# Fingerprinting Simulated Marine Oil Spills with Gasoline-range Compound Specific Isotope Correlation

by

Michael David Kory
B.Sc., University of Victoria, 1986

A Thesis Submitted in Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

in the School of Earth and Ocean Sciences

# Supervisory Committee

**Fingerprinting Simulated Marine Oil Spills with Gasoline-range Compound Specific Isotope Correlation**

by

Michael David Kory
B.Sc., University of Victoria, 1986

**Supervisory Committee**

Dr. Michael J. Whiticar, Supervisor
(School of Earth and Ocean Sciences, University of Victoria)

Dr. Eileen Van der Flier-Keller, Departmental Member
(School of Earth and Ocean Sciences, University of Victoria)

Dr. Eleanor Setton, Outside Member
(Department of Geography, University of Victoria)

***Supervisory Committee***

Dr. Michael J. Whiticar, Supervisor
(School of Earth and Ocean Sciences, University of Victoria)

Dr. Eileen Van der Flier-Keller, Departmental Member
(School of Earth and Ocean Sciences, University of Victoria)

Dr. Eleanor Setton, Outside Member
(Department of Geography, University of Victoria)

# ABSTRACT

Environmental liability cases involving spilled or released petroleum products into ocean ecosystems require oil identification techniques that are unambiguous and conclusive, even in situations where oils have been subjected to secondary environmental processes, such as, evaporation and dissolution.

The ability and functionality of the Compound Specific Isotope Correlation (CSIC) technique is tested to determine its reliability to characterize released petroleum using the carbon isotope ratios ($^{13}C/^{12}C$) of the individual gasoline-range compounds ($C_5$-$C_9$). In particular, this thesis studies the potential of CSIC as a robust diagnostic tool, to identify and correlate marine releases of oil with their sources, especially those having undergone evaporative weathering.

Three crude oils (Alberta Sweet Mixed Blend, Lacula and Louisiana) added to synthetic seawater were exposed to mechanically simulated wave energy and controlled evaporative weathering at 10 $^{o}$C. Time-series sampling of the gasoline-range vapour fractions from the headspace employed Solid Phase Micro Extraction (SPME). SPME-

Continuous Flow-Isotope Ratio Mass Spectrometry (SPME-CF-IRMS) determined the molecular abundances and stable carbon isotope ratios ($\delta^{13}C$) of the gasoline-range compounds of the original and weathered oils.

Evaporation rates over the maximum 20 hour period varied for the 3 study oils. Most (74%) of the individual compounds measured in the oils display a $\delta^{13}C$ enrichment with progressive evaporation with approximately half of the compounds in all 3 oils showing fractionation of the carbon isotopes ≤ 0.5‰ within measurement precision. The magnitude of carbon isotope shift observed in compounds pre-vs. post-weathering ranges from 0 to 2.8 ±0.6‰. There is no clear relationship identified between the degree of $^{13}C$ enrichment in the oils and groupings such as chemical class, structure or carbon number. The overall weighted average $^{13}C$ enrichment for all compounds in the 3 oils is approximately 1‰. Toluene was the only compound consistently exhibiting comparatively high $^{13}C$ enrichment (1.6‰, 1.8‰ and 2.8‰) in all 3 oils after evaporative weathering.

Hierarchical Cluster Analysis (HCA) treatment of the CSIC data set can reliably discriminate between the 3 oils despite evaporative weathering and $\delta^{13}C$ changes. HCA is also able to unambiguously relate the three weathered oils back to their respective original unweathered oil.

Diagnostic shifts in $\delta^{13}C$ of individual compounds in an oil may potentially be used to trace weathered oils back to the source, and possibly give a estimation of time since release. However the typically rapid rate of evaporation for the gasoline-range fractions limits the time that an oil can be successfully identified by CSIC.

# TABLE OF CONTENTS

# LIST OF TABLES

# LIST OF FIGURES

# ACKNOWLEDGMENTS

I would like to express my sincerest gratitude to Dr. Michael Whiticar, Dr. Kathryn Gillis, Dr. Patricia McKenzie, Ms. Allison Rose, Dr. Eileen Van der Flier-Keller, Dr. Eleanor Setton and every single one of the University of Victoria administrative staff involved for the opportunity, the consideration, the support and the enormous patience required to help a man finish what he started.

The Science Council of British Columbia and the taxpayers of British Columbia for their generous funding throughout the program.

Janice and Julia Kory for the support, encouragement, patience and sacrifices necessary to allow to me finish what was started……so other things could be started.

Dr. John Harper who provided the many opportunities to get me started.

Mrs. Karyn Drysdale, who gave me the opportunity to do what made me want to start in the first place.

All of the EOS 110 students who convinced me it was worthwhile starting.

Dr. Murray Erasmus for the numerous surgeries that kept my retinas in place long enough for me to finally finish what I started.

Any and all "*gods*" that may exist, for the *focus* required to allow a man with the attention span of a newt, to finally swallow a bite thought too big to chew.

# CHAPTER 1. INTRODUCTION

***Statement of Purpose***

The primary purpose of this study is to develop and evaluate the use of a Compound Specific Isotope Correlation (CSIC) approach to characterize fugitive releases of crude oils. CSIC in this study uses stable carbon isotope ratios ($^{13}C/^{12}C$) of individual hydrocarbon compounds in the gasoline-range of an oil to provide a diagnostic signature, or fingerprint, for specific oils. A primary component of this thesis was the development of a technique to perform stable carbon isotope ratio analyses on experimentally weathered oil samples. This consisted of a CSIC procedure using Solid Phase Microextraction (SPME) combined with Continuous Flow-Isotope Ratio Mass Spectrometry (CF-IRMS). An immediate application is the potential identification and tracking of oils released into the environment. A particular emphasis of this research is the application of CSIC to oils spilled at sea. This study investigates whether the carbon isotope signatures for the gasoline-range compounds of oils are suitably reliable as a diagnostic tool, specifically testing the magnitude of molecular and stable isotope ratio changes in 3 released oils after evaporation.

## 1.1 RESEARCH OBJECTIVES

Gasoline-range fractions were chosen for Compound Specific Isotope Correlation (CSIC) research because of their relative abundance in crude oils, compound class representation (e.g., paraffins, napthenes, aromatics) and analytical resolvability (Whiticar and Snowdon, 1999). Gasoline-range studies using the CSIC technique for oil-

oil and oil-source rock correlation applicable to the petroleum exploration industry have been pioneered at the Biogeochemistry Facility at the School of Earth and Ocean Sciences (BF-SEOS), (e.g. Murphy, 1994; Harris et al., 1999; Whiticar and Snowdon, 1999). The primary focus of these initial studies was to develop and advance CSIC methodology to characterize or fingerprint conventional petroleum from crude oils and reservoirs. CSIC takes advantage of the fact that oils and/or gasolines can have unique carbon isotope ratio signatures, based on the $^{13}C/^{12}C$ ratios of individual n-, iso, and cycloalkanes as well as the aromatics. CSIC is based on Continuous Flow-Isotope Ratio Mass Spectrometry (CF-IRMS), a methodology developed at the BF-SEOS to analyze individual compounds in bulk or complex mixtures. Early studies investigated the use of different stable carbon isotope ratios of bulk oils or their main fractions (aliphatic, aromatic, heteroatomic) to characterize them (Stahl, 1979; Sofer et al., 1984; Mango, 1997). Although there were some successes based on these bulk isotope ratio methods, in many cases the bulk isotope signatures were not sufficiently diagnostic to distinguish between oils. The initial studies found that large carbon isotope ratio differences exist in the gasoline-range fractions between crude oils from a variety of geological settings (Bjorøy et al., 1994; Rooney et al., 1998; Whiticar and Snowdon, 1999). These preliminary investigations also suggested that there is not an appreciable change in the isotopic signatures during the degradation process in reservoir settings.

However, fugitive releases of petroleum, especially in marine settings, present a dramatically different environment to reservoired crudes (Smallwood et al., 2002; Wang and Stout, 2007; Li et al., 2009). As a consequence, this study researches the fidelity of carbon isotope ratio signatures of crude oils after being released into a simulated marine environment.

This study investigates some of the physical changes anticipated due to evaporation and solubilization of crude oil in a three-phase (oil-water-air) system. The potential effects of other natural weathering processes such as biodegradation and photoxidation are not addressed.

The following criteria must be met for the CSIC technique to be effective for oil spill fingerprinting investigations:

1. Hydrocarbon compounds of interest must be present in sufficient concentrations for reliable isotope ratio measurements,
2. The stable isotope ratio signatures of the individual oils must be significantly and diagnostically different to provide a distinguishing fingerprint,
3. Secondary effects, e.g., evaporation, if applicable must have minimal or a predictable influence on the isotope signature,
4. The CSIC analytical technique must be practical, efficient and generate universally accepted results; it must be litigatively sound.

Based on these criteria, it is the objective of this study to determine the potential for using the CSIC technique to use carbon isotope ratios to fingerprint and identify the source of fugitive releases of crude oils into the marine environment, specifically onto the ocean surface. By systematically measuring the carbon isotope ratios of the available gasoline-range compounds over time, in various crude oils exposed to the surface of synthetic seawater, the robustness of the isotope signatures after initial weathering (evaporation) can be investigated. Results can be used to further develop and evaluate the usefulness of the CSIC methodology in fugitive marine petroleum spill scenarios.

Evaporation affects the temporal availability of the gasoline-range fractions and potentially influences changes to the initial isotope signatures. This study attempts to observe any changes in the post weathering isotope signatures of gasoline-range compounds analyzed from the equilibrated headspace above crude oil samples.

There are analytical challenges associated with the collection, isolation and measurement of gasoline-range compounds. Although liquid at room temperature (25 $^{o}$C), the pentanes with boiling points in the range of normal ambient temperatures (i.e. iso-pentane b.p. 28$^{o}$ C), represent the phase boundary between gases and liquids in the alkane (aliphatic) series.

Many of the gasoline constituents in oils, especially those in the $C_5$-$C_6$ range can shift more from the liquid towards the gas phase at typical lab temperatures. Therefore care must be taken to minimize the evaporative loss during sample collection and analysis. Conventional methods that focus on higher molecular weight fractions in whole oils normally require that the samples be diluted with a low boiling point solvent, such as n-hexane, prior to injecting the sample into the gas chromatograph (GC). These solvent peaks often co-elute and can drastically interfere with isotope measurements (Whiticar and Snowden, 1999). To avoid this interference, techniques involving solventless extraction, such as purge and trap (P&T) were developed to collect these volatile constituents from oil samples. An early P&T method for analyzing the volatile components in oil using a helium purge and a liquid nitrogen trapping system was developed by Dr. Lloyd Snowdon in the late 1970's which allowed gasoline-range hydrocarbons to be effectively analyzed by GC (Snowden, 1978). Subsequently at BF-SEOS, Murphy (1995) and Whiticar and Snowdon (1999) utilized a modified P&T technique for capturing the gasoline-range compounds from a headspace above an oil

sample for CF-IRMS. Although efficient for volatile analyte extraction, the system is laborious, time consuming and susceptible to evaporative losses. In addition, controlling the amounts of sample introduced into the CF-IRMS is challenging.

To circumvent P&T limitations, Harris et al. (1999) developed at BF-SEOS, a Solid Phase Micro Extraction (SPME) technique to sample the gasoline-range fractions from the headspace above fresh and weathered crude oil samples. Classical SPME involves exposing a fused silica fibre coated with a liquid polymeric coating (in this case polymethylsiloxane) to a sample by either direct immersion into an aqueous phase or into the headspace above it. Application of the SPME technique to the headspace above the liquid sample is more specifically referred to as Headspace SPME or HSPME. After an equilibration period for analyte adsorption, the fiber, housed in a handheld syringe mechanism (Figure 2.3), is removed, then directly inserted into the GC injector housing for introduction onto the GC column.

Harris et al. (1996) reported that although the majority of studies using SPME have involved immersion of the fiber to extract analytes from an aqueous medium (e.g., Arthur and Pawliszyn, 1990; Arthur, et al., 1992a,b; Louch et al., 1992; Potter and Pawliszyn, 1994; Dias and Freeman, 1997); a number of authors also used HSPME to analyze complex headspace mixtures in oils, pesticides, flavor volatiles and sludges (Zhang and Pawliszyn, 1993a,b, 1994; MacGillivary et al., 1994; Steffen and Pawliszyn, 1996; Boyd-Boland et al., 1996; Hunkeler and Aravena, 2000; Abrams and Logan, 2010). A detailed use of HSPME methodology for this study is given in Analytical Methodology section (Section 2).

The current study involves the application of 3 different crude oils as surface films in containers of water and air. The study examines the time-series related changes to the

molecular and carbon isotope ratios of the oils before, during and after evaporative weathering experiments. Headspace samples of the hydrocarbons above the surface oil are collected using HSPME, and the $^{13}C/^{12}C$ ratios of resolvable gasoline-range compounds in the oil are determined over the experimental time-series. The study attempts to relate the temporal changes in relative molecular abundances of the oils to changes in their isotope signatures.

## 1.2 BACKGROUND

### 1.2.1 Petroleum Releases

Petroleum release into marine waters occurs from four major sources:

1. Natural seeps (ocean bed fissures, sedimentary rock erosion),
2. Releases that occur during the extraction of petroleum (land and offshore drilling platforms),
3. Transportation of petroleum products (refinery terminal loading, vessel spills, operation discharges from cargo washing) and
4. Consumption of petroleum products (urban runoff, discharges from commercial and recreational marine vessels).

The percentages of main input sources of petroleum into the marine environment are shown in Figure 1.1.

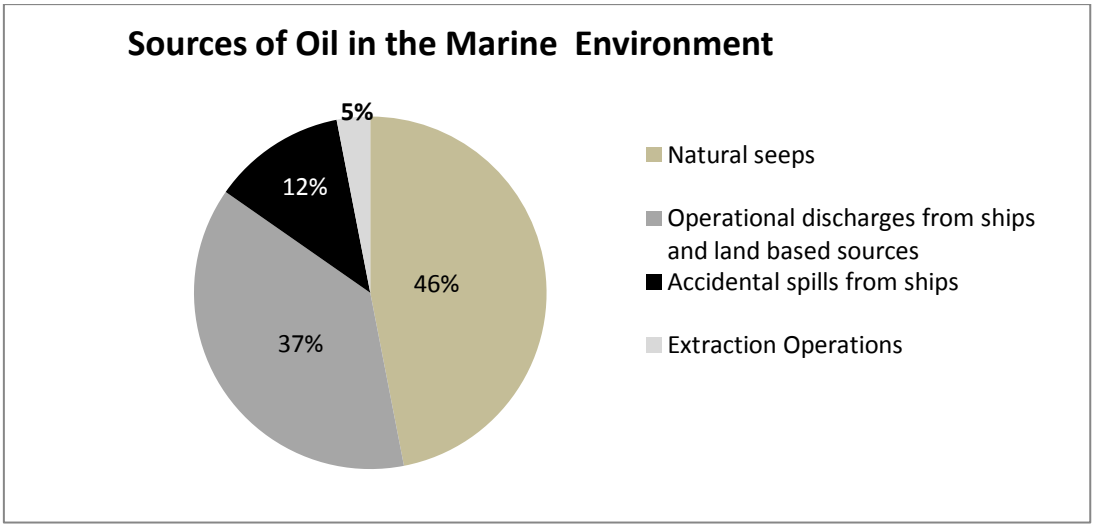



*Figure 1.1. Main input sources of petroleums into the environment. Source percentages from NRC, 2003.*

Based on a 2003 National Research Council (NRC) report, the average total worldwide annual release of oils into the sea from all known sources has been roughly estimated to be 1.3 million tonnes per year (NRC, 2003). The NRC report does acknowledge that there is a wide range, up to a possible 8.4 million tonnes, attributed to the complexities of estimating land based runoff, inaccurate spill volume reporting and potential fugitive releases.

These huge quantities of spilled or released petroleum products enter our ocean ecosystems and contaminate coastlines, potentially causing extensive and lasting damage to marine organisms, terrestrial life, human health and natural resources. Costs associated with oil spill cleanup, such as the 1989 *Exxon Valdez* tanker spill in Alaska's Prince William Sound, can total hundreds of millions and even billions of dollars in restorative and stakeholder compensative expenses (Anderson, 1983; Dickens et al., 1990; Galt, et. al., 1991; Hostettler and Kvenvolden,1994: Thompson et al. 1991).

The recent *Deepwater Horizon* drilling platform oil spill (also known as the Gulf of Mexico Oil Spill or the BP Oil Spill), is estimated to have released roughly 5 million barrels (650,000 tonnes) of Louisiana crude oil into Gulf of Mexico before the well was initially plugged and subsequently sealed Sept. 19, 2010. In a worst-case scenario, BP's cleanup liability is estimated to be between 12 and 16 billion dollars, which would account for the entire loss of all fishing and tourism revenues for coastal states closest to the spill (Mouawad, 2010).

The National Pollution Funds Center, a subsidiary of the U.S. Coast Guard responsible for recovering oil spill cleanup costs from responsible parties, reports that about 40% of spills in U.S. waters are "mystery" spills, and the costs go unrecovered (Ramseur, 2008). For example, for many years it has been common practice to dump oil-contaminated ballast water and tank washings directly into the sea. So while most of the known source large-scale spills result from grounded tankers or tanker collisions, the cumulative contamination from numerous relatively small accidents, leaks, and intentional fugitive discharges can actually surpass that of large spills from shipping (Epstein and Selber, 2002). Hampton et al. (2003) believe that the process of oil tanker cargo tank washing between reloading dissimilar petroleum cargoes remains the greatest oil spill threat to seabirds, aside from catastrophic accidents. A recent review of Transport Canada observation flights between 1998 and 2007 (Serra-Sogas, 2010), identified what was believed to be more than 500 spills along the coast of British Columbia. Observed spills were relatively small, ranging up to as much as 1000 liters. The review identified particular areas of higher likelihood for oil spills from engine residue, tank washing, bilge water and even "mystery" leaks that have no confirmed source: Johnstone Strait; the

Sunshine Coast; the Fraser River belt; and concentrated marine areas surrounding higher density urban areas such as Nanaimo.

Due to the potentially severe effects associated with even a relatively small spill, the ability to characterize and correlate oil releases to their sources is important for assessing potential environmental damage, prediction of long term impacts, spill response and effective cleanup strategies. In addition, the unambiguous identification of fugitive oil releases in many cases is critical for determining and assigning environmental liability. In certain cases potential defendants seek to demonstrate that the petroleum products associated with their activities is not the source of the contamination in question, therefore analytical techniques are required to discriminate between multiple contaminant sources.

### 1.2.2 Weathering of Crude Oils

When crude oil or a petroleum product is spilled or released into the ocean it is subject to a variety of transport and physicochemical transformation processes collectively known as weathering (Figure 1.2). The fate and behavior of spilled oils in the environment depends on a number of factors including evaporation, dissolution, emulsification, microbial degradation, photo-oxidation, and interaction between oil and sediments. The combined effects of weathering can dramatically modify or remove many of the compounds or parameters used to correlate oil with the source based on GC or GC/MS analysis or other traditional techniques. Correlation of spilled oil to its suspected source requires fingerprinting techniques that are relatively insensitive or resistant to the effects of the weathering process.

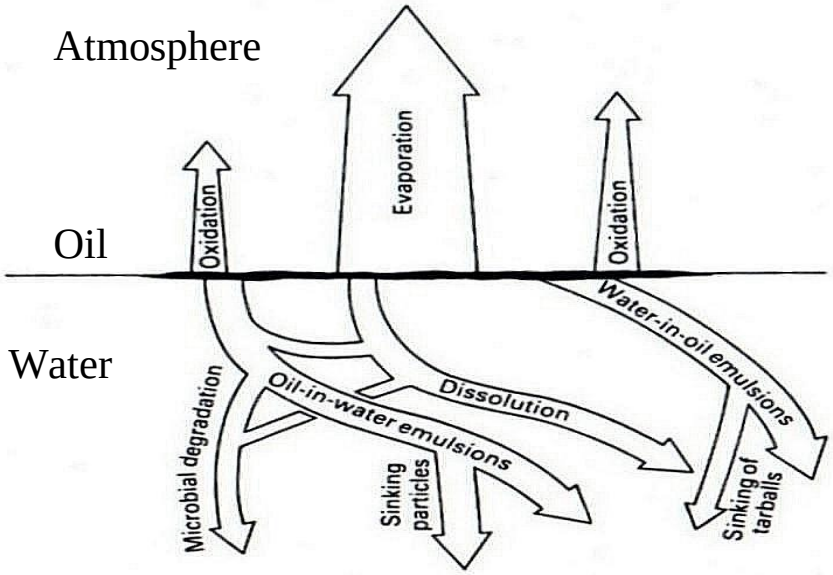



*Figure 1.2. Gross weathering processes of oil spills on the seawater surface. (from Doerffer, 1992).*

### *1.2.2.1 Evaporation*

The dominant initial process is typically evaporation, with other processes becoming significant later in the spill stages (NRC, 1989; Stiver and Mackay, 1989; Doerffer, 1992; Fingas, 1997; Wang and Fingas, 2003). Except for the situations where natural conditions rapidly disperse a spill, evaporation is responsible for the largest mass balance change in a body of spilled oil. Depending on the weather and sea state, medium to light crude oils can lose between 40 and 75% of their volume in only a few days after a spill (Mackay and Matsugu, 1973; Wang et al., 1999). For many crude oils, it is not uncommon for 25% of the total volume of an oil spill to evaporate within one day of the spill (Fingas et al., 1979). Fingas (1995) reports that oil evaporation is not similar to water evaporation due to the heterogeneous chemical composition of a crude oil, containing up to thousands of

different chemical compounds. Pure compounds evaporate in a linear manner, whereas crude oils, which have many compounds evaporating simultaneously, evaporate in a logarithmic manner (Fingas, 1997). Each component of a crude oil may have its own physicochemical parameters; however they are modified and obscured by the oils bulk characteristics. Initial rapid loss of the more volatile gasoline-range fractions is followed by progressively slower loss of the less volatile components. Gasoline-range fractions are the most volatile and can typically comprise between 20% and greater than 40% of most crude oils (Hocking, 1985; McDonald et al., 1984). For example, the bulk composition of the *Exxon Valdez* crude oil was approximately 20% $C_1$-$C_{10}$ volatiles (Bence et al., 1996).

Evaporation of petroleums spilled at sea is reviewed in detail by many authors including: Bobra, (1992); El-Nemr, (2006); Fingas et. al., (1979, 1995, 1997, 2003); Mackay and Matsugu, (1973); McAuliffe, (1977, 1986) Riazi and Edalat, (1996); Reijnhart and Rose, (1982), Striver et. al., (1989) and Wang et. al., (1999).

The rate of evaporation and the subsequent temporal availability of the gasoline-range compounds is important with regards to determining the diagnostic usefulness of the CF-IRMS technique used in this study. Furthermore, the various physicochemical changes observed in the study oils during the simulated weathering process provide useful insight into specific weathering and evaporation characteristics and subsequent availability of gasoline-range compounds in different oil types under a variety of spill scenarios.

#### *1.2.2.2 Emulsions*

One of the various secondary processes that can occur as a result of crude oil being spilled on water with turbulence is emulsification. Emulsification of crude oils typically refers to the process by which minute water droplets (1-20μm) become dispersed in the oil through physical mixing by wave energy (Fingas et. al., 2003). The formation of emulsions is a complex process and whether an oil will form an emulsion depends on its physicochemical properties and prevailing environmental conditions (Payne and Phillips, 1985; Bobra et. al., 1992). Emulsion formation has been shown to be a result of the stable suspension of water droplets in the oil by the surfactant action of asphaltenes, resins and waxes (Aske et. al., 2002; Bobra, 1991; Bridie et. al., 1980). Also, in a study by Canevari and Fiocco (1997) it was established that a concentration of over 15 ppm concentration of vanadium and nickel (trace metal components of asphatltenes), is required in order for a fresh crude oil to form a stable emulsion; more weathered oils may form emulsions with lower vanadium and nickel concentrations. Volatile aromatic compounds (BTEX) in crude oils act as solvents to stabilize the asphaltenes and resins. When these volatile fractions are depleted through weathering, asphaltenes and resins precipitate, which act to reduce the surface tension of the oil-water interface initiating emulsification (Auflem, 2002; Bobra, 1992; Langevin et. al., 2004). Even crude oils containing lower quantities of these volatile compounds or BTEX (benzene, toluene, ethylbenzenes, xylenes) will form emulsions given sufficient turbulent sea surface energy (Fingas et. al., 2003).

When emulsions are formed, they can have very different characteristics from the spilled parent crude oil, increasing in volume 3 to 5 times; similar to the volume increases observed in this study. Formed water-in-oil emulsions in crude oils have different classes of stability based on the asphaltene and resin contents, as well as differences in the

viscosity of the initial oil. Oils with an asphaltene content greater than 0.5% can form stable emulsions. When both asphaltenes and resins are present in quantities greater than 3%, stable water-in-oil emulsions can be formed which persist for months after the initial spill (Fingas et. al., 1995a). Wax content can also influence the general stability of an emulsion once formed (Bobra, 1992). Due to the stability and frothy consistency, stable water-in-oil emulsions are sometimes called “chocolate mousse” or “mousse” by oil spill workers (Fingas et. al., 1995). Oils containing a lower percentage of asphaltenes are less likely to form emulsions and are more likely to disperse. Less stable emulsions may separate into oil and water again if heated by sunlight under calm conditions (Aske et. al., 2002).

#### *1.2.2.3 Biodegradation*

Biodegradation is considered during the design stage of this study and efforts to prevent microbial growth are implemented. Since the process of bacterial degradation can contribute significantly to hydrocarbon weathering, a brief and general discussion of biodegradation is presented to support the assumed absence of any microbial influence on either relative abundance losses or biologically induced isotope effects.

More than 200 genera of bacteria, cyanobacteria, fungi, and algae are known to degrade or transform hydrocarbons, using them for energy and carbon (Margesin and Schinner, 2001). Many of these organisms consume mainly saturated hydrocarbons, while others can metabolize even the normally toxic aromatic hydrocarbons, and these fractions can be largely removed within a few weeks by biodegradation (Head et al., 2006). The early stages of biodegradation are characterized by the loss of n-alkanes followed by the acyclic isoprenoids (norpristane, pristine and phytane, etc.), with highly

branched and cyclic saturated hydrocarbons as well as aromatics being increasingly more resistant (Goodwin et al., 1983).

The natural degradation of petroleum hydrocarbons occurs in either water or soil wherever the essential nutrients, water and oxygen are present in sufficient supply to meet the requirements of the specific petroleum degrading microorganisms. Normally the hydrocarbon-degrading organisms are diverse and widespread but uncommon in the marine environment. When crude oil is introduced however, these organisms are favored by the new conditions, and their populations can bloom and become very abundant in a short time (Ludzack and Kinkead, 1956). Under favorable biological conditions, specific to the species present, significant hydrocarbon losses and isotopic fractionation (0.5 to 5‰), particularly in the alkanes, are reported by various authors including (Stahl, 1980; Zang et al., 2004).

Early biodegradation studies by Atlas and Bartha (1972) showed that even with oils added to seawater supplemented with cultured petroleum degrading microorganisms and optimal amounts of phosphorous and nitrogen, mineralization was not observed until after approximately 30 days at 10 $^{o}$C. Biodegradation was based on measured $CO_2$ evolution rates; no measurable $CO_2$ evolution was observed in the crude oils exposed to unsupplemented seawater, at any of the study temperatures (5, 10, 15 or 20 $^{o}$C). The lag period in the study was attributed to the lower temperatures inhibiting organism multiplication; the initial populations of hydrocarbon degraders require sufficient time to multiply into concentrations able to produce measurable amounts of $CO_2$; and evaporation of the more toxic constituents (i.e. BTEX) which retards biodegradation. To test the above factors, Atlas and Bertha (1972) used weathered oils exposed to the same inoculants. Evolution of $CO_2$ was observed after approximately 10 days. Stahl (1980) also

studied biodegradation rates using water from the North Sea (due to its known populations of hydrocarbon degraders) with supplemental nutrient solutions of nitrogen and phosphorus at 18 $^{o}$C. Biodegradation was observed in the biologically active flasks, however no appreciable effects were observed in the blanks void of nutrient solutions after 21 days.

Walker et al (1978) report that lower water temperatures suppress the microbial growth and metabolic activity of the hydrocarbon degraders and/or inhibit growth as a result of increased retention of more toxic volatiles not evaporated at the lower temperatures. Also microbial growth may be inhibited by increased solubility of potentially toxic compounds at higher sea water temperatures.

A synthetic mixture rather than natural seawater is used in this study, prepared using de-ionized water and a mineral solution mimicking the mineral content of a typical seawater mixture. Raw seawater is not used in an effort to eliminate the chance of natural petroleum degrading microbes being initially present in the experimental mixtures. All experimental saltwater batches of the de-ionized water and mineral salt mixtures are prepared and utilized within a 48 hour period. Based on previous research, the relatively short weathering times (less than 20 hours) and the10 $^{o}$C temperature of these trials, it is assumed that biodegradation has no effect on relative abundance losses or carbon isotopic fractionation of the measured gasoline range fractions in this study.

#### *1.2.2.4 Dissolution*

Although the process of dissolution may play some role in regards to potential effects on carbon isotope ratios, no analyses of oily-water mixtures are performed and thus solubilized concentrations of hydrocarbons are not investigated. Riazi and Edalat (1996)

found that the rate of dissolution of both a crude oil and kerosene, under normal sea surface conditions, is about 0.1% the rate of evaporation. Lafargue and Theiz (1996) report that compounds with the same carbon number, the aromatics are removed first, the n-alkanes second and finally the cycloalkanes. Overall, general solubility ranges from less than 1 part per million (ppm) in light fuels to 100's ppm in heavy oils such as Bunker C (Fingas et. al., 2003). For gasoline-range fractions in this study, reported solubility ranges from about 35 ppm ($nC_5$) to 490-627 ppm (Toluene); BTEX (benzene, toluene, ethylbenzene and xylene) fractions are considered the most soluble (El-Nemr, 2006).

Since evaporative rates are generally much faster than the dissolution process, much of these volatile BTEX fractions are removed from a spill by evaporation (El-Nemr, 2006). Dissolution is however considered important environmentally, as many of the BTEX compounds are highly toxic to marine organisms.

### 1.2.3 Forensic Techniques for Petroleum Identification

A wide variety of forensic techniques commonly referred to as petroleum fingerprinting, have been developed to characterize and identify hydrocarbons in waterborne environmental samples. These chemical fingerprinting methods have played an important role in the identification of mystery oil spills. More recent applications of these and other methods currently used for the forensic characterization of escaped petroleum hydrocarbons have been summarized by numerous authors including: Bence 1996; Kaplan et al., 1997, Wang et al., 1994, Wang and Fingas, 1999; Stout et al., 2001; Stout et al., 2005; Wang and Fingas, 2003 and Alimi et al., 2003.

Initially, hydrocarbons were characterized using bulk parameter methods, such as specific gravity ($API^{o}$), viscosity, metal and sulfur content, octane rating, cetanes, or API distillation profiles. With the appearance of more advanced analytical methods, petroleums are now routinely characterized using gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS), high-performance liquid chromatography (HPLC), infrared spectroscopy (IR), supercritical fluid chromatography (SFC), thin layer chromatography (TLC), ultraviolet (UV), fluorescence spectroscopy, and isotope ratio mass spectrometry (IRMS).

Correlations are made on the basis of bulk molecular patterns and distribution of aliphatic and aromatic hydrocarbons, or more specifically biomarker fingerprints (Wang et al., 1994). However in certain situations, GC and GC/MS data can be ambiguous or inconclusive due to secondary environmental effects after the oil is released into the marine environment.

The most common approach to the characterization of a fugitive oil spill and identification of its potential source relies on analyses by GC and gas GC/MS and more recently Gas Chromatograph Isotope Ratio Mass Spectrometry (GC-IRMS) (Mansuy et al., 1997; Whiticar and Snowdon, 1999; Mazeas and Budzinski, 2002; Smallwood et al., 2002; Wang and Stout, 2007; Li et al., 2009).

Beginning with the early isotope investigations by Harold C. Urey et al. (1932) and his classic paper in 1947, in which he observed and calculated stable isotope distribution factors between species of geochemical interest, there has been a steady increase in the use of stable isotope variations for the natural earth sciences. Early pioneers such as Craig (1953) analyzed hundreds of samples establishing ranges of values for the relative abundances of the carbon isotopes in marine and terrestrial materials.

Stable isotope methods for oil-oil correlation were pioneered by researchers such as Silverman (1964), and Stahl (1977). Later, analyses and characterization of petroleum hydrocarbons using $^{13}C/^{12}C$ isotope ratios typically focused on bulk/whole oil carbon compositions, major saturates ($C_{15}$ +), aromatics, asphaltenes, polycyclic aromatic hydrocarbons (PAH) and N,S,O fractions, e.g., Silverman, (1964); Stahl, (1979); Chung et al., (1981); Macko et al., (1981); Sofer, (1984); Farran et al., (1987), Kvenvolden et al, (1995). Although these bulk isotope and molecular approaches to oil correlation are useful and often successful they can be ambiguous and inconclusive in situations where oils have been subjected to secondary environmental effects, i.e., evaporation, water washing, biodegradation etc.

In the past few decades, organic geochemistry has benefited from the continuing development and application of monitoring isotope ratios using a combination of Continuous Flow Gas Chromatography, and Mass Spectrometry. The combination of a gas chromatograph, an on-line combustion unit and an isotope ratio mass spectrometer allows the GC separation and combustion of individual compounds into carbon dioxide which can be isotopically measured by the mass spectrometer. Many researchers have applied this CF-IRMS technique in the petroleum exploration and drilling industry for developing oil-oil and oil-source correlations, e.g. Freeman et al., (1990); Hayes et al., (1990); Bjorøy et al., (1994); Carpentier et al., (1996); Murphy, (1994); Abrajano and Lollar, (1999); Harrington et al., (1999); Harris et al., (1999); Huang et al.,(1999); Whiticar and Snowdon, (1999). Numerous others have employed CF-IRMS techniques to monitor or source correlate contaminants in the aquatic and marine environment, e.g. O'Malley et al., (1994); Mansuy et al., (1997); Slater et al., (1999); Wang et al. (1999);

Smallwood et al., (2002); Wang and Fingas, (2003); Mazeas and Budzinski, (2002) and Alimi et. al., (2003).

The development of CF-IRMS permits researchers to determine and characterize the isotope ratios of individual components of complex mixtures such as crude oils. In many of the studies, compounds analyzed are in the $C_{10}$-$C_{40}$ range, with n-alkanes, isoprenoids (i.e. pristine, phytane), and PAH's being those commonly studied. Many of these compounds are generally abundant in crude oils and possess relatively established analytical protocols.

Although many CF-IRMS studies have been performed on the C15+ range hydrocarbons, the gasoline-range hydrocarbons ($C_5$-$C_{10}$) have been largely ignored until the last decade, due the volatile nature and associated handling concerns of the compounds. Since many crude oils are comprised of between 20-40% gasoline-range fractions they are a dominant and readily available fraction consisting of a range of compound classes (Hocking, 1985). Straight and branched chain alkanes (paraffins), cyclic alkanes (napthenes) and aromatics are all represented in the gasoline-range ($C_5$-$C_{10}$) series. In addition, compounds in this lower molecular weight series provide good analytical separation due to the limited number of structural isomers that must be resolved during the GC component of the CF-IRMS analysis. For example, as the carbon number increases in the paraffin homologous series the number of possible structural isomers also increases. Hexane, for example, has 5 structural isomers; and heptane has 6. All of the 18 isomers of octane have been defined, as have the 35 isomers of nonane (Hocking, 1985). The accuracy and reproducibility of CF-IRMS data are mainly affected by chromatographic resolution (co-eluting compounds) and background as defined by column bleed and unresolved complex mixtures (UCM) from increasingly complex

higher molecular weight petroleum hydrocarbon fractions (Mansuy, 1997, Abrajano and Sherwood Lollar, 1999).

## 1.3 STABLE CARBON ISOTOPE DEFINITIONS, EFFECTS AND FRACTIONATION

Isotopes are atoms of the same element with the same number of protons and electrons (atomic number), but with a different number of neutrons (atomic mass). Because they have the same number of electrons, isotopes of a particular atom have very similar chemical properties and differ only in characteristics associated with their atomic mass differences. Carbon has two known naturally occurring isotopes that are considered stable; $^{12}C$ (mass=12μ) and $^{13}C$ (mass=13μ). $^{12}C$ is the most abundant in nature at 98.89% compared to $^{13}C$ with an abundance of 1.11% (Faure, 1986).

However, through the many natural chemical and physical processes that occur, molecules may be influenced by *isotope effects* that can result in observable amounts of isotope fractionation. Isotope fractionation refers to the change in an isotope ratio between phases that arises as a result of some chemical or physical process.

An isotope effect is a physical phenomenon, not directly observable, that potentially leads to isotopic fractionation which is an observable effect measured by changes in isotopic abundances (Hayes, 1982). Isotope fractionation is a consequence of the fact that certain thermodynamic properties of molecular interaction are dependent on the masses of the component atoms and molecules as studied by numerous authors including; Urey, (1947); Bigeleisen and Mayer, (1947); Bigeleisen, (1952, 1965); Broeker and Oversby, 1971).

Mass differences lead to fractionation due to the influences on both the molecular mobility and the bond energies of reacting atoms and molecules. In simple terms, the average kinetic energy (KE) of a molecule is related as $KT = {}^{1}/_{2}\,mv^{2}$. Hence if the mass of an isotope species is larger it must have a lower average velocity. This lowered mobility of the heavier species results in lower diffusion velocities and lower collision frequencies leading to lower reactivity compared to the lighter species.

During isotopic fractionation, heavy and light isotopes partition differently between two compounds or phases. Because the bond energy of each isotope is slightly different, the heavier isotopes have stronger bonds and slower reaction rates. Since the difference in bonding energy and reaction rates are proportional to mass differences between isotopes, lighter elements are more likely to exhibit isotopic fractionation compared to heavy isotopes. For example, the relatively light $^{12}C$ and $^{13}C$ isotopes have an 8% mass difference and undergo stable isotope fractionation. Those isotopes especially influenced by fractionation are elements that are among the most abundant on earth: H, C, N, O, and S (White, 1997; Faure, 1986).

It is this fractionation, or partitioning, of atoms and molecules that make isotopes useful for scientific investigations. A substance or product that undergoes fractionation resulting in a change in the relative isotopic abundances is said to have become either enriched or depleted in the heavy $^{13}C$ isotope. Those enriched in $^{13}C$ are said to be heavy (or heavier), those depleted in $^{13}C$ are said to be light (or lighter).

Isotope fractionation can originate from isotope effects of which the two pertinent types are *kinetic isotope effects* (KIE) and *equilibrium isotope effects* (EIE); KIE are generally irreversible wherein EIE can reversibly exchange isotopes during reactions, e.g., Craig, 1953; Bigeleisen, 1965; Hayes, 1982; O'Neil, 1986; Wen, 1991. Isotopic ratio

measurements involved in this study are discussed in more detail in section 1.3.1. following.

### 1.3.1 Isotope Ratio Measurements

Isotopes of an element are generally not measured as absolute abundances or concentrations; rather they are made as ratios relative to an internationally accepted reference standard. This is based on instrumental and reporting reasons (Mook, 2000; Werner and Brand, 2001).

The normal form to report the magnitude and direction of isotope differences between phases is the delta (δ) notation. Units of delta (δ) are "‰" or "per mil", calculated using the following equation;

$$\delta^{13}C = \left[ \frac{(^{13}C/^{12}C)_{sample} - (^{13}C/^{12}C)_{standard}}{(^{13}C/^{12}C)_{standard}} \right] \times 1000 \qquad \text{(equation: 1.1)}$$

where: $(^{13}C/^{12}C)$ is the carbon isotope ratio in the sample or standard.

The comparison of isotope ratio data from different laboratories is made against an internationally accepted isotope standard such as the V-PDB (Vienna PDB) (Coplen, 1994). The original PDB, now exhausted, is based on the $^{13}C/^{12}C$ for the carbonate shell of a Cretaceous belemnite (cephalopod: *Belemnitella Americana*) from the Pee Dee Formation in South Carolina. The standard ratio ($R_{standardVPDB}\,^{13}C/^{12}C$) is presently defined as 0.0111802 ± 0.0000028 (Werner and Brand, 2001). Samples are either more enriched or depleted in $^{13}C$ compared to the standard.

Petroleum is believed to derived from various precursor plant and animal residuals that have been deposited in prehistoric marine and freshwater basins; the processes by which this precursor material is converted in petroleum is still not clearly understood. The carbon contained in fossil fuels (coal, natural gas and petroleum) is strongly depleted in $^{13}C$ relative to the V-PDB standard. This depletion is related to fractionation (depletion) in the plant precursor material, wherein the lighter $^{12}C$ containing $CO_2$ molecules are favored during the photosynthetic processes. The bulk $\delta^{13}C$ values of petroleum range typical from -18 to -34 ‰ (Stahl, 1979).

As previously mentioned, when oil is spilled into the environment, secondary weathering effects such as evaporation and water washing, can lead to isotope fractionation. More recently researchers have performed preliminary laboratory investigations into effects of evaporation and water washing (BTEX primarily) on the fractionation of carbon isotopes in both neat gasolines, BTEX compounds and these same gasoline-range compounds as individual components in whole crude oils (Bojrøy, et al., 1994; Carpentier et al., 1996; Lafargue and Thiez, 1996; Mansuy et al., 1997; Harrington et al., 1999; Huang et al., 1999; Sherwood Lollar et al, 1999; Smallwood et al., 2002). Most of these studies involved laboratory bench-top petri dish evaporation and/or closed system separatory funnel water-washing in distilled water.

In this study, CF-IRMS coupled with SPME are utilized to characterize and monitor the $\delta^{13}C$ values for individual gasoline-range ($C_5$-$C_9$) hydrocarbon compounds in three crude oils exposed to simulated weathering effects, employing mechanically induced wave energy on a synthetic seawater medium.

# CHAPTER 2. ANALYTICAL METHODS

## 2.1 CRUDE OIL SAMPLES

Three different crude oils are used in this study. Each oil has a unique hydrocarbon composition and carbon isotope ratio signature. The oil samples were obtained courtesy of Environment Canada Emergencies Science Division in Ottawa.

The crude oil samples used for the study are:

1. Alberta Sweet Mixed Blend (ASMB)
2. Lacula
3. Louisiana

The bulk physical properties of the three oils listed in Table 2.1 were provided by Environment Canada and are determined using methods listed in the Catalogue of Crude Oil and Oil Product Properties, Appendix of Methods, published by Environment Canada Emergencies Science Division in Ottawa (Jokuty et al., 1999).

All three crude oils are stored at 5 $^{o}$C prior to being shipped in high-density polyethylene *(nalgene*) 4 liter containers to SEOS. To lower vapour pressures of the gasoline-range compounds of interest and therefore inhibit evaporative losses, the oils are stored at 3 $^{o}$C in the BF-SEOS refrigerator until they were required for experimentations.

As a larger goal of the thesis is to assess molecular and isotope changes to released oils in marine settings, the experiments are designed to simulate spill-like conditions. The experiments are performed in an environmental chamber on simulated seawater at

10 $^{o}$C. Alberta and Louisiana oils are stored in their sealed containers in the chamber to ensure both water and oil are consistently 10 $^{o}$C. Lacula oil is warmed outside the chamber for 1 hour in order for it to be poured (18 $^{o}$C pour point).

*Table 2.1. Physical and chemical properties of the experimental crude oils. (Environment Canada, 1999).*

| **PROPERTY** | **ASMB** | **LACULA** | **LOUISIANA** |
|---|---|---|---|
| API Gravity | 36.1 | 33.4 | 34.5 |
| Density (g/ml) 0 $^{o}$C (0% Evaporation) | 0.8548 | 0.8709 | 0.8628 |
| Density (g/ml) 15 $^{o}$C (0% Evaporation) | 0.8434 | 0.8574 | 0.8518 |
| Pour Point ($^{o}$C) | -27 | 18 | -28 |
| **Hydrocarbon Groups (Weight %) (0% Evaporation)** | | | |
| Saturates | 65 | 67 | 73 |
| Aromatics | 27 | 22 | 21 |
| Resins | 5 | 8 | 4 |
| Asphaltenes | 3 | 4 | 0 |
| Waxes | 6 | 13 | 4 |
| **Volatile Organic Compounds (ppm) (0% Evaporation)** | | | |
| Benzene | 860 | 370 | 800 |
| Toluene | 7060 | 1070 | 2190 |
| Ethylbenzene | 1360 | 210 | 710 |
| Xylenes | 8490 | 1900 | 5360 |
| C3-benzenes | 11,250 | 2690 | 5710 |
| Total BTEX | 17,770 | 3550 | 9060 |
| Total BTEX + C3-benzenes | 29,020 | 6240 | 14,780 |
| **Dynamic Viscosity (mPa$*$s or cP) 15 $^{o}$C (0% Evaporation)** | 7 | 43 | 8 |

***Chester Laboratory Reference Oil***

Chester (NA1) oil, collected from an Alberta oil production well, is used as the laboratory reference to compare the experimental results and to check the operating condition of the CF-IRMS. Chester is a light to medium crude with abundant gasoline-range hydrocarbons. The Chester reference has been used by other investigators in previous studies performed at the BF-SEOS, e.g., Harris (1999), Murphy (1994) and Whiticar and Snowdon (1999). Isotope ratio values for the measureable gasoline-range compounds from daily Chester standard test runs are used to check the functioning of the CF-IRMS instrumentation and to provide isotope ratio values for normalizing subsequent experimental runs. A more detailed description of the isotopic characterization of the Chester standard oil and the methods used for normalizing weathered oil IRMS runs are presented in Section 2.5.2.

### 2.1.1 Overview of Methods

The methodology flow chart Figure 2.1 presents an overview of the principal tasks of the study. Headspace samples from fresh Chester reference and the 3 study oils are characterized using CF-IRMS to establish initial baseline (unweathered ) isotope ratio values and the analytical variation for individual gasoline-range compounds. Study oil samples are then subjected to time-series weathering experiments in an environmental chamber (10 $^{o}$C) using a reciprocating platform table to provide simulated low wave energy ocean surface conditions. After specified weathering periods, experiment sample containers are sealed to arrest evaporation to the atmosphere. Aliquots of the gasoline-range hydrocarbon analytes are collected from the headspace using Headspace Solid

Phase Micro-Extraction (HSPME) (Harris 1999). Samples are then injected into the CF-IRMS to obtain $^{13}C/^{12}C$ measurements and abundance values.

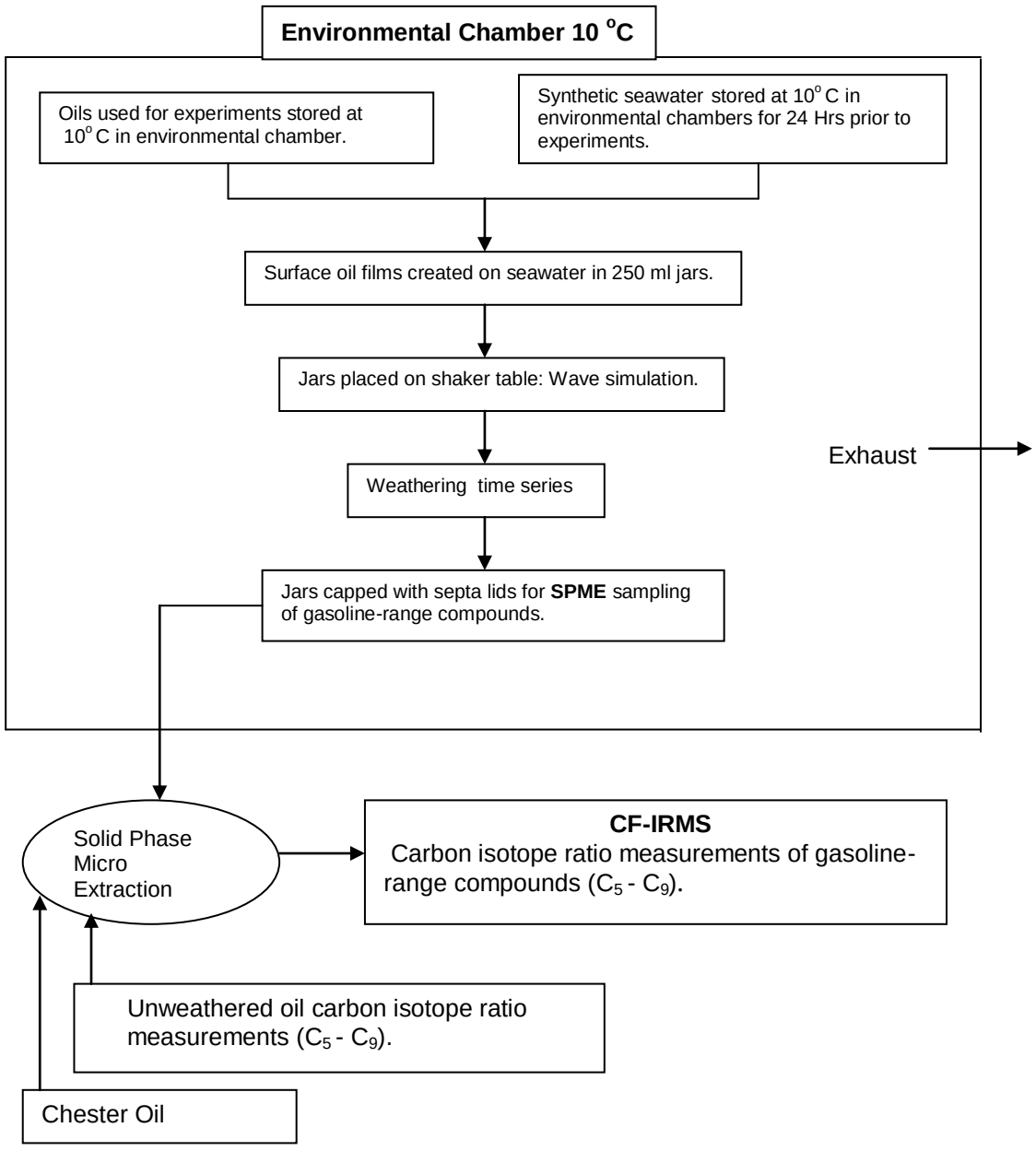



*Figure 2.1. CSIC Analytical flow chart.*

## 2.2 TIME-SERIES WEATHERING

### 2.2.1 Environmental Chamber

Oil weathering experiments are performed in a Percival model 50036 environmental chamber, with an interior volume of approximately 0.4 cubic meters. Chamber temperature precision is stated on the manufactures plate as ± 0.5 $^{o}$C. Interior chamber temperature was set to maintain a temperature as close to 10 $^{o}$C as possible; temperature cycling from 9.6 $^{o}$C to 10.3 $^{o}$C over a 10 minute period was observed with the chamber thermostatic temperature control set to 9.8 $^{o}$ C.

The intermediate temperature of 10 $^{o}$C was selected as it closely approximates an average summer open sea-surface temperature off Victoria's well mixed waters (Thomson, 1981). The 10 $^{o}$C air temperature above the water in the environmental chamber actually reflects a more temperate winter climate for the Victoria area; actual air temperatures above the water in summer around Victoria range from about 15 to 24 $^{o}$C (Thomson, 1981).

The chamber interior is dark during weathering trials as light fixtures are disconnected in order to prevent electrical arcing, mitigating the potential for ignition of hydrocarbon vapours within the chamber. Low volume exhaust fans continuously vent vapours from inside the chamber through 15 cm diameter flexible ducting through an exterior wall to the outside, mitigating cross contamination and explosive risks.

### 2.2.2 Salt Water Medium

A commercially produced synthetic salt water (*Instant Ocean*) is used for the experiments, mixed to a salt concentration of 30 ‰ (parts per thousand). The synthetic mixture, approximating salt and mineral characteristics of "typical" seawater, is used to maintain water quality consistency throughout the trials. Natural seawater contains varying numbers and species of micro and macro-organisms. Using the synthetic seawater mixture ensures a homogenous, consistent and relatively microbe free medium during each trial. Although none were observed, any developing microbe populations would have resulted from any species present or introduced during a similar lab mixing process and therefore common to all prepared batches.

Deionized water from a *Modulab* deionization unit (Fisher Scientific) is used for the salt water mixture to maintain consistency. The saltwater mixture is stored in a sealed 10 liter *nalgene* carboy, in the environmental chamber for 24 hours prior to its use for the oil experiments to ensure a uniform 10 $^{o}$C. All saltwater is used within 48 hours of the initial mixing. Any water remaining after the 48 hour period is discarded and a new 10 liter batch prepared.

### 2.2.3 Weathering Vessels

Standard wide-mouthed 250 ml glass preserving (mason) jars are used to contain the oil and water mixtures during the simulated oil spill weathering experiments. The jars are approximately 7.2 cm in diameter and 6 cm deep. Standard mason jars are supplied with threaded screw top sealing rings and a gasket lined metal lid to provide an air-tight seal necessary for the preserving process. The basic sealing assembly, with lid modifications

for HSPME sampling, is used to stop further evaporation from the jars and to contain the volatile components immediately after each set of time-series experiments. To facilitate HSPME sampling without removing the lids and the associated loss of volatile fractions, ½ dram *teflon* lined septa capped glass vials are incorporated into the metal lids (Figure 2.2). Lid fabrication involves first removing the bottom of each ½ dram glass vial and then attaching the open cut end of the vial into hole (11 mm in diameter) closely matching the diameter of the dram vial, cut into the center of the metal lid. The vial is inserted approximately 3 mm into the hole then a bead of adhesive applied both on the top and bottom areas of the lid/vial interface. The adhesive bead is continuous to provide a sealed attachment. A methyl ethyl ketone based adhesive (*Seal All*) is used to join the components as the product is guaranteed to be unaffected by gasoline or oil. After curing for 24 hours, three empty septa modified jars are sampled and analyzed using SPME and CF-IRMS to confirm the absence of any adhesive sealant contamination. These trials also confirmed the initial absence of any residual hydrocarbon contaminants in the CF-IRMS instrumentation. The *teflon* lined septa screw cap facilitated the penetration of the SPME sampling needle apparatus into the sealed headspace above the oil water mixtures. A new septa vial lid assembly is used for each experiment.

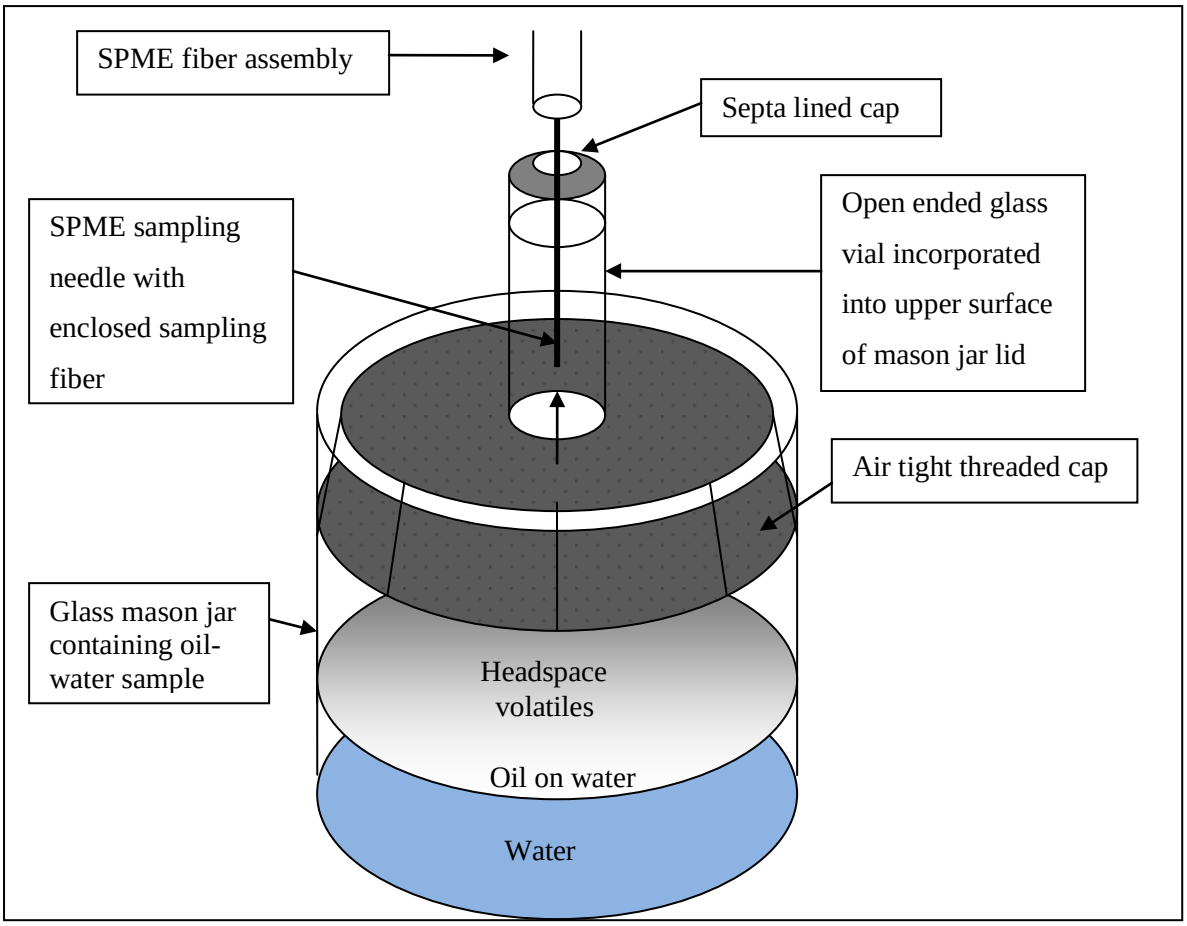



*Figure 2.2. Weathering jar with sampling assembly. Septa lined vial incorporated into air-tight lid allows for headspace SPME sampling.*

### 2.2.4 Oil Film Thickness

All weathering experiments are performed using approximately 17 ml of oil added to the surface of 150 ml of synthetic sea water, corresponding to a 4mm oil film thickness and a water depth of approximately 3.6 cm. Simulated oil spill studies performed by Tasaki and Ogawa (1995) concluded that the evaporative process is not affected by oil thickness in the range of their tests (1mm-4mm), although no conclusions regarding evaporation of an oil film greater than 4mm thick are presented. In spill studies where oil films are greater than 4mm, such as those performed by Doerffer (1992), it is reported

that evaporation rates are influenced by oil type and spill volume since surface/volume ratios change as oil film thickness increases. As the primary objective of this study was to test the stability of the gasoline-range carbon isotope ratio signatures over time, sufficient oil was used to attempt longer time-series investigations.

### 2.2.5 Simulated Wave Energy

A laterally reciprocating shaker table is used to simulate light wave action within each of the experimental jars within the chamber. Table stroke is approximately 8 cm laterally, approximately 30 oscillations per minute. Surface wave amplitude is roughly determined to be approximately 1 to 1.5 cm. Initially a total of 12 jars containing water and oil are prepared inside the chamber and placed on the shaker table at the onset of each experimental run. After a specified weathering time interval, three jars (triplicates) are then quickly sealed and removed from the chamber. After each removal, three new experimental jars are quickly prepared and added to the table along with the remaining jars from the initial setup and their time of placement recorded. During the rapid additions, chamber temperature normally increases to a maximum of approximately 12 $^{o}$C during the sampling events and returns to normal temperatures within 5 minutes.

### 2.2.6 Weathering Time-Series

Unweathered samples of all three study oils are taken directly from storage carboys, transferred to septa capped vials and analyzed without exposure to saltwater or weathering protocol. Weathered samples of all three oils are collected after the initial 0.5, 1, 2 and 3 hours. Alberta samples are collected after a further 4, 6, 8, 9, 10, 12, and 14

hours of weathering in the chamber. Lacula samples are further collected at intervals of 4, 5, 6, 7, 8, 10, 12, 16, to a maximum of 20 hours. Table 2.2 shows the time-series and maximum evaporation time for each of the three oils. The maximum evaporation times listed correlate with the onset of the lack of reliable amounts of gasoline-range hydrocarbons below $nC_6$ being present in the headspace. Sample intervals are stated as $T_{\text{sample hr}}$ ,i.e the 1 hour sampling interval is stated as $T_1$, the 8 hr sample $T_8$; unweathered samples are $T_0$, the final sample $T_f$.

*Table 2.2. Experimental time-series and sampling periods.*

| Oil Type | Number of Experiments | Experiment Sampling Intervals (Hrs) | Maximum (Hrs) |
|---|---|---|---|
| Alberta | 33 | 0, 0.5, 1, 2, 3, 4, 6, 8,9 10, 12, 14 | 14 |
| Lacula | 36 | 0, 0.5, 1, 2, 3, 4,5, 6,7 8, 10, 12, 16, 20 | 20 |
| Louisiana | 15 | 0, 0.5, 1, 2, 3 | 3 |

## 2.3 SAMPLE COLLECTION

### 2.3.1 Unweathered Oils

All three initial unweathered oils ($T_0$) are sampled and analyzed using fresh samples from *nalgene* carboys stored in the BF-SEOS freezer (3 $^{o}$C). A one drop sample of each oil is transferred by Pasteur pipette to a ½ dram glass vial (pre-fired at 450 $^{o}$C to remove contaminants). The vial is then quickly sealed with a *teflon* lined septa cap to facilitate SPME. Initial vials are left to stand in the CF-IRMS lab for approximately 2 hours to reach room temperature (the CF-IRMS facility is maintained at a constant 21 $^{o}$C) prior to SPME analysis. The 3 unweathered oils are analyzed in triplicate (using fresh vials for

each run) to determine the initial $T_0$ gasoline-range compound carbon isotope ratios. Laboratory reference oil (Chester) is analyzed identically to the $T_0$ study oil samples.

### 2.3.2 Weathered Oils

Upon completion of the temporal weathering trials, sample jars are immediately sealed with the septa lid assembly and secured tightly with a threaded clamp ring to ensure an air tight seal, stopping further loss of volatile gasoline-range fractions. Jars are then carefully transported to the CF-IRMS laboratory for analyses, minimizing agitation of the oil-water mixture. All jars are allowed to stand in the CF-IRMS laboratory for at least 2 hours in an attempt to ensure all headspace samples are collected at the same room temperature. Although previous research (Harris, 1999) showed that the resulting $\delta^{13}C$ values of most compounds differed very little ($< \pm 0.3$ ‰) over a vial temperature range of 0 to 42 $^{o}C$, sampling temperatures are kept at a relatively constant 21 $^{o}C$ laboratory temperature during SPME analyses to decrease potential differences arising from any vapour pressure/temperature isotope effects.

Three sacrificial oil and water mixtures, prepared from each of the oils and left sealed in jars at 10 $^{o}C$ overnight, were all found to have reached room temperature after approximately 1 hour and 30 minutes after arrival at the lab.

All experiments are performed in triplicate wherein 3 separate sample jars are prepared for each specific time series. One HSPME sample is taken from each of the 3 jars.

### 2.3.3 Solid Phase Microextraction

Solid Phase Micro-Extraction (SPME) is a solvent-free sample preparation technique in which a fused silica fiber coated with a polymeric phase is introduced into an aqueous sample or into the headspace above it to collect selected analytes. As previously discussed, Headspace SPME (HSPME) refers to using the technique to specifically extract, capture and concentrate the volatilized organic analytes in the headspace above a sample and transfer them to the analytical instrumentation for analysis. Compared with direct SPME sampling from an aqueous phase, the HSPME technique can be used to extract volatile target organic compounds from complex matrices such as petroleum hydrocarbons, oily water or even human foods. Sampling from the headspace avoids the difficulties arising from the fiber coating being enclosed by a film of oil or grease or being impaired by large protein molecules (Zhang and Pawliszyn, 1993a).

The specific composition of the SPME fiber coating chosen for sampling is dependent on the characteristics of the compounds being analyzed. In this study a polydimethylsiloxane (PDMS) coating is chosen based on its performance in previous studies by Harris (1999), Louch et. al. (1992), and Zhang and Pawliszyn (1993b) for analysis of non-polar volatile hydrocarbon compounds. PDMS is hydrophobic, therefore compared with conventional headspace extraction, the amount of moisture and oxygen is substantially reduced. The PDMS fiber coatings are very similar to the stationary phase of the GC column used in analysis (Zhang and Pawliszyn, 1994) and are thermally stable throughout the range of sampling temperatures and analysis encountered in this study. The fiber is preconditioned in the GC before use, using the manufacturer's suggested protocol.

The SPME fiber used for these experiments is housed in a syringe device to facilitate ease of handling. When not in use, the fiber component is withdrawn and housed within a narrow gauge stainless steel needle (Figure 2.3). During sampling the syringe needle is then used to punch through the septa on the unweathered sample vial caps and the lid assemblies of the weathering sample jars. The fiber component is then extruded from the needle to expose it to the headspace above the oil sample by manually depressing the plunger on the syringe and locking it into a preset exposed position. Exposure to the headspace for a period of 25 minutes establishes equilibrium between the PDMS fibre coating, the headspace and the oil sample matrix.

A headspace exposure time of 25 minutes is chosen based on previous SPME equilibration studies by Dias and Freedman (1997) and most recently by Harris (1999) at the SEOS isotope laboratory, showing the establishment of molecular and isotopic equilibrium after 15 minutes of fiber exposure. Harris et al. (1999) exposed the SPME fiber to the vial headspace above an oil droplet for periods of 30 seconds to 1 hour. As in the Dias and Freeman (1997) investigations, Harris (1999) measured the resulting peak areas, signal amplitude and $\delta^{13}C$ ratios of 14 gasoline-range ($C_5$-$C_9$) compounds until equilibrium was established (when all three variables remained constant).

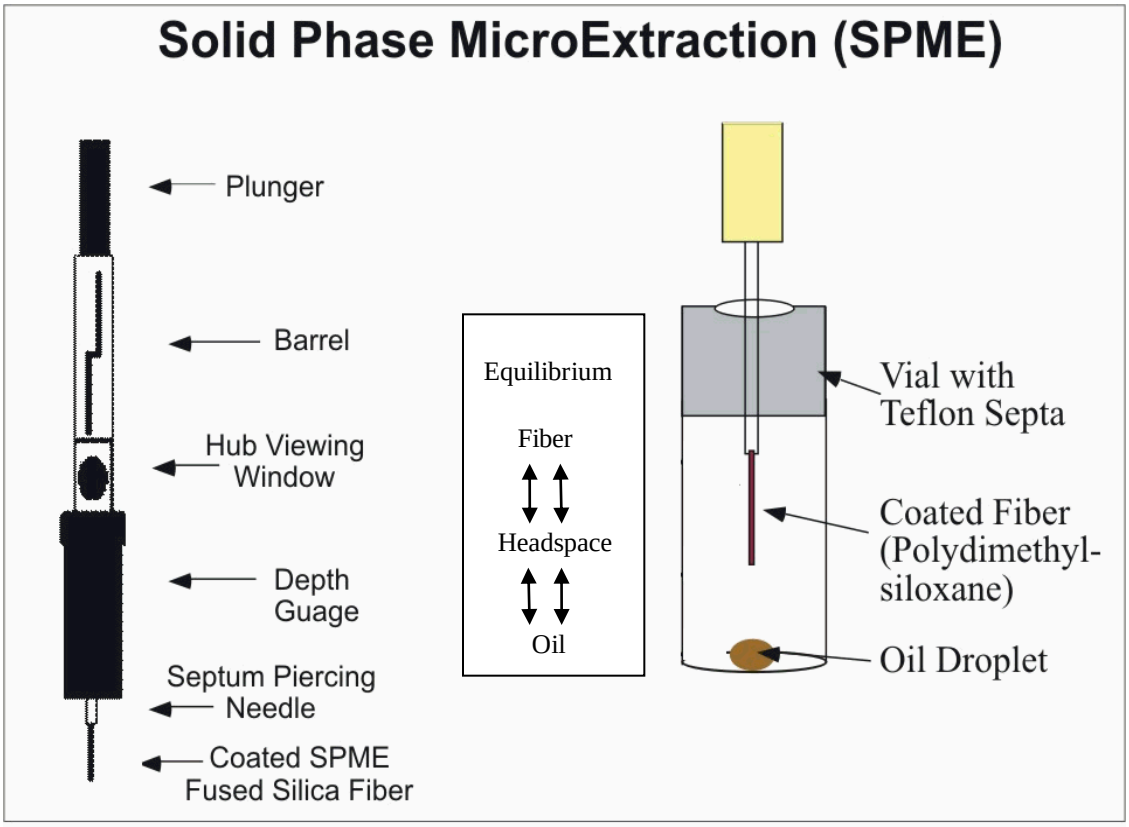



*Figure 2.3. Schematic of SPME syringe and fiber assembly (after Harris, 1999).*

Although many of the compounds achieved stability after 5 minutes, those fractions greater than $C_8$ did not achieve molecular equilibrium until after 15 minutes of fiber exposure. Results of the molecular equilibrium times, measured by peak areas (normalized to $nC_7$) are shown in Figure 2.4a. The establishment of isotopic equilibrium was more rapid, occurring after 5 minutes of fiber exposure (Figure 2.4b). Regardless of the molecular weight or compound chemical class, variability in the $\delta^{13}C$ values of all the measured compounds decreased significantly after 5 minutes (Figure 2.5b). Zhang and Pawliszyn (1993a) also found that for BTEX compounds, molecular equilibrium is reached after 5 minutes. The fiber exposure time of 25 minutes established for this study is used to ensure that the minimum headspace equilibrium period of 15 minutes was

surpassed, and also providing an additional 10 minute margin in the event of the need for last minute instrumentation adjustments prior to analysis.

After the 25 minute exposure time, the fiber is retracted into the syringe needle and the assembly removed from the headspace through the septa. The syringe is then immediately transferred to the GC split/splitless injector where the fiber is extended into the injection port (260 $^{o}$C) where the analytes are thermally desorbed and carried to the GC column component of the CF-IRMS system. The injector utilizes a glass inlet specially designed for SPME applications. The inlet has a smaller inside diameter (0.75mm) than conventional inlets (2mm) that promotes a more rapid, and thorough heating of the SPME fiber and thus a faster desorption of the analytes. The inlet also serves to focus the sample, improving GC peak shape and resolution (Harris et al, 1999).

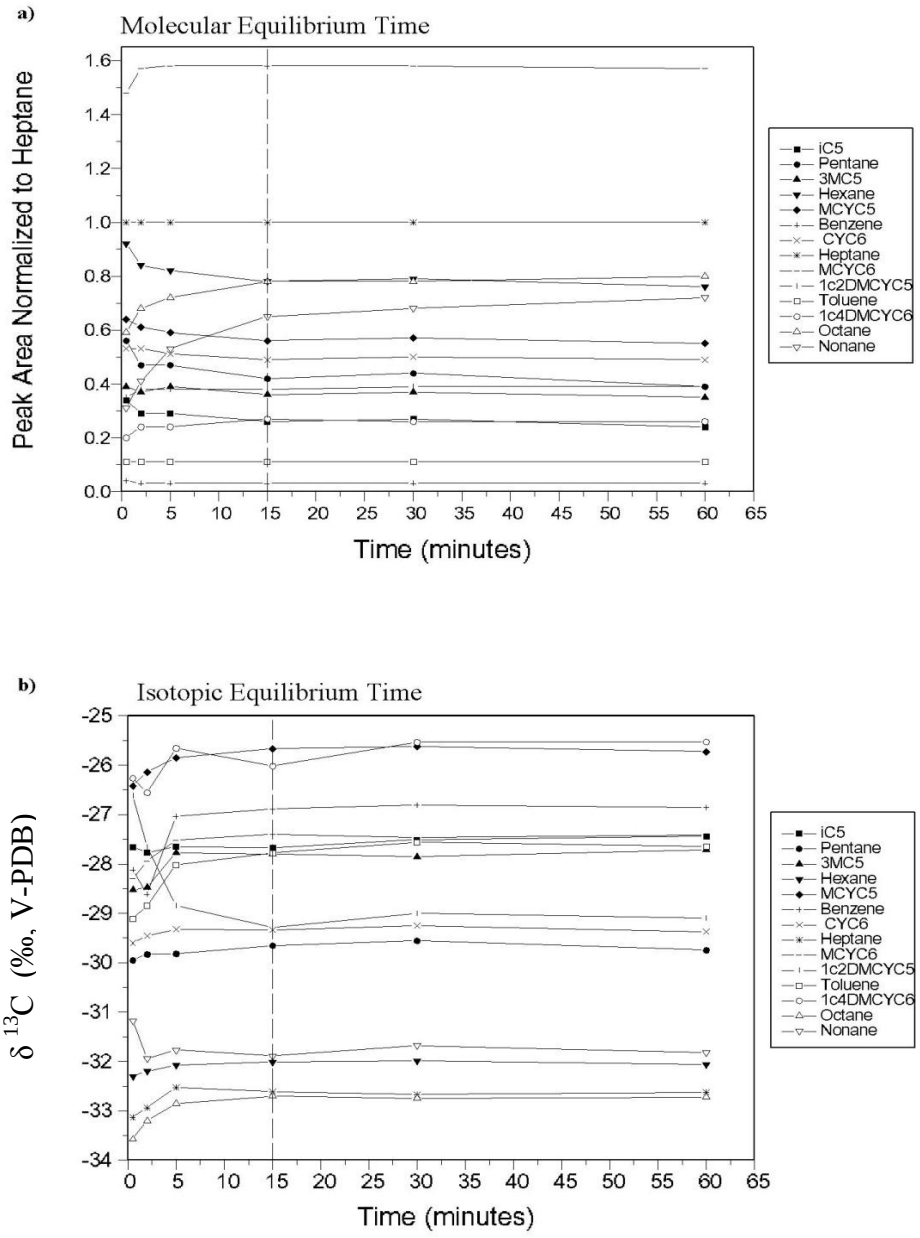



*Figure 2.4. Minutes required for a) molecular and b) isotopic equilibrium between SPME polydimethylsiloxane coated fiber and headspace analytes. The dashed line at 15 min. represents minimum adsorption time (after Harris, 1999).*

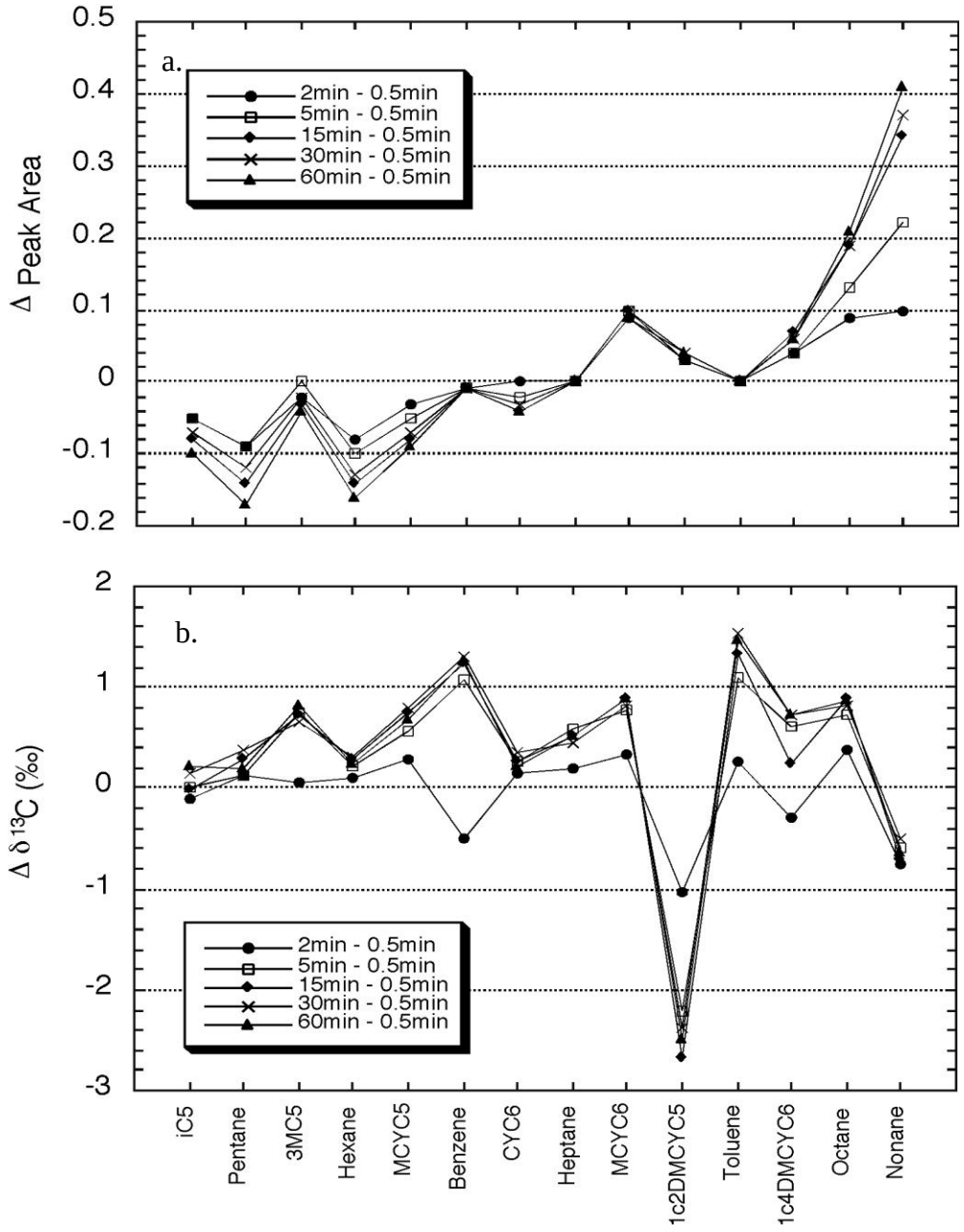



*Figure 2.5. Variation in peak area a) and isotope ratios b) for gasoline-range analytes from 2 to 60 minutes. (after Harris, 1999).*

## 2.4 CARBON ISOTOPE CHARACTERIZATION OF OILS

### 2.4.1 Analytical Instrumentation

The carbon isotope ratios of the gasoline-range compounds of the oils are analyzed by Continuous Flow Isotope Ratio Mass Spectrometry (CF-IRMS) at BF-SEOS. A schematic of the analytical system is shown in Figure 2.6.

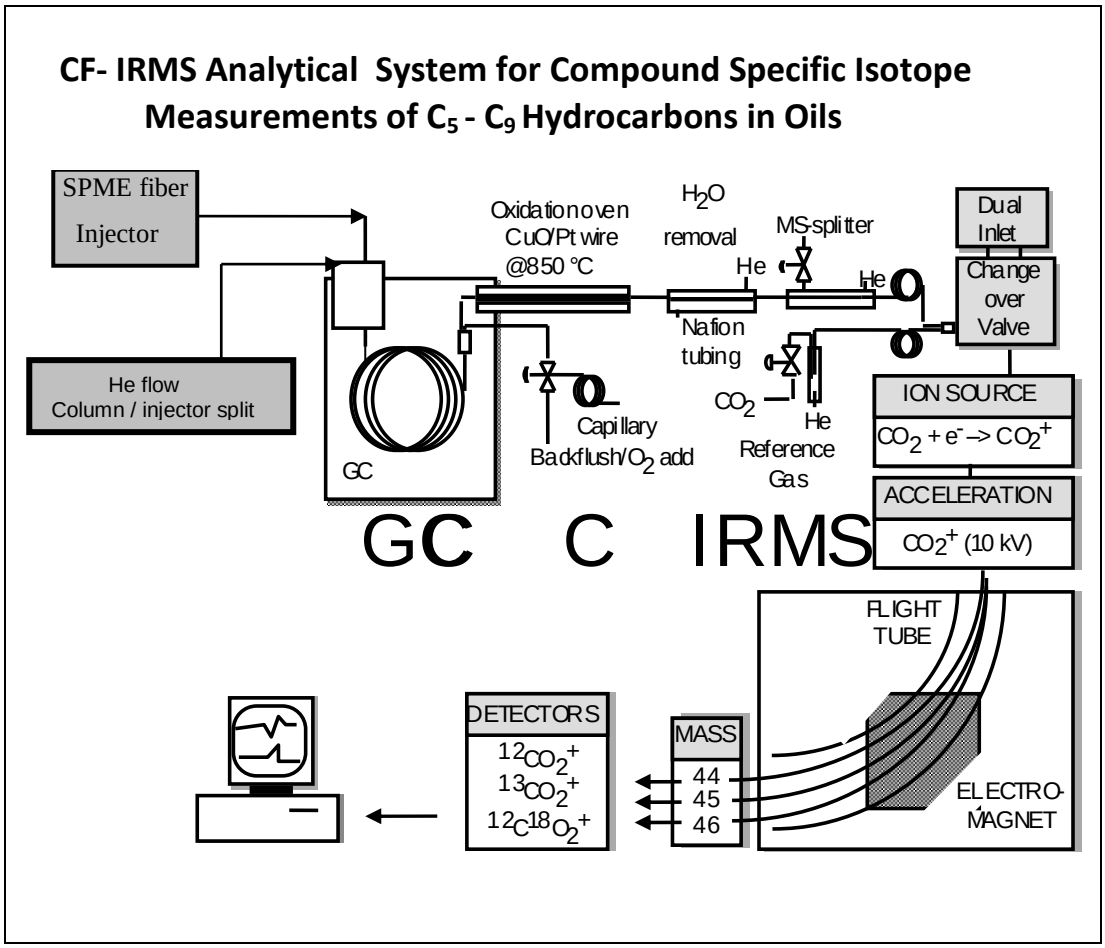



*Figure 2.6. Schematic of the SPME/CF-IRMS instrumentation.*

CF-IRMS has been used in numerous studies to measure the isotopic ratios of single compounds in a complex mixture such as an oil sample (i.e. Matthews and Hayes, 1978; Santrock et al., 1995; Boutton, 1991; Habfast, 1991; Bjorøy et al., 1994; Merritt et al.,

1994; Ricci et al., 1994; Murphy, 1994; Mansuy et al. 1997; Harris, 1999; Whiticar and Snowden, 1999; Hunkeler and Aravena, 2000; Li et al., 2009; Smallwood et.al.; 2002; Woulé Ebongué et. al., 2009a; Abrams and Logan, 2010). The instrument used in this study is a combination of a Varian 3400 GC, coupled to a Finnigan-Mat 252 Isotope Ratio Mass Spectrometer (IRMS) via an on line micro-combustion oven (Figure 2.6). Previous studies refer to the instrumentation as GC-C-IRMS, based on the sequence of individual components of the analytical system. Contemporary studies now refer to the process generically as Continuous Flow-Isotope Ratio Mass Spectrometry (CF-IRMS).

***Gas Chromatographic Column***

Sample analytes are injected from the SPME fiber into the injector port of the Varian 3400 GC. The fused silica column separates the compounds in the complex oil mixture according to their boiling points (Table 2.3) and resultant relative retention time (RRT) on the column. The *Petrocol* fused silica column used for these analyses was chosen since it is specifically designed for petroleum hydrocarbon applications. Column specifications are as follows:

- Column name/manufacturer *Petrocol* $^{TM}$ , SUPELCO
- Liquid stationary phase : DB-1 (non-polar), bonded methyl silicone
- Film thickness : 0.5 μm
- Column length : 100 m
- Column diameter : 0.25 mm
- Maximum temperature : 320 $^{o}$C

*Table 2.3. Boiling and melting points for various gasoline-range hydrocarbons. (CRC Handbook of Chemistry and Physics, 1992).*

| **Compound Name** | **Abbreviation** | **Melting ($^0$C)** | **Boiling ($^0$C)** | **Phase** |
|---|---|---|---|---|
| ethane | C2 | -172 | -89 | |
| propane | C3 | -187.0 | -42.0 | *gas* |
| butane | C4 | -135 | -0.5 | |
| isopentane | $iC_5$ | -159.9 | 27.8 | |
| normal pentane | $nC_5$ | -130.0 | 36.1 | |
| 2,2-dimethylbutane | $22DMC_4$ | -99.9 | 49.7 | |
| cyclopentane | $CYC_5$ | -93.9 | 49.2 | |
| 2,3-dimethylbutane | $23DMC_4$ | -128.5 | 58.0 | |
| 2-methylpentane | $2MC_5$ | -153.7 | 60.3 | |
| 3-methylpentane | $3MC_5$ | -118.0 | 63.3 | |
| normal hexane | $nC_6$ | -95.0 | 69.0 | |
| methylcyclopentane | $MCYC_5$ | -142.4 | 71.8 | |
| benzene | ben | 5.5 | 80.1 | |
| cyclohexane | $CYC_6$ | 6.5 | 80.7 | |
| 2-methylhexane | $2MC_6$ | -118.3 | 90.0 | |
| 1,1-dimethylcyclopentane | $11DMCYC_5$ | -69.6 | 87.5 | |
| 2,3-dimethylpentane | $23DMC_5$ | -135.0 | 89.8 | |
| 3-methylhexane | $3MC_6$ | -119.0 | 92.0 | |
| 1cis, 3-dimethylcyclopentane | $1c3DMCYC_5$ | -134.0 | 91.0 | *liquid* |
| 1trans, 3-dimethylcyclopentane | $1t3DMCYC_5$ | -137.0 | 91.0 | |
| 1trans, 2-dimethylcyclopentane | $1t2DMCYC_5$ | -117.4 | 92.0 | |
| normal heptane | $nC_7$ | -90.6 | 98.4 | |
| methylcyclohexane | $MCYC_6$ | -126.6 | 100.9 | |
| 1cis, 2-dimethylcyclopentane | $1c2DMCYC_5$ | -53.7 | 109.0 | |
| 2,5-dimethylhexane | $25DMC_6$ | -91.2 | 108.0 | |
| 2,4-dimethylhexane | $24DMC_6$ | | 109.2 | |
| 2,2,3-trimethylpentane | $223TMC_5$ | -112.3 | 110.0 | |
| toluene | toluene | -95.0 | 110.6 | |
| 3-methylheptane | $3MC_7$ | -121.0 | 115.8 | |
| 1cis,4-dimethylcyclohexane | $1c4DMCYC_6$ | -87.4 | 124.3 | |
| normal octane | $nC_8$ | -56.8 | 125.7 | |
| normal nonane | $nC_9$ | -53.0 | 151.8 | |

The *Petrocol* column has a smaller diameter (0.25mm versus 0.32mm) and is longer (100m versus 60m) than previous columns used for CSIC investigations at SEOS, in attempts to increase efficiency and associated peak resolution. Column efficiency is a description of its ability to separate and resolve compounds distinctly as a function of sample residence time (Bruno, 1991). Column diameter has an influence over parameters such as efficiency, retention capacity, carrier gas flow rate and column pressure. High column efficiency is beneficial since less peak separation is required to completely resolve narrow peaks. Narrower peaks mean higher resolution and less overlap (co-elution) of compound peaks.

Harris (1999) showed that the *Petrocol* column appeared to be more efficient at resolving a greater number of peaks; reducing co-elution of peaks of $CYC_5$ with $23DMC_4$ (peaks 4 and 5); $MCYC_5$ with $24DMC_5$ (peaks 10 and 11); and $MCYC_6$ with $1c2DMCYC_5$ and $EtCYC_5$ (peaks 25, 26 and 27) as observed in previous CSIC studies at SEOS (Murphy, 1994; Harris, 1999). Decreased co-elution and increased resolution of these peaks resulted in more reliable isotope ratio measurement of some additional individual gasoline-range compounds (Figure 2.7) in this present study. Due to low abundances of some compounds during the study (i.e., $CYC_5$, $24DMC_5$) and other factors, some additional compounds have unreliable isotope ratios. One disadvantage to the longer column was the chromatographic analyses required more time compared to the 60m predecessor, increasing run times to approximately 70 minutes (as per experimental column temperature and pressure regimes).

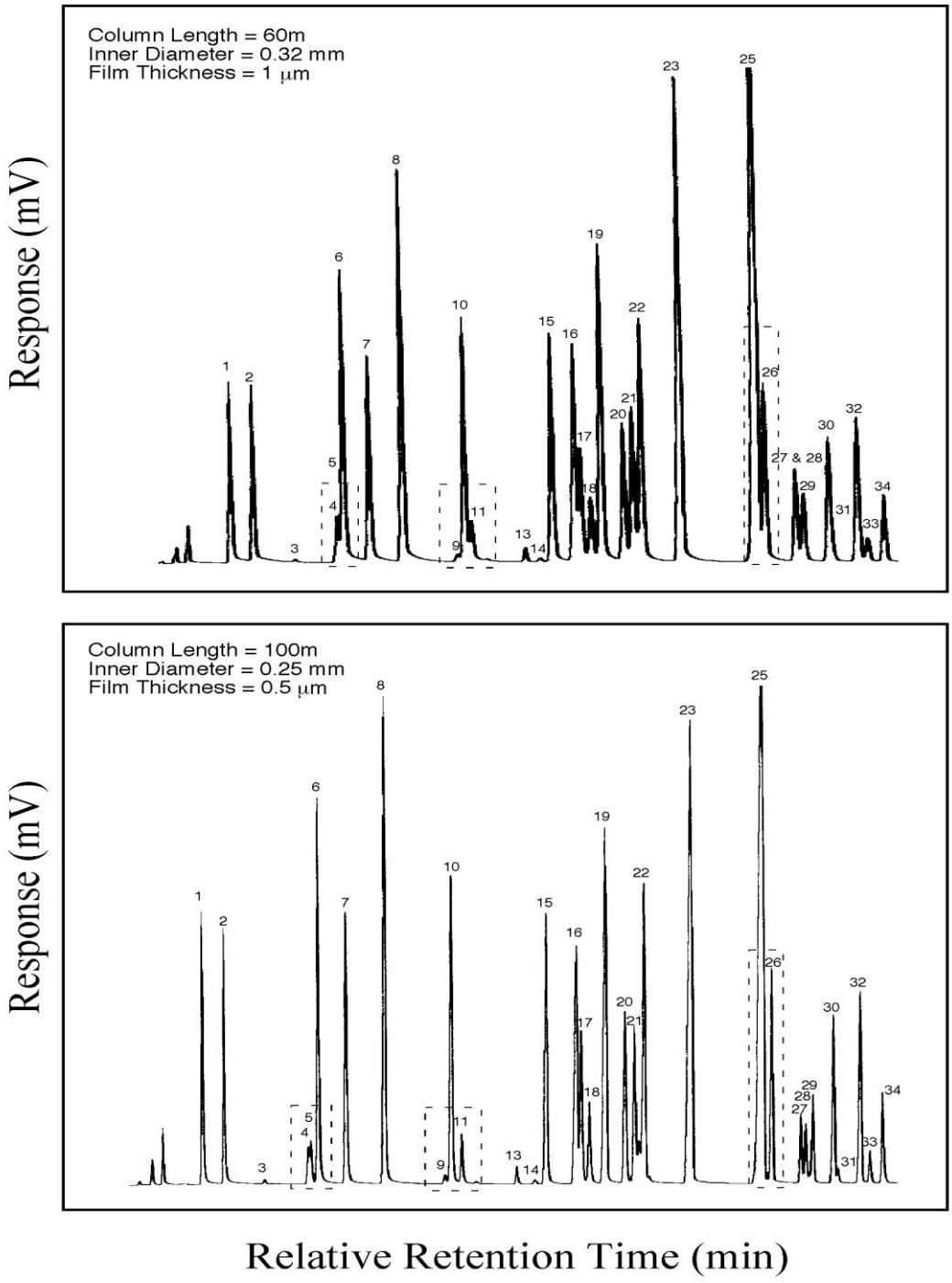



*Figure 2.7. Comparison of peak separation in Chester oil; 60m versus 100m Petrocol (Varian 3400 GC). Improved resolution is observed on Compounds $MCYC_5$ and $MCYC_6$. See table 3.1 for the corresponding peak names (after Harris, 1999).*

### 2.4.2 Gas Chromatographic Operating Conditions

***Column/Split Flows***

CF-IRMS requires a constant inert gas (helium) flow to carry the analytes through the GC column and to input into the GC injector split flow valve. The injector split flow is set to control the amount of sample applied to the column so as not to saturate the IRMS detector amplifiers. Harris (1999) experimented with column flow rates ranging from 1.8 to 3.0 mls/min (16–22 psi) on the SEOS CF-IRMS to test the effects of higher flow rate on combustion to $CO_2$ efficiencies. Since a much longer column was used in these experiments, 100m versus 60m, higher pressures were required. A flow rate of 2.8mls/min was adopted.

Injector split and column flows are checked prior to each run. Split flows are adjusted regularly, in order to account for the successive decreases in the concentration of the compounds as the time series evaporation progresses, maintaining a measureable range of analytes for the CF-IRMS detectors/amplifiers. For example, the $T_{0.5}$ samples injector split flow was adjusted to as high as 120 mls/min, $T_8$ samples may use 10 mls/min, while final analyses may use 0 mls/min.

Gas flows used for analyses were as follows:

- He through column : 2.8 mls/min
- Injector split : variable depending on GR concentrations
  : 40 mls/min unweathered droplet/vial samples
  : 0 – 120 mls for weathering experiments
- Open split flow : 3.0 mls/min

***Column heating protocol***

Column heating regimes are important in order to produce well partitioned and sharp peaks with minimum run time. Numerous column temperature programs, based on boiling points (see Table 2.3) were investigated in order to determine the parameters optimal to gasoline-range peak resolution on the *Petrocol* column for the types of oils used in this study. All unresolved compounds ($>C_{10}$) present on the GC column after the programmed run terminates, are automatically back flushed from the column prior to entering the combustion oven. This prevents unnecessary depletion of the limited amounts of oxygen available within the oven.

The column temperature program chosen was as follows:

- Initial column temperature : 30 $^{o}$C
- Column hold time : 1 min
- Temperature rate increase : 2 $^{o}$C/min
- Final column Temperature : 120 $^{o}$C
- Hold time : 1 min
- Temperature rate increase : 20 $^{o}$C/min
- Final temperature : 280 $^{o}$C
- Hold time : 15 min
- End time : 70 min

  Final column backflush

### 2.4.3 On-line Combustion Oven

Column helium flow carries the elutants to the on-line micro-combustion oven (Figures 2.6, 2.8). The oven consists of an alumino-silicate capillary tube containing a fine wire composed of copper and platinum. The resulting copper oxide is the source of oxygen for combustion, the platinum acts as a combustion catalyst. The oven was

operated at 850 $^{o}$C during CF-IRMS operation, producing a slow, continuous oxygen bleed for combustion. To conserve oxygen, the oven was turned down to 400 $^{o}$C when not in use. Low oxygen levels can result in incomplete combustion of the hydrocarbons which could lead to anomalous isotope measurements.

Oxygen levels in the oven are periodically replenished to ensure total combustion of all desired compounds, performed by reducing the temperature to 400 $^{o}$C, with an introduced oxygen stream overnight.

Eluted hydrocarbons entering the oven are oxidized into $CO_2$ and $H_2O$ (Figure 2.8). The combustion water is removed by a *Nafion* membrane water trap (Perma Pure™) prior to the $CO_2$ and helium entering the differentially-pumped IRMS. Water entering the ion source of the IRMS can react with $^{12}C^{16}O_2$ (mass 44) to form $^{1}H^{12}C^{16}O_2^{+}$ (mass 45), simulating the heavier $^{13}CO_2$ to produce artificially high $^{13}C/^{12}C$ ratios (Leckrone and Hayes, 1998).

### 2.4.4 Isotope Ratio Mass Spectrometer

The dynamic range of CF- IRMS system amplifiers is limited (approx. 0.35-7 Volts, mass 44 amu; equivalent to 1 to 10 nmoles of $CO_2$). Compounds must elute in amounts that produce a signal within this range for precise/reproducible carbon isotope ratio measurements . Compounds present in quantities outside the dynamic range of the detectors usually fail to produce reliable values (Whiticar and Snowdon, 1999). If the amount of sample is too low, it may not be detected. If the amount of sample is too high it will saturate the detectors or prematurely deplete oxygen in the combustion oven. Although many compound peaks are discerned on the chromatogram trace, only those

within the voltage limits of the detectors and that exhibit distinct peak baseline separation produce reliable values.

A reference $CO_2$ gas (with known proportions of mass/atomic number 44/45/46) is automatically injected into the IRMS before and after each sample run for internal calibration of the detector system. All isotope values are presented in delta (δ) notation as per mil (‰) differences from the lab standard gas, referenced to the V-PDB standard as described in the Introduction (Section 1.3.1).

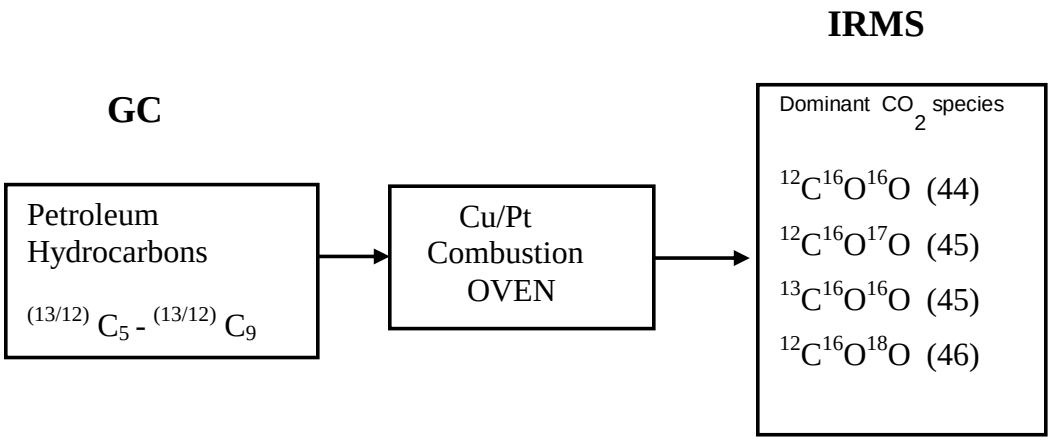



*Figure 2.8. Predominant $CO_2$ species analyzed in the IRMS*

## 2.5 REPRODUCABILITY

### 2.5.1 Data Sources

The main sources of data for the study are from the CF-IRMS instrumentation printed outputs; specifically the GC traces, peak amplitudes (Volts) and δ $^{13}C$ values for all resolvable gasoline-range compounds measured. With the exception of the daily Chester reference oil run , all of the δ $^{13}C$ data obtained from unweathered and weathering analyses are reported as the average δ $^{13}C$ values for triplicate CF-IRMS runs. This

involved a separate HSPME analysis from each one of three triplicate experiment jars for a given oil and time-series weathering period. All $\delta^{13}C$ values are stated relative to the V-PDB standard.

All of the standard deviations calculated for the data in this study are obtained using equation 2.1.

$$\text{standard deviation} = [(\sum (x_i - x)^2)/n-1]^{1/2} \qquad \text{(equation 2.1)}$$

where $x_i$ = individual data value

$x$ = mean

$n$ = number of data values

Errors associated with combining independent measurements such as those resulting from calculating the changes (differences) over time in $\delta^{13}C$ values ( $\Delta\delta^{13}C$) with associated errors are calculated using equation 2.2:

If two independent $\delta^{13}C$ measurements A and B, with errors $\Delta A$ and $\Delta B$, are combined, this gives the quantity $X$ which has the associated error $\Delta X$.

If $X = A - B$ ,

$$\text{then: } \Delta X = [(\Delta A)^2 + (\Delta B)^2]^{1/2} \qquad \text{(equation 2.2)}$$

### 2.5.2 Chester Reference Oil

Chester was used as the external laboratory reference oil (see section 2.1). The oil is stored at 3 $^{o}$C. Chester has an abundance of gasoline-range hydrocarbons typical of most light to medium crude oils (Figure 2.9). Each day the HSPME/IRMS analytical system is checked with at least one run of a fresh vial of Chester oil. The data outputs are viewed in attempt to ensure that resulting chromatogram peaks are well defined and carbon isotope ratio values are realistic. The instrumentation are also checked for system leaks and

sufficient oxygenation for the combustion of the target compounds. If chromatograms show poor peak resolution or anomalous isotope ratio values, necessary adjustments or repairs are performed and additional Chester test runs made prior to further analyses.

A total of 83 Chester runs were made over the study period, of which 46 verified operational instrumentation. Of these 46 runs, 37 runs corresponded to specific days or periods in which sample oils were also analyzed. Figure 2.9 shows a gas chromatogram of the standard Chester oil showing the typical gasoline-range peaks observed in both the standard and experimental oil chromatogram traces. Compound names associated with peak numbers are given in Table 2.4.

Many of numerous compound peaks in the GC trace (Figure 2.9) are not baseline resolved. Due to isotopic heterogeneity across an eluting peak (Matthews and Hayes, 1978; Ricci et al., 1994) compounds that have partial co-eluting compounds, and do not have baseline separation, typically do not have reliable isotope ratio measurements. As previously described, compounds present in quantities outside the instrument dynamic range (0.35V to 7V) do not yield useable isotope ratio values (Whiticar and Snowdon, 1999). For example, the $\delta^{13}C$ measurements on $CYC_5$ (peak 4) may be contaminated by $23DMC_4$ (peak 5) due to their poor separation as illustrated in Figure 2.9.

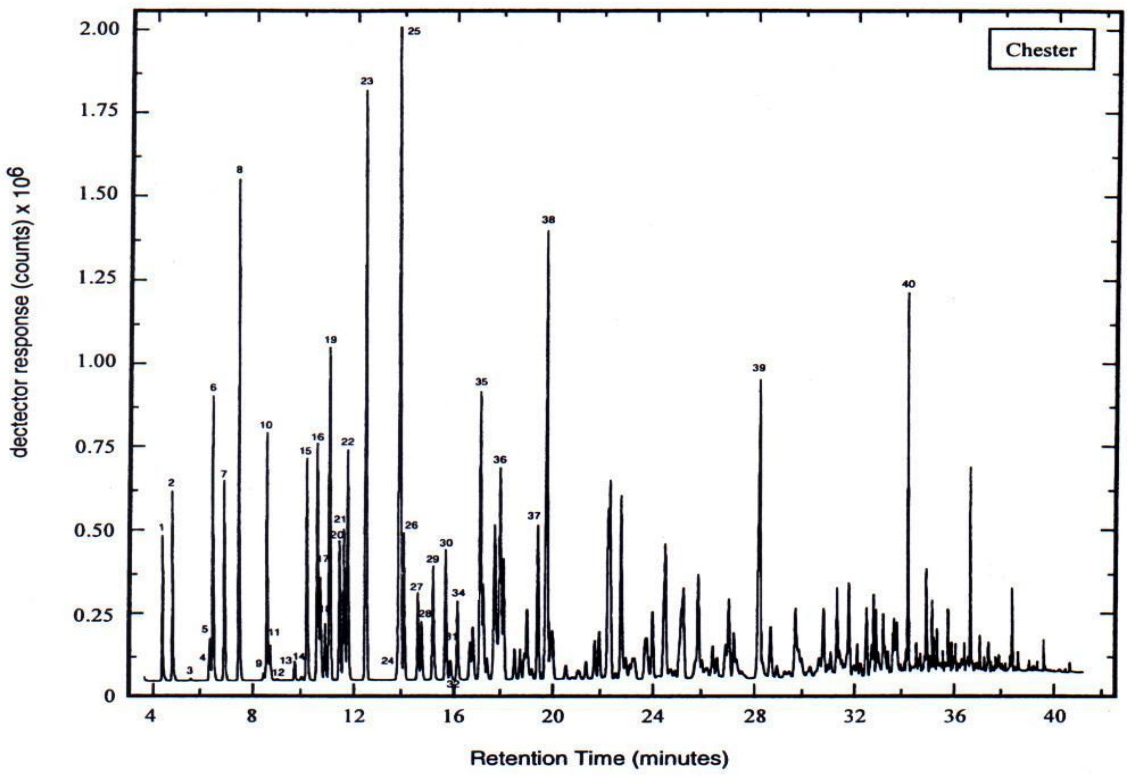



*Figure 2.9. Representative gasoline-range chromatogram of Chester laboratory reference oil sampled using HSPME (Harris,1999). Peak numbers and specific peaks identified for isotopic analysis are listed in Table 2.4.*

Although a total of 27 compound peaks are reliably resolved in the Chester reference oil, only those compounds consistently resolved in all study oils are used in order to provide a reference for normalization of experimental runs, discussed further in the next section. The oils being measured have different physicochemical properties and therefore may have different analytical characteristics, wherein various compounds are not consistently measurable in all 3 study oils for all time-series sampling periods.

*Table 2.4. List of compounds and associated peak numbers shown in Figure 2.9. Those compounds with reliable values in at least one oil are highlighted.*

| Compound | Abbreviation | Chemical name |
|---|---|---|
| 1[a.b.] | **i**$C_5$ | **iso-pentane** |
| 2[a.b.] | **n**$C_5$ | **n-pentane** |
| 3 | 22DM$C_4$ | 2,2-dimethylbutane |
| 4 | CY$C_5$ | cyclopentane |
| 5 | 23DM$C_4$ | 2,3-dimethylbutane |
| 6[a.b.] | **2M**$C_5$ | **2-methylpentane** |
| 7[a.b.] | **3M**$C_5$ | **3-methylpentane** |
| 8[a.b.] | **n**$C_6$ | **n-hexane** |
| 9 | 22DM$C_5$ | 2,2-dimethylpentane |
| 10[a.b.] | **MCY**$C_5$ | **methylcyclopentane** |
| 11 | 24DM$C_5$ | 2,4-dimethylpentane |
| 12 | 223TM$C_4$ | 2,2,3-trimethylbutane |
| 13 | Benz | benzene |
| 14 | 33DM$C_5$ | 3,3-dimethylpentane |
| 15[a.b.] | **CY**$C_6$ | **cyclohexane** |
| 16[a.b.] | **2M**$C_6$ | **2-methylhexane** |
| 17[a.] | **23DM**$C_5$ | **2,3-dimethylpentane** |
| 18[a.b.] | **11DMCY**$C_5$ | **1,1-dimethylcyclopentane** |
| 19[a.b.] | **3M**$C_6$ | **3-methylhexane** |
| 20[a.b.] | **1c3DMCY**$C_5$ | **1-cis-3-dimethylcyclopentane** |
| 21[a.b.] | **1t3DMCY**$C_5$ | **1-trans-3-dimethylcyclopentane** |
| 22[a.b.] | **1t2DMCY**$C_5$ | **1-trans-2-dimethylcyclopentane** |
| 23[a.b.] | **n**$C_7$ | **n-heptane** |
| 24 | 22DM$C_6$ | 2,2-dimethylhexane + co-elute |
| | 113TMCY$C_5$ | 1,1,3 trimethylcyclopentane (minor) |
| 25[a.b.] | **MCY**$C_6$ | **methylcyclohexane** |
| 26[a] | **1c2DMCY**$C_5$ | **1-cis2-dimethylcyclopentane** |
| 27[a.b.] | **EtCY**$C_5$ | **ethylcyclopentane** |
| 28[a.b.] | **25DM**$C_6$ | **2,5-dimethylhexane** |
| 29[a] | **24DM**$C_6$ | **2,4-dimethylhexane** |
| 30[a] | **1t2c4TMCY**$C_5$ | **1-trans-2-cis-4-trimethylcyclopentane** |
| 31 | 33DM$C_6$ | 3,3-dimethylhexane |
| 32 | 1t2c3TMCY$C_5$ | 1-trans-2-cis-3-trimethylcyclopentane |
| 33 | 223TMCY$C_6$ | 2,2,3-trimethylcyclohexane (minor) |
| 34[a.b.] | **Toluene** | **toluene** |
| 35[a.b.] | **2M**$C_7$ | **2-methylheptane** |
| 36[a.b.] | **3M**$C_7$ | **3-methylheptane** |
| 37[a.b.] | **1c4DMCY**$C_6$ | **1-cis-4-dimethylcyclohexane** |
| 38[a.b.] | **n**$C_8$ | **n-octane** |
| 39[a.b.] | **n**$C_9$ | **n-nonane** |

[a] Results recorded for a maximum of 27 specific compounds between $C_5$ and $C_9$ based on high resolution and abundances in the series of sample oils Alberta and Lacula during the initial un-weathered analyses.

[b] Results recorded as above for a maximum of 23 specific compounds in Louisiana oil.

### 2.5.3 Normalization Using Chester Oil Reference

Changes in the instrumental operating conditions lead to detectable variations in the isotope ratio measurement output of the IRMS software. IRMS carbon isotope ratio value outputs for resolvable compounds in the Chester standard did vary slightly outside the expected level of precision for the unweathered oils in instances throughout the study. Although the reasons for the variations in data output are generally undetermined, $\delta^{13}C$ output values at one point suddenly were observed to be generally more negative (depleted in $^{13}C$) by about -1.5‰ relative to the initially established Chester reference oil $\delta^{13}C$ values. The instrumentation shift or difference was not consistent for all compounds during the IRMS runs.

In order to correct for the instrumentation shift, all isotope values obtained for the weathered oil CF-IRMS runs are normalized to a Chester reference (referred to as Chester A for this explanation), based on the isotopic values obtained for initial Chester reference oil prior to observed instrumentation shifts. Chester A is established by determining the average $\delta\ ^{13}C$ values for the resolvable gasoline-range compounds in 19 runs of the initial Chester. The differences (offsets) between compound $\delta\ ^{13}C$ values obtained for the 19 pre and 18 post instrumentation shift Chester runs are calculated to obtain the numerical offsets necessary to apply to each compound in the experimental runs to correct for instrumentation output shift. Since a Chester reference oil was run prior to all experimental runs on any given day, each set of compound offsets is applied to the specific day (and instrumentation conditions ) or series of study oil IRMS runs.

Figure 2.10 shows the averaged $\delta\ ^{13}C$ values for the 27 resolvable compounds in the Chester A and post shift Chester (referred to as Chester B) reference oil. Standard deviations for resolvable compounds in Chester A over a 10 month period ranged from ±

0.3 ‰ ($iC_5$, $nC_5$) to as much as ± 1.6 ‰ ($23DMC_5$, $1c2DMCYC_5$). Table 2.5 lists the averaged values of the compounds in Chester A with their associated standard deviations. Chester A will be referred to simply as Chester in the remaining chapters of this study.

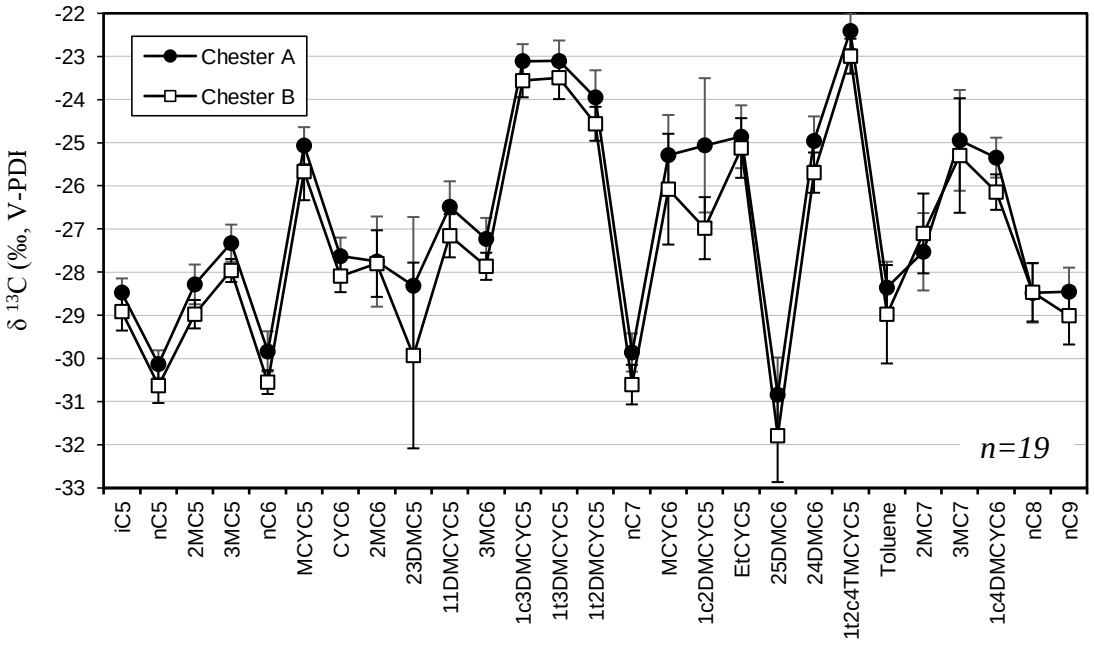



*Figure 2.10. Instrumentation differences between the average compound δ $^{13}C$ values obtained for Chester reference oil.*

Some examples of the isotope ratio variability observed in the Chester (A and B) $\delta^{13}C$ values are shown in the Figures 2.11-2.13. The figures include $\delta^{13}C$ values for compounds from various n-alkanes, iso-alknes, cyclic and aromatic compounds.

*Table 2.5. Average δ13C values and standard deviations for individual gasoline-range compounds for the Chester A oil reference.*

| Peak No. | Compound | Chester A Average $\delta\ ^{13}C$ $n = 19$ | Chester A Standard Deviation $n = 19$ |
|---|---|---|---|
| 1 | $iC_5$ | -28.5 | 0.3 |
| 2 | $nC_5$ | -30.1 | 0.3 |
| 6 | $2MC_5$ | -28.3 | 0.5 |
| 7 | $3MC_5$ | -27.3 | 0.4 |
| 8 | $nC_6$ | -29.8 | 0.5 |
| 10 | $MCYC_5$ | -25.1 | 0.4 |
| 15 | $CYC_6$ | -27.6 | 0.4 |
| 16 | $2MC_6$ | -27.8 | 1.1 |
| 17 | $23DMC_5$ | -28.3 | 1.6 |
| 18 | $11DMCYC_5$ | -26.5 | 0.6 |
| 19 | $3MC_6$ | -27.2 | 0.5 |
| 20 | $1c3DMCYC_5$ | -23.1 | 0.4 |
| 21 | $1t3DMCYC_5$ | -23.1 | 0.5 |
| 22 | $1t2DMCYC_5$ | -24.0 | 0.6 |
| 23 | $nC_7$ | -29.9 | 0.4 |
| 25 | $MCYC_6$ | -25.3 | 0.9 |
| 26 | $1c2DMCYC_5$ | -25.1 | 1.6 |
| 27 | $EtCYC_5$ | -24.9 | 0.7 |
| 28 | $25DMC_6$ | -30.8 | 0.9 |
| 29 | $24DMC_6$ | -25.0 | 0.6 |
| 30 | $1t2c4TMCYC_5$ | -22.4 | 0.4 |
| 34 | Toluene | -28.4 | 0.6 |
| 35 | $2MC_7$ | -27.5 | 0.9 |
| 36 | $3MC_7$ | -25.0 | 1.2 |
| 37 | $1c4DMCYC_6$ | -25.4 | 0.5 |
| 38 | $nC_8$ | -28.5 | 0.7 |
| 39 | $nC_9$ | -29.0 | 0.7 |

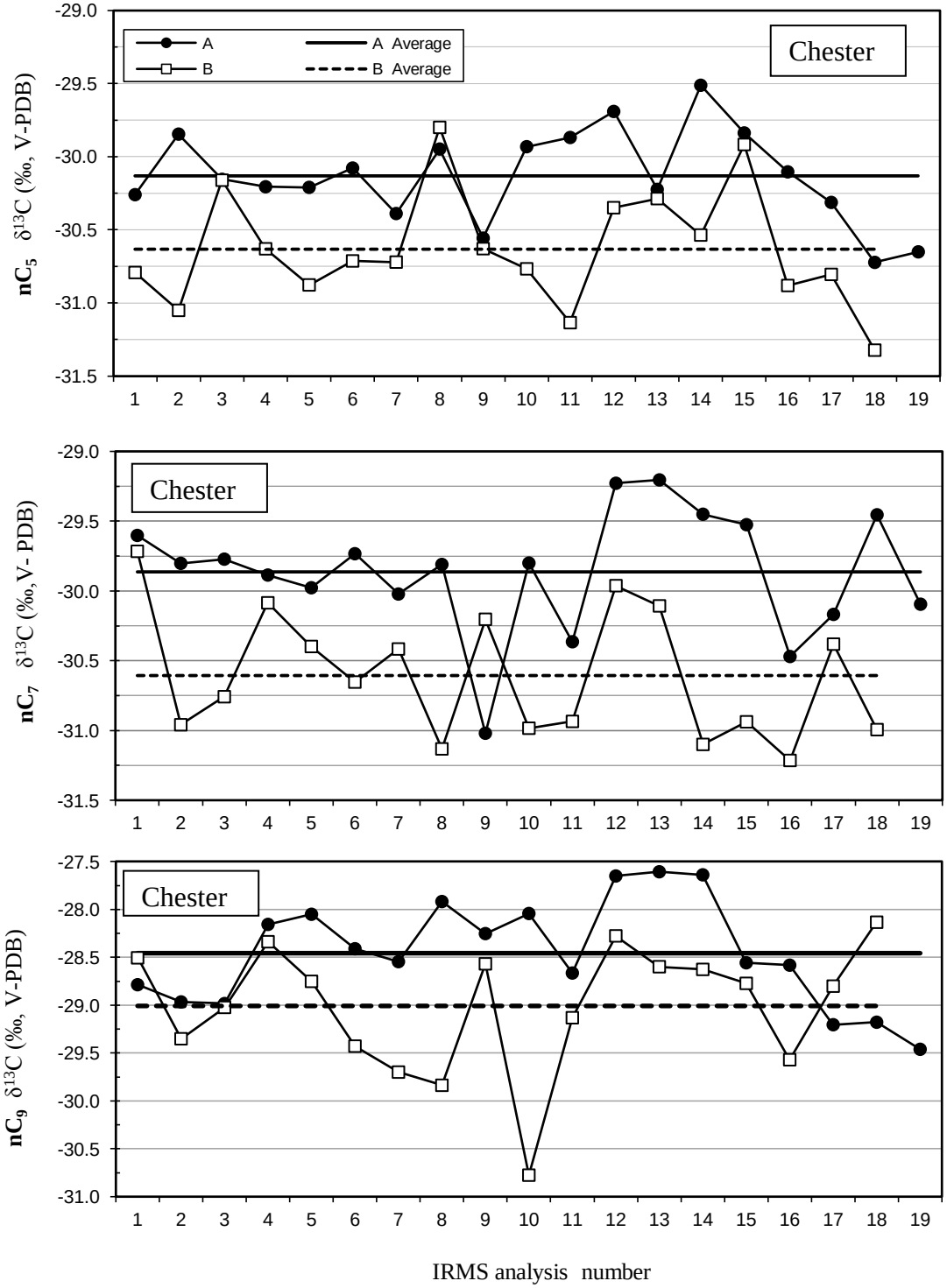



*Figure 2.11. Instrument variability in $\delta^{13}C$ values between Chester (A and B) reference oil for various n-alkanes.*

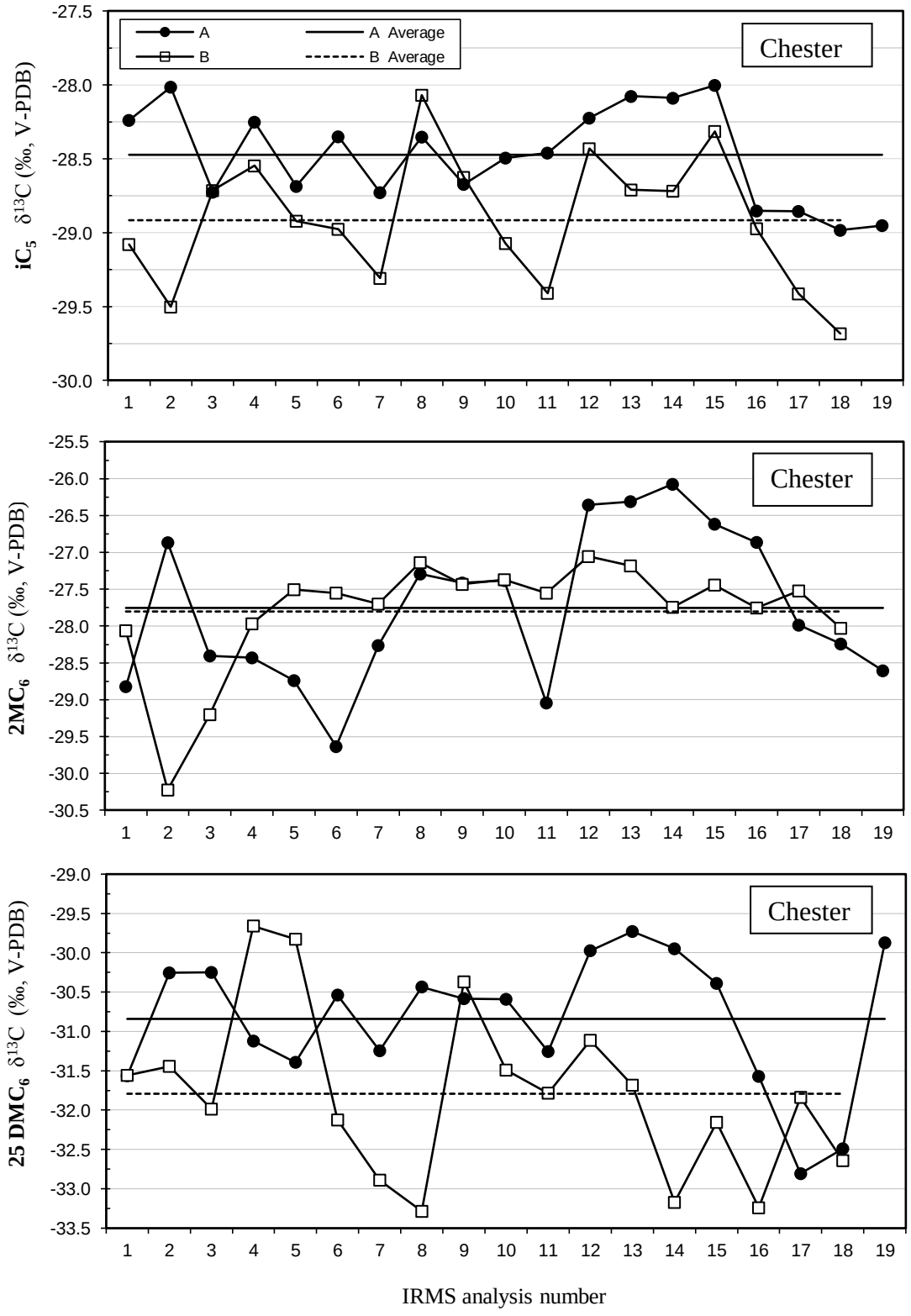



*Figure 2.12. Instrument variability in $\delta^{13}C$ values between Chester (A and B) reference oil for various iso/branched alkanes.*

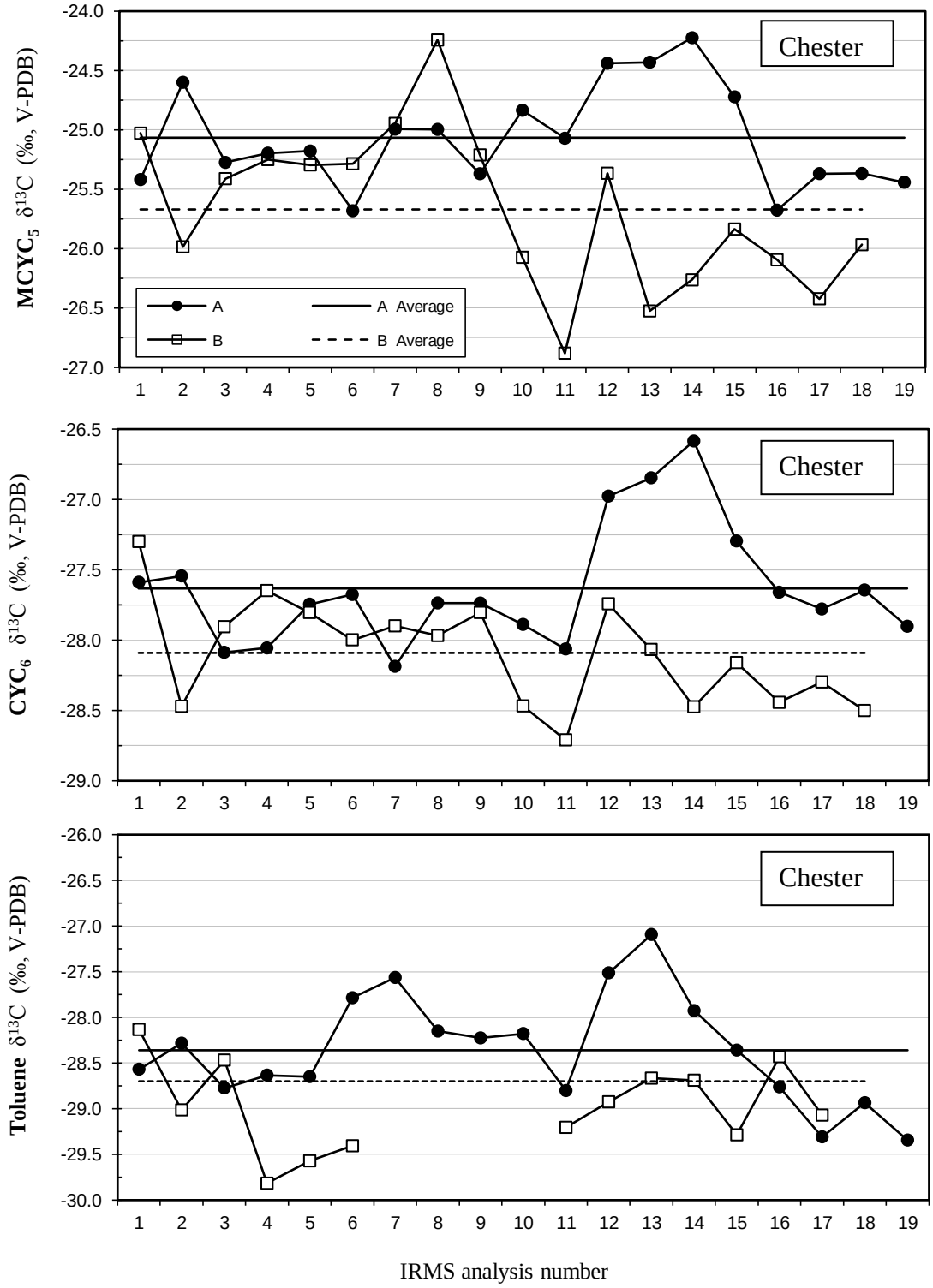



*Figure 2.13. Instrument variability in δ $^{13}$C values between Chester (A and B) reference oil for various cyclic alkanes and toluene.*

# CHAPTER 3. RESULTS

## 3.1 UNWEATHERED OILS

Copies of the gas chromatograms (GCs) produced by the CF-IRMS analysis for each of the unweathered ($T_0$) oil samples are presented in Figures 3.1a-c. The GC traces show the differences in initial gasoline-range compound abundances between the 3 oils. Although a full range of compounds are represented by the peaks on the traces, many are not resolved to baseline, limiting the ability of the CF-IRMS software to produce a reliable molecular or isotopic signature. As previously mentioned, as a general rule, all samples analyzed by GC-C-IRMS have to be within a certain size range for detection (equivalent to 1 to 10 nmoles of $CO_2$; 0.35 -7 Volts). Amounts of sample too low go undetected, amounts too high lead to anomalous results. Peaks exhibiting poor baseline separation resulting from co-elution or insufficient partitioning of adjacent hydrocarbon compounds result in a blending of isotopic signatures within the data processing software, also producing imprecise or unreliable values

The three small compound peaks occurring prior to $iC_5$ in the three initial oil headspaces (Figure 3.1) were not characterized due to their rapid evaporation rates, exhibiting below threshold or undetectable abundances within 0.5 hours of simulated weathering.

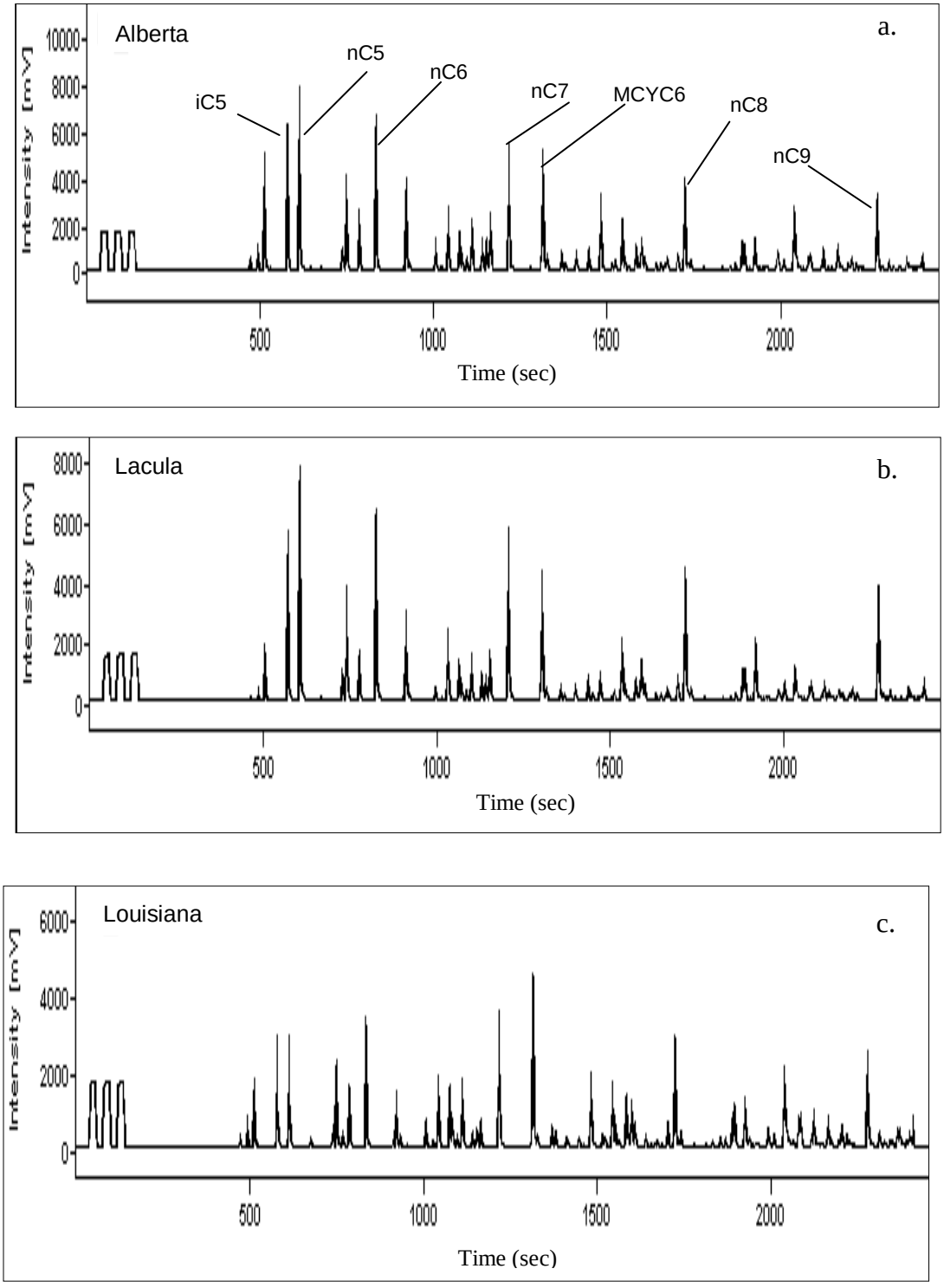



*Figure 3.1. Chromatograms of HSPME samples from the three unweathered oils showing the variability in concentrations of gasoline-range fractions within an oil. a) Alberta; b) Lacula; c) Louisiana.*

All three oils differed in their abundances of the measured gasoline-range fractions, most noticeably with Louisiana having lesser amounts of the lighter end peaks (ie. $iC_5$, $nC_5$) compared to the Alberta or Lacula oils. Refer to Table 2.1 for the chemical and physical properties of the three study oils.

Figures 3.2 through 3.5 are referred to as "*isotopograms*" (Whiticar and Snowdon, 1999) and display the carbon isotope ratio signatures of the three unweathered oils. A total of 27 gasoline-range compounds in the unweathered Alberta and Lacula oils and 23 in Louisiana are characterized based on their carbon isotope ratios. The compounds $23DMC_5$ (peak 17), $1c2DMCYC_5$ (peak 26), $24DMC_6$ (peak 29) and $1t2c4TMCYC_5$ (peak 30) were not diagnostically reliable consistently throughout the Louisiana trials.

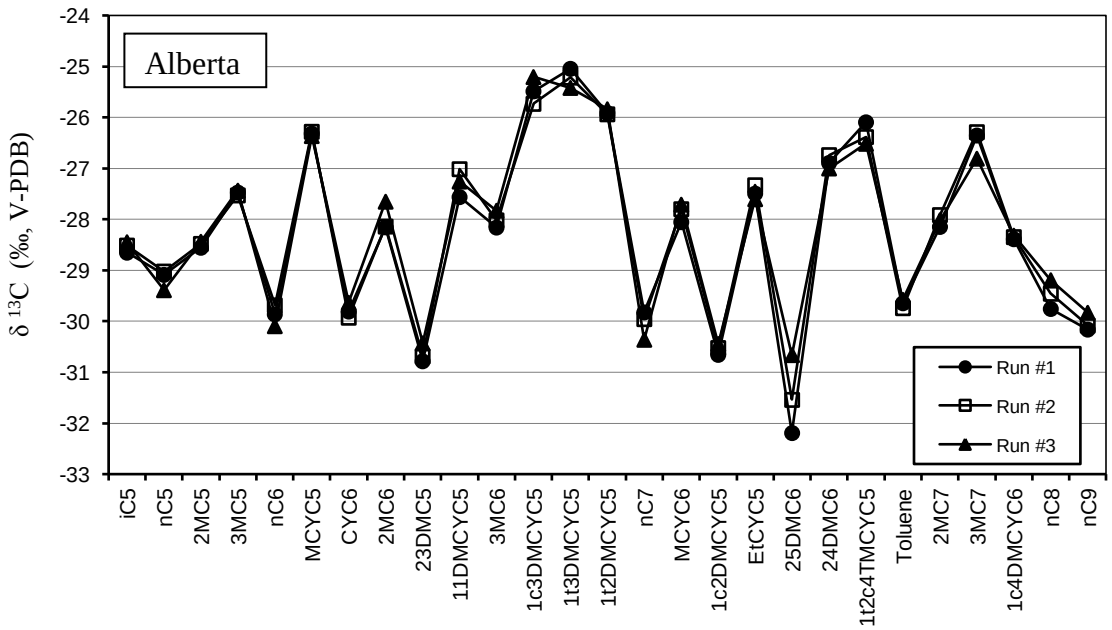



*Figure 3.2. $\delta^{13}C$ values for resolvable gasoline-range compounds in triplicate runs of unweathered ($T_0$) Alberta Oil.*

Compounds identified in the Alberta oil show good repeatability in $\delta^{13}C$ values obtained from three runs. All compounds but $25DMC_6$ have a standard deviation of lower

than ±0.3 ‰. Due to an initially high (120 mls/min) injector split flow being required to capture the full range of compounds in a single CF-IRMS run, the initial molecular abundance of $25DMC_6$ was near the lower IRMS range limits (0.37 volts) which may have caused the larger uncertainties ( ±0.8 ‰). As injector split flows were decreased to 40 mls/min at the $T_1$ samples, molecular abundances of $25DMC_6$ increased to reliably measurable levels with a resulting standard deviation of ± 0.4‰ for the triplicate runs.

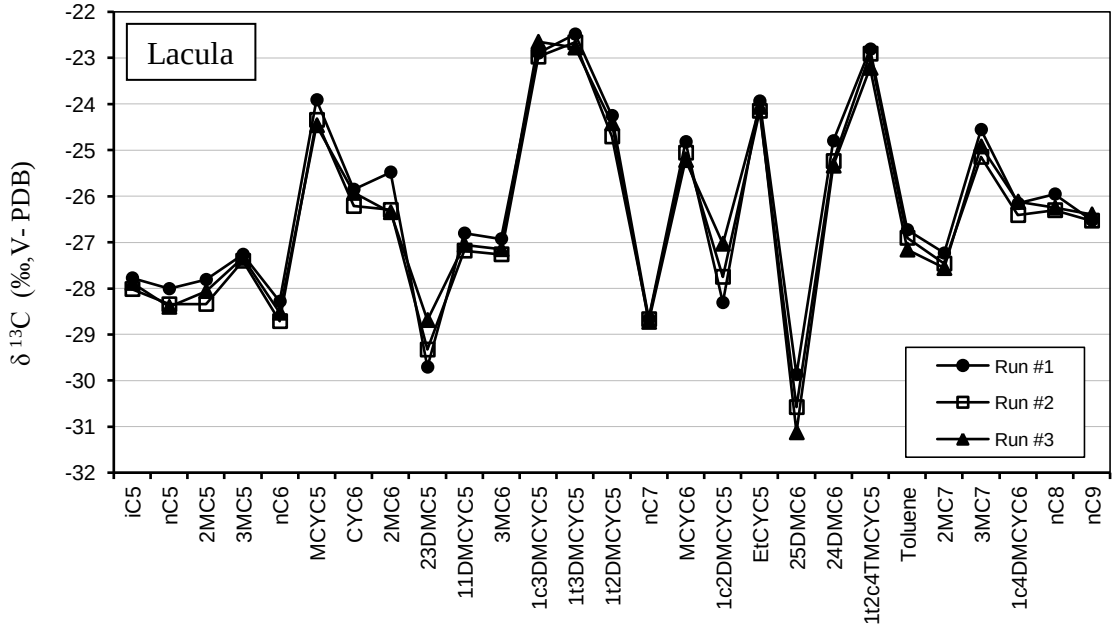



*Figure 3.3. $\delta^{13}C$ values for resolvable gasoline-range compounds in triplicate runs of unweathered ($T_0$) Lacula Oil.*

Compounds in the Lacula oils also show good repeatability over the three unweathered runs, with all compounds but four having a standard deviation of less than ± 0.3‰ (Figure 3.3). $2MC_5$ and $2DMC_5$ both show a standard deviation of ±0.5‰; $1c2DMCYC_5$ and $25DMC_6$ show variations of ±0.6‰. As in the unweathered Alberta oil runs, the necessary high injector split flows for the Lacula analyses resulted in diagnostically marginal molecular abundances for $25DMC_6$.

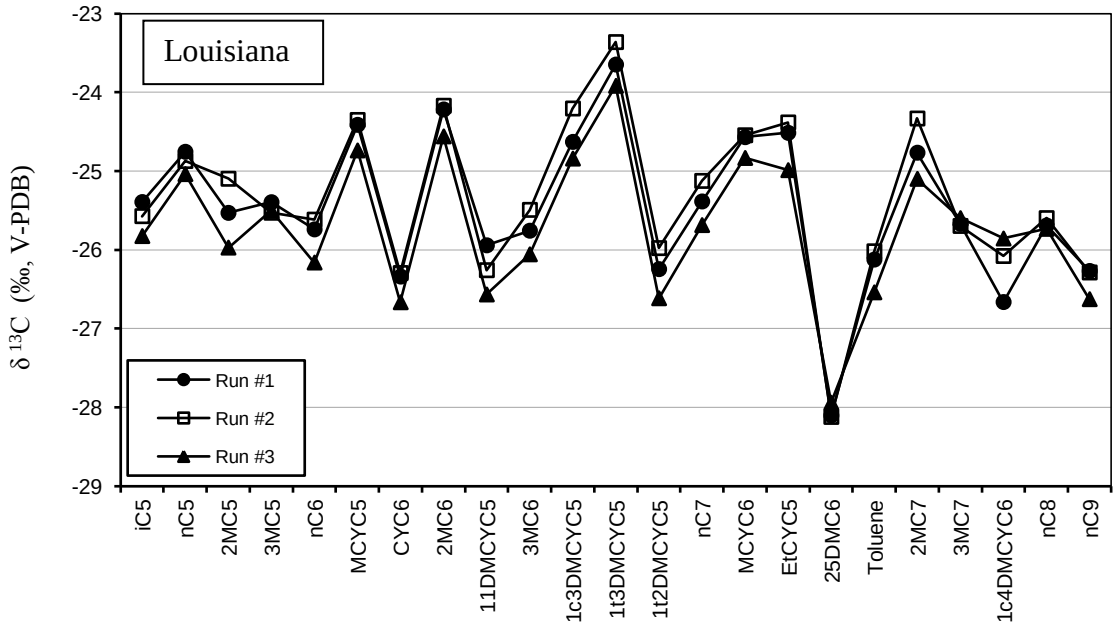



*Figure 3.4. $\delta^{13}C$ values for resolvable gasoline-range compounds in triplicate runs of unweathered ($T_0$) Louisiana Oil.*

Good repeatability is also shown in the 23 unweathered Louisiana oil measurements, with the compounds $2MC_5$, $2MC_7$ and 1c4DMCY$C_6$ having a standard deviation of ±0.4‰, all others show a standard deviation of ± 0.3‰ or less.

Based on the unweathered oil $\delta^{13}C$ values, and associated precision, the isotopograms show that the 3 oils are isotopically different for 17 of the resolvable study compounds (Figure 3.5). Generally, the measured compounds in the Alberta oil appear to be isotopically lighter (more depleted in $^{13}C$), having 22 of the 27 resolvable compounds less enriched in $^{13}C$ than the other two oils. The $\delta^{13}C$ values for Alberta compounds ranged from -31.5 ‰ ($25DM_6$) to -25.2 ‰ (1t3DMCY$C_5$), exhibiting a overall range of 6.3‰. Louisiana was observed to be generally heavier, with 13 of 23 compounds more enriched in $^{13}C$ than the other two oils. Louisiana $\delta\ ^{13}C$ values ranged from -28.1‰ ($25DMC_6$) to -23.6 ‰ (1t3DMCY$C_5$) for an overall range of 4.5‰.

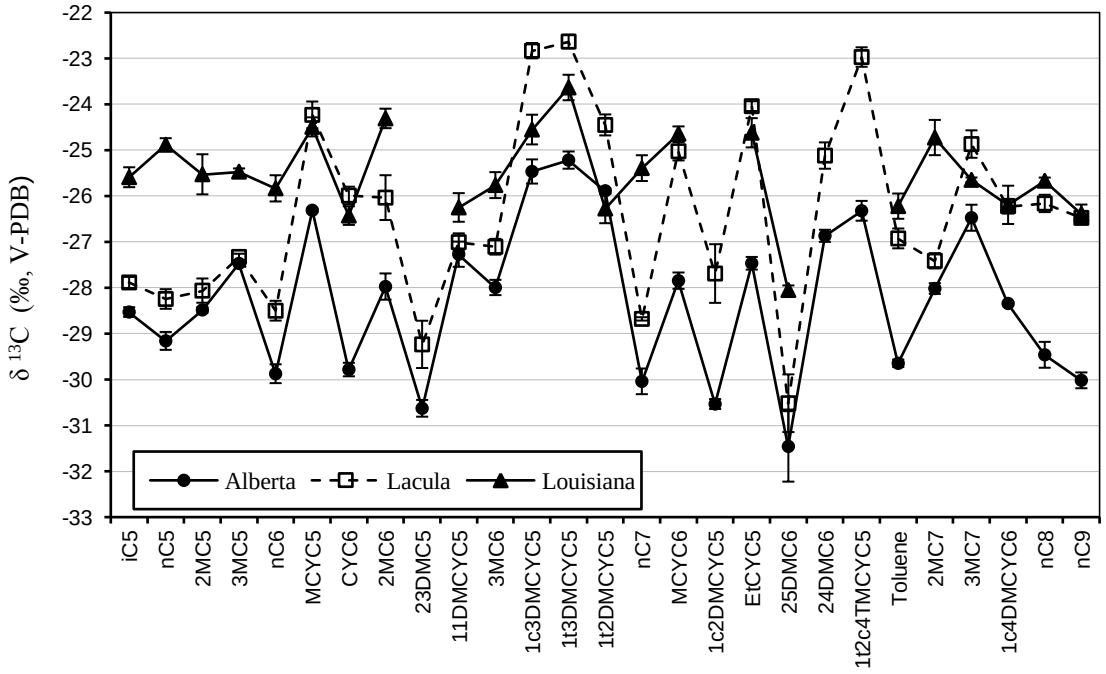



*Figure 3.5. $\delta^{13}C$ values for resolvable gasoline-range compounds in the 3 unweathered ($T_0$) study oils.*

The most $^{13}C$ enriched of all $\delta^{13}C$ measurements in the study are observed in the Lacula oil, with 6 compounds being more $^{13}C$-enriched than those in the other two oils, i.e., $1c3DMCYC_5$, $1t3DMCYC_5$. $1t2DMCYC_5$, $24DMC_6$, $1t2c4TMCYC_5$ and $3MC_7$. As observed in the other 2 oils, the compounds $25DMC_6$ (-30.5‰) and $1t3DMCYC_5$ (-22.6‰) in the Lacula oil also showed the largest overall isotopic range (7.9‰) between individual compounds.

## 3.2 RESULTS OF TIME SERIES WEATHERING EXPERIMENTS

### 3.2.1 Molecular Abundance Changes

This study focuses primarily on stable carbon isotope signatures and measured changes in the individual gasoline-range compounds of oils over time, however there is additional diagnostic value in observing the molecular abundance changes in the gasoline-range compounds. As mentioned in the introduction, traditionally molecular abundance changes are used to identify and characterize the weathering of oils (GC). The calculated changes in the compound abundances associated with evaporation of oils, investigated here, provides information regarding the variability of weathering patterns and any associated changes in isotopic composition over time in different oils. Furthermore, it is important to monitor the compound abundances to ensure sufficient quantities for reliable CF-IRMS measurements.

Weathering of the Alberta and Louisiana oils proceeded until the compounds $iC_5$ and $nC_5$ diminished to concentrations below the analytical limit of the IRMS. Louisiana oil exhibited the most rapid loss of after only 2 hours of weathering in the environmental chamber; in Alberta these compounds are measurable up to approximately 12 hours of weathering. The Lacula oil headspace continued to have concentrations of $iC_5$ and $nC_5$ near 60% of IRMS detector limits after 20 hours of weathering even with an injector split flow dilution.

Factors such as the use of varying injector split flow dilutions, difficulties associated with calculating the absolute concentrations of compounds absorbed onto the SPME fiber and calculating mass loss in an water-oil mixture, require that molecular amounts be presented as “normalized abundances”. Normalized abundances are calculated by

comparing measured IRMS detector voltage outputs for the individual compounds in each run, to those measured for $nC_9$, a compound with the lowest vapour pressure and assumed to have the least abundance change over the trial periods. Normalized abundances are expressed as the numerical ratio representing the abundance relative to $nC_9$ ($[C_x]/[nC_9]$) in an individual IRMS analysis. Depending on the individual compound, normalized abundance is either less than, equal to, or greater than 1; $nC_9$ always having an abundance of 1. Although imprecise, the method does provide successive values of molecular abundance losses over time for interpretation and comparison of compound abundance changes. The method unfortunately excludes the calculation of any abundance changes in the compound $nC_9$. Carbon isotope ratio measurements are unaffected.

Relative abundances, wherein the percentage of a particular compound IRMS detector voltage output relative to the total of all compound outputs in a sample, were considered for monitoring molecular abundance changes, but abandoned due to the inverse relationship between the changes observed in the lower molecular weight, more volatile components (e.g. $nC_5$, $nC_6$) and those of the heavier compounds (e.g. $nC_8$, $nC_9$) as evaporation progressed. Relative abundance values of the lower molecular weight compounds do decrease with time but higher molecular weight values begin to increase as they gradually constitute more of a fraction of the remaining oil. Comparison of the results of calculating abundances using relative abundance (% of total) and abundance normalized to $nC_9$ are shown in Figures 3.6a and b respectively. The abundance normalized to $nC_9$ method is clearly more representative of the actual abundance decreases in the oil over the course of evaporation. From this point in this thesis, abundances normalized to $nC_9$ will be referred to simply as abundances.

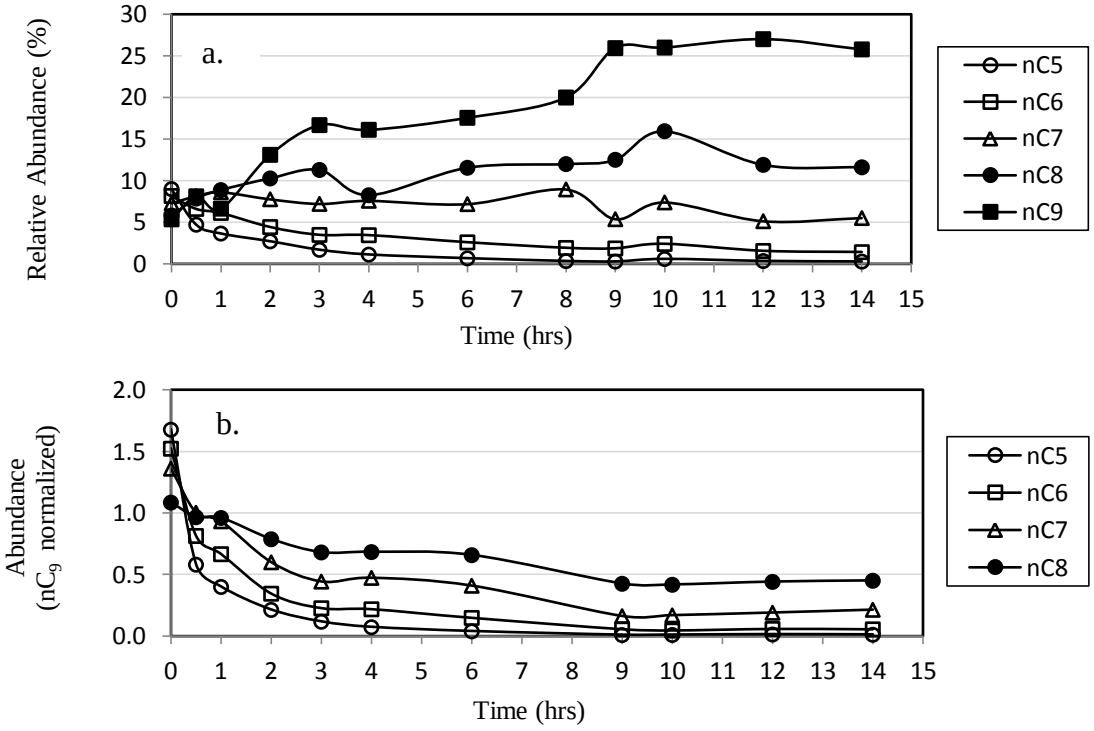



*Figure 3.6. Comparison of plots using a.) relative abundance (% of total sample) and b.) abundance normalized to $nC_9$.*

### *3.2.1.1 Alberta Sweet Mix Blend*

Figure 3.7 shows the change in abundance of headspace compounds in the Alberta oil over 14 hours of weathering. Due to a large range in compound concentrations in the $T_8$ samples, IRMS detector exceedences prohibited values for this sampling event being included in Figure 3.7.

Compounds $iC_5$, $nC_5$, $nC_6$, $nC_7$, $MCYC_6$ and $nC_8$ show abundances larger than 1 (the value of assigned to $nC_9$) in the unweathered signature, characteristics supported by compound peak (molecular abundances) distributions shown on the unweathered Alberta GC trace (Figure 3.1a). A significant decrease (i.e. average 78%) in abundance is shown in all compounds after 14 hours of weathering.

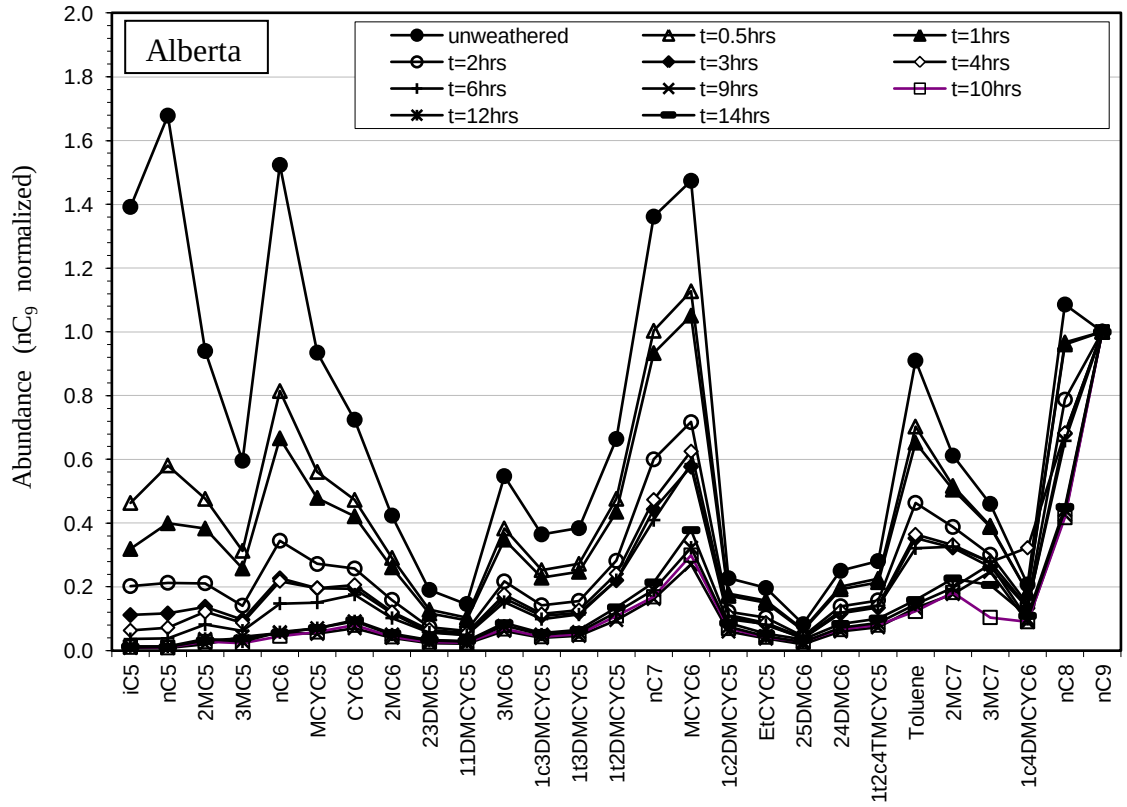



*Figure 3.7. Changes in abundances of gasoline-range compounds in Alberta oil over 14 hours of experimental weathering.*

Abundance losses at 14 hours range from greater than 99% ($iC_5$, $nC_5$) to approximately 47% in $1c4DMCYC_6$ (Figure 3.7). All compounds eluting up to and including $2MC_6$ decreased by at least 90%. The compound $nC_8$ decreased in abundance by approximately 59 %. The higher molecular weight compounds $nC_7$ and $MCYC_6$, present in larger molecular abundances in the unweathered oil, show overall decreases of 84% and 74% respectively. Figure 3.8 illustrates the amount of abundance decrease in Alberta compounds after 14 hours of evaporative weathering.

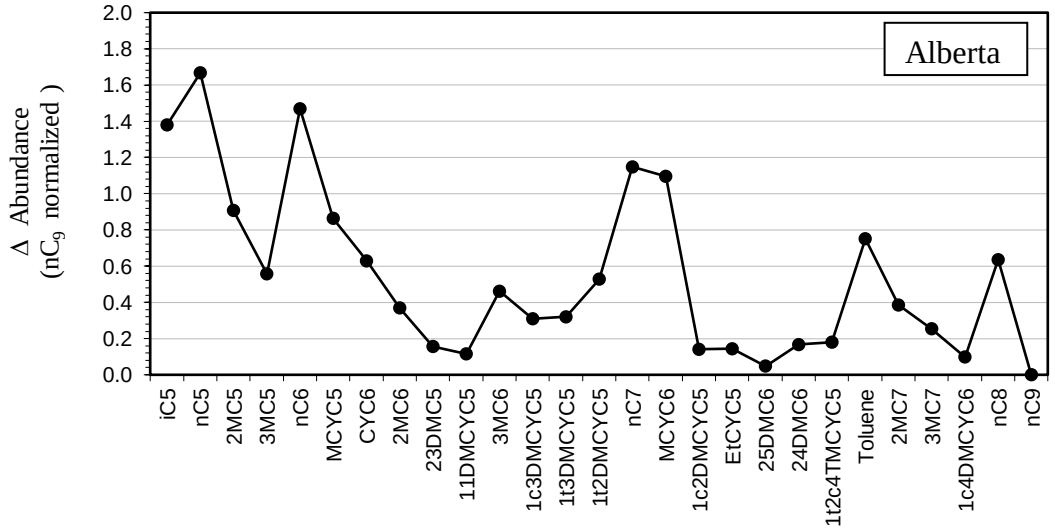



*Figure 3.8. Amount of decrease in abundance of Alberta headspace compounds after 14 hours of experimental weathering.*

Abundance changes in the Alberta oil over time for the various chemical classes of compounds; alkanes (paraffins), cycloalkanes (naphthenes) and the aromatic hydrocarbon toluene are shown in Figure 3.9 a through d.

Rapid decreases in abundances are seen in the compounds $iC_5$ (67%) and $nC_5$ (65%) in the first 0.5 hours (Figure 3.9a and b). Compounds $2MC_5$, $3MC_5$ and $nC_6$ also show rapid decreases of 49%, 47% and 47% respectively in the $T_{0.5}$ sampling. In comparison, the higher molecular weight $1c4DMCYC_6$ and $nC_8$ decreased by approximately 11% in the same period. At $T_3$ $iC_5$ and $nC_5$ have a greater than 90% decrease in abundances. In all of the classes shown, the highest rate of decreases in most compounds occurred in the first 3 hours. All compounds eluting up to and including $nC_6$ had decreased abundance values greater than 90% at $T_6$. Despite decreases in abundance by over 90% by $T_9$, $iC_5$ and $nC_5$ were present in enough quantity for reliable isotopic measurement up to 12 hours.

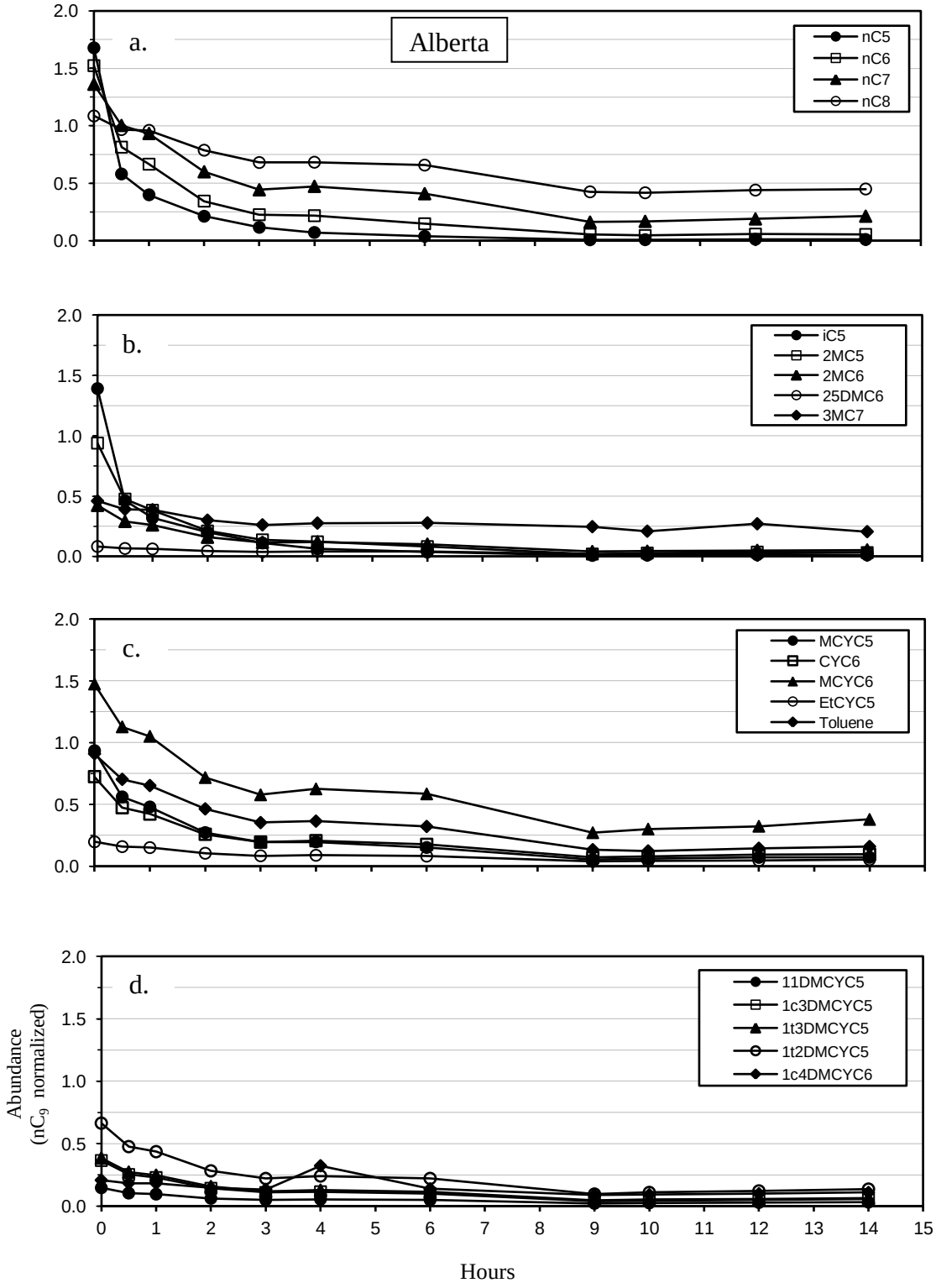



*Figure 3.9. Abundance vs weathering periods for gasoline-range compounds in Alberta oil. a.) n-alkanes; b.) branched alkanes; c and d) cyclic alkanes/aromatic.*

### *3.2.1.2 Lacula*

Figure 3.10 shows the change in abundance of headspace compounds in the Lacula oil at sampled intervals throughout 20 hours of weathering. As observed in the original GC trace (Figure 3.1 b), the compounds $iC_5$, $nC_5$, $nC_6$, $nC_7$, $MCYC_6$ and $nC_8$ all show high abundances in the unweathered trace on Figure 3.10.

Unlike the Alberta oil, Lacula still had comparatively larger abundances of all measured gasoline- range compounds in the headspace at $T_{20}$. In addition the $T_{20}$ samples are diluted with a 16 mls/min injector split flow.

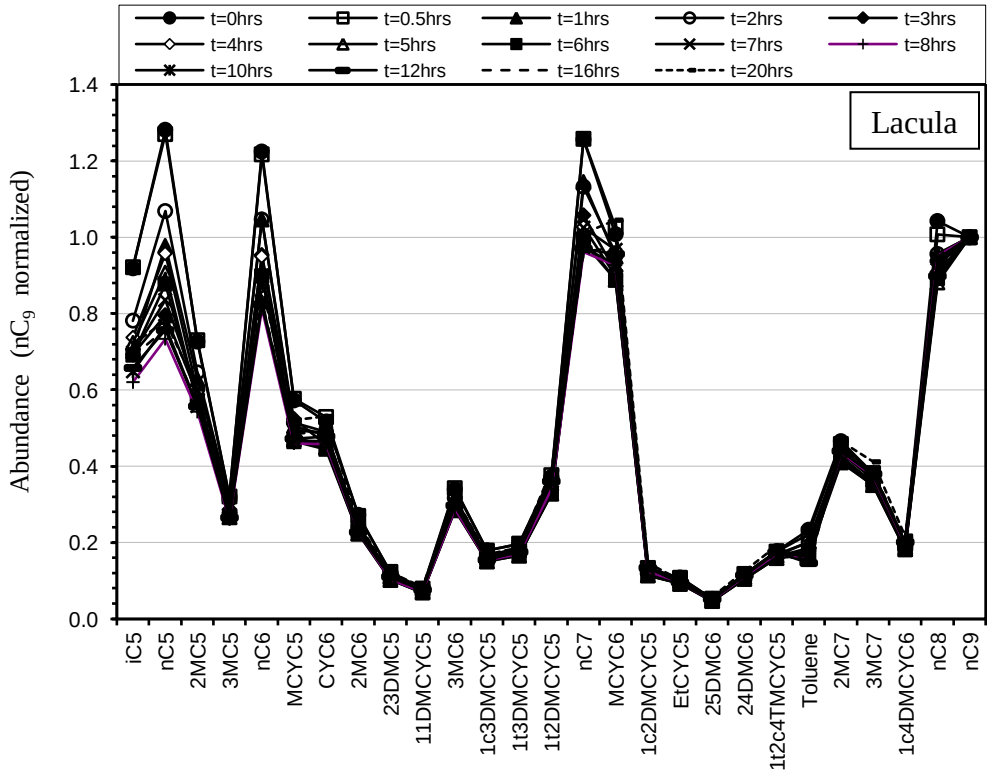



*Figure 3.10. Changes in abundance of gasoline-range compounds in Lacula oil over 20 hours of experimental weathering.*

Only those compounds with initial high abundances ($iC_5$, $nC_5$, $nC_6$, $nC_7$, $MCYC_6$ and $nC_8$) show easily observable changes over the 20 hour period (Figure 3.10). The overall average decrease in abundance is approximately 14%. Although not observable in Figure 3.10, some compounds, such as $11DMCYC_5$ have anomalous increases in abundances of 11% after 20 hours. This compound has a very low abundance ratio (0.08) in the unweathered samples and although Figure 3.10 does not clearly show significant change, due to very small values, abundance ratio calculations in small numbers produce significant differences when converted to percentages.

Overall compound abundance decreases range from 0% to 39% at 20 hours. Compound $nC_5$ has the largest decrease with 39%, followed by toluene (37%), $nC_6$ (29%), $iC_5$ (22%) and $nC_7$ at 20%. The higher molecular weight compound $nC_8$ decreased in abundance by only about 11% as compared to an approximate 59% decrease in the same compound in the Alberta oil.

Unlike the Alberta oil, Lacula headspace compounds show only very slight decreases (1-5%) in abundance in the first half hour. Even the more volatile lower molecular weight compounds $iC_5$ and $nC_5$ had decreases of 0% and 1% respectively, compared to over 65% in their Alberta counterparts. Toluene had the largest decrease in this early sampling period with 5%. More significant changes are seen at $T_1$, wherein both $iC_5$ and $nC_5$ show a 24% and toluene a 14% decrease in abundances.

The overall amount of abundance change is displayed in Figure 3.11. As stated previously, the majority of the compounds with the highest unweathered abundances show the largest decreases. $MCYC_6$ is also high in abundance in the unweathered oil headspace (Figure 3.1b, 3.9) but had a negligible decrease after 20 hours (Figure 3.10).

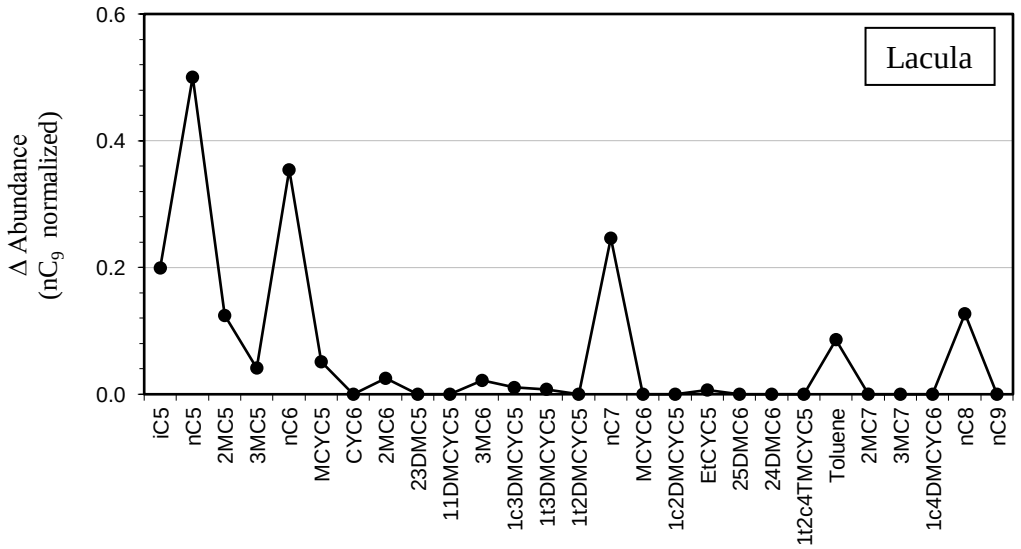



*Figure 3.11. Amount of decrease in abundance of headspace compounds in Lacula oil after 20 hours of experimental weathering.*

Abundance changes over time for various compound classes in Lacula are plotted in Figure 3.12a-d. Generally, the trends are considerably different than those seen in the Alberta oil, with a smaller range and a comparatively slower rate of change, especially during the early weathering periods.

Similar to the trend observe in the Alberta oil, the majority of compounds show their maximum decrease in abundance hours prior to the final sampling period ($T_f$). In the case of Lacula this occurred at $T_8$. This trend is more prevalent in the n-alkanes and various lower molecular weight compounds (e.g., $iC_5$ and $2MC_5$), (Figure 3.12a, b) but is evident to some degree in all of the chemical classes.

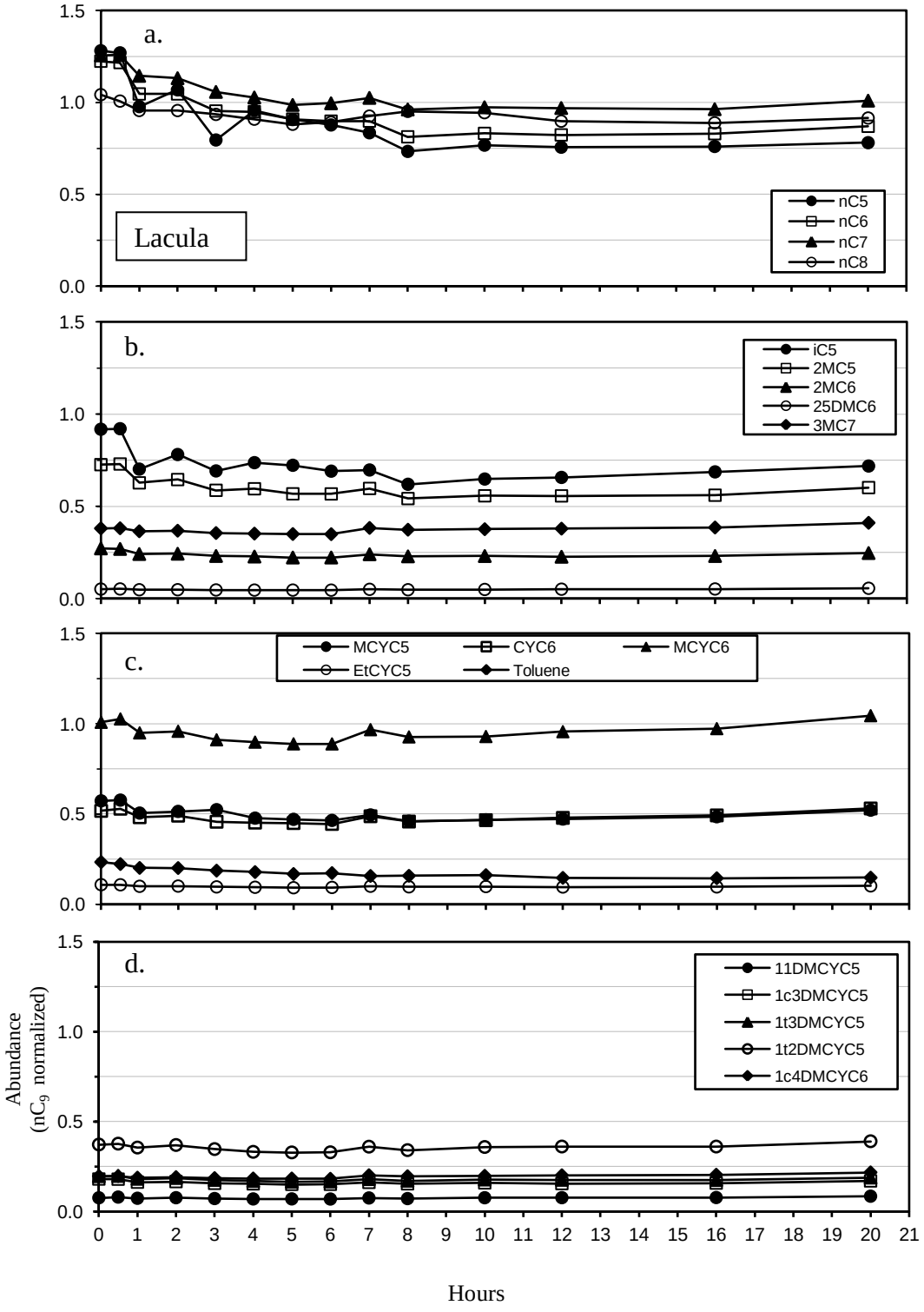



*Figure 3.12. Abundance vs weathering times for gasoline-range compounds in Lacula oil. a.) n-alkanes; b.) branched alkanes; c.) cyclic alkanes; d.) cyclic/aromatics.*

All but 2 compounds ($nC_8$, toluene) generally show no change in abundance during the period from $T_8$ to $T_f$. Some compounds e.g., $iC_5$ and MCYC6, show a slight increase from 8 hours to 20 hours, attributed to diminishing abundances of $nC_9$, affecting ratio calculations and much slower evaporation losses as compared to the other 2 study oils.

More relevant perhaps to slower evaporative rates in Lacula, was the tendency for the Lacula oil to form a waxy surface film, observed upon removal of the oil jars from the weathering chamber, even during the early sampling periods. Elaboration on wax content and its effects on evaporation, will occur in the Discussion section of this document.

#### *3.2.1.3 Louisiana*

Abundances in the Louisiana oil exhibit rapid changes over the reasonably short weathering time of 3 hours (Figure 3.13). As observed in GC trace (Figure 3.1c) the compounds $nC_6$ and $MCYC_6$ are present in high molecular abundances in the unweathered oil. Overall there was an 87% decrease over 3 hours in compound abundances in the Louisiana oil, compared to 78% in Alberta ($T_f$=14 hrs) and 14% in Lacula ($T_f$ =20 Hrs).

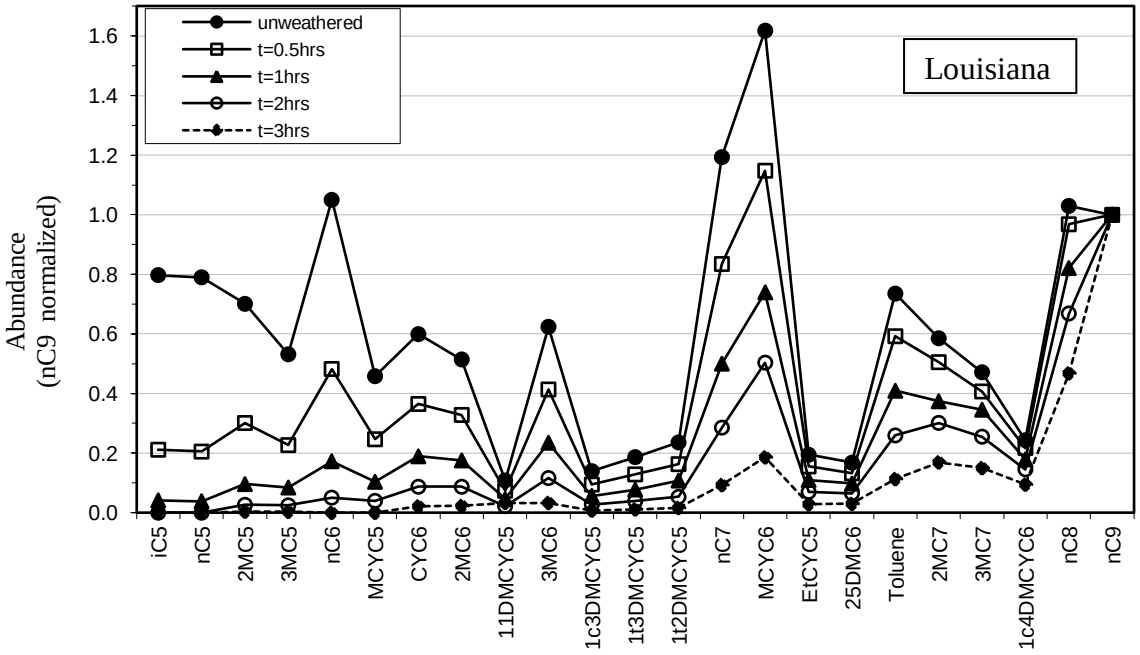



*Figure 3.13. Changes in abundance of compounds in Louisiana oil over 3 hours of experimental weathering.*

In the first 0.5 hour of weathering, compounds $iC_5$, $nC_5$ show an abundance decrease of approximately 74%. Other compounds showing high initial abundances such as $nC_6$, $nC_7$ and $MCYC_6$ also show considerable decreases (i.e.,) in the first 0.5 hour with 54%, 30% and 29% respectively. Compound $nC_7$ shows a decrease of about 92% relative to $nC_9$ at the $T_3$.

Abundances in all compounds eluting just before $nC_6$ diminished to relatively low levels at $T_3$ (Figure 3.13). Molecular abundances were very close to IRMS threshold limits, however isotope ratio measurements were still obtainable for $2MC_5$ and $3MC_5$. All compounds, except $11DMCYC_5$, eluting up to and including $nC_7$ show a decrease in relative abundance of greater than 90% at $T_3$. Compound $nC_8$ has the lowest overall decrease in relative abundance with 55% at $T_f$.

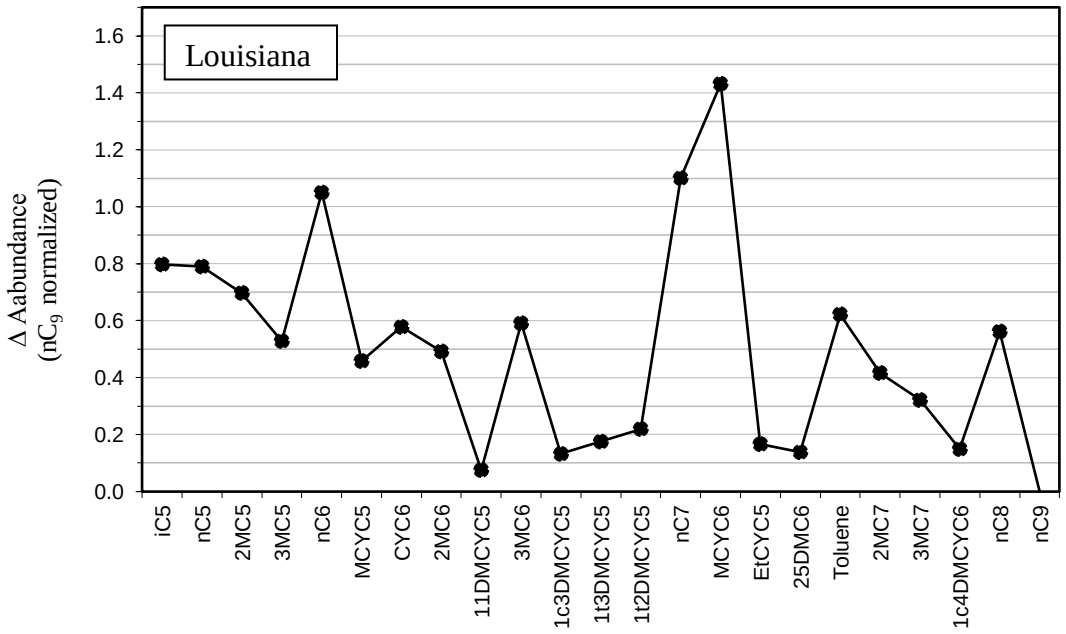



*Figure 3.14. Amount of decrease in abundance of compounds in Louisiana oil after 3 hours of expeimental weathering.*

Figure 3.15a-d. shows the change in abundances over time for the compound chemical classes. In comparison to the other study oils, the plots show a rapid and successive decrease in abundances for all chemical classes.

Unlike the results from the other two study oils, abundance decreases are constant until final sampling. Similar to the other oils, was a point in the weathering regime where a large portion of the relative abundance changes occurs. In Louisiana the most significant reduction in abundances is observed during the first hour of weathering, with compounds such as $iC_5$ and $nC_5$ decreasing by approximately 95%. Those compound eluting up to and including $nC_6$ decreased by more than 80% during this first hour. This rapid evaporation first hour trend is seen in members of all chemical classes, although to a lesser degree in the multi-branch cyclic compounds (3.15d).

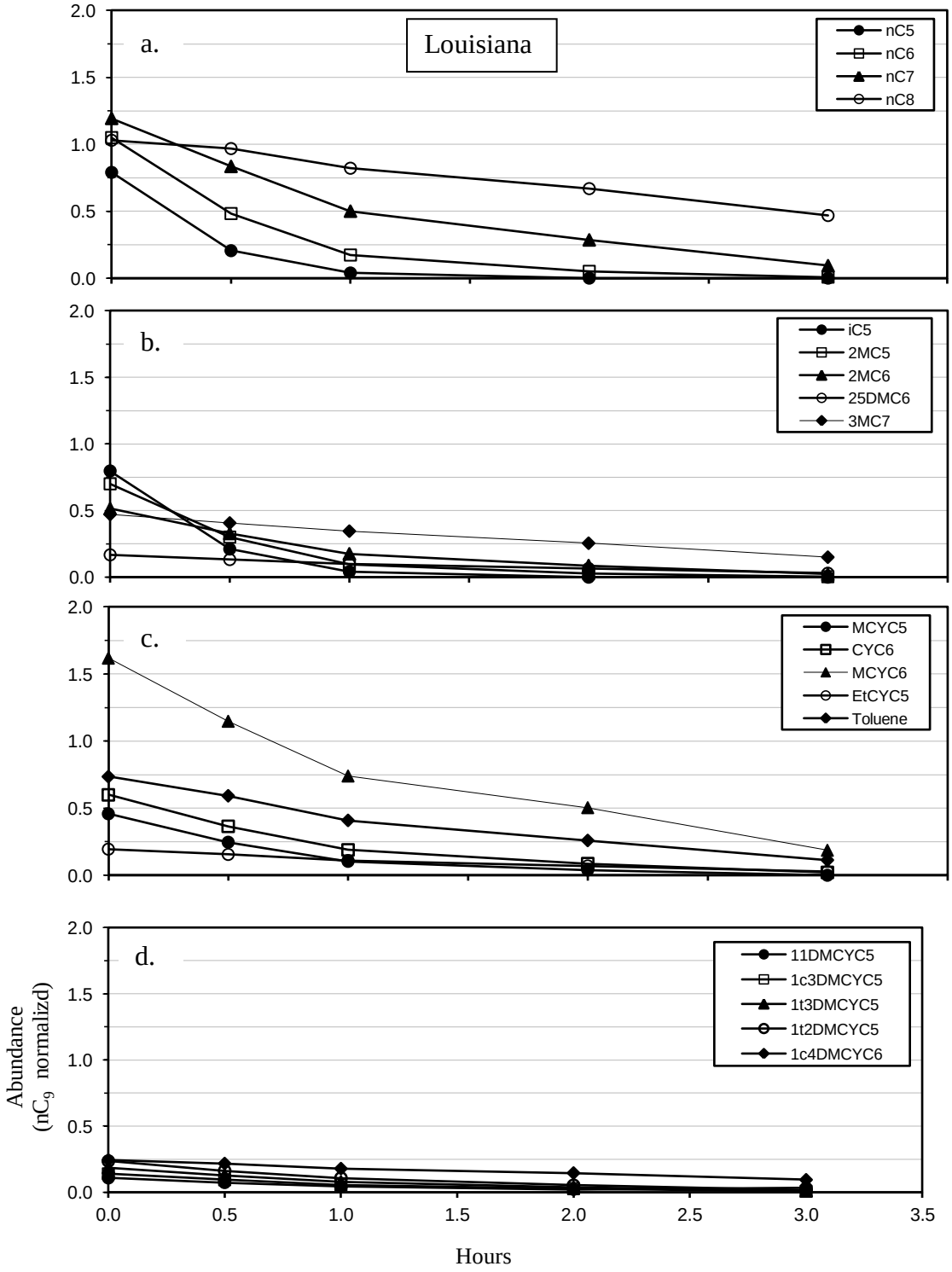



*Figure 3.15. Abundance vs weathering times for gasoline-range compounds in the Louisiana oil. a.) n-alkanes; b.) branched alkanes; c.) cyclic/aromatics; d.) cyclic alkanes.*

Multi branched cyclic alkanes show a small change in abundance ratio (Figure 3.15c) however their abundances were initially low in the unweathered oil so the relative change compared to $nC_9$ is expected to be smaller.

The monocyclic compound $MCYC_6$, in highest abundance in the unweathered oil, showed a decrease in abundance of approximately 88% at $T_3$; $MCYC_5$ decreased by approximately 98% and toluene decreased by about 85% at $T_3$. Abundance change trends, although more rapid in the Louisiana oil, were more similar to those observed in the Alberta oil than in Lacula.

Unique to Louisiana oil, was the formation of a surface emulsion during the weathering experiments sampled after the $T_{0.5}$, $T_1$ and $T_2$ hour weathering periods. Emulsion thicknesses on the triplicate $T_{0.5}$ sample surfaces (1.8, 1.9 and 2.0 cm) were approximately five times the original thickness of the oil initially added to the surface (4.0 mm). Emulsion thicknesses observed at $T_2$ were approximately 8mm, still double that of the original oil thickness applied.

### 3.2.2 Carbon Isotope Ratio Signatures

#### *3.2.2.1 Alberta Sweet Mixed Blend*

The isotopogram showing the $\delta^{13}C$ values for the 27 compounds measured on 11 sampling intervals over 14 hours is shown in Figure 3.16a. Unweathered and final sampling intervals with standard deviations are presented in Figure 3.16b to more clearly show the overall change in the $\delta^{13}C$ values.

After 14 hours of weathering, molecular abundances of the lower molecular weight fractions $iC_5$ and $nC_5$ diminish to quantities below required for reliable IRMS measurements. The resulting 14 hour isotopic signature, generally enriched in $^{13}C$, does parallel the unweathered trace for many of the compounds, compounds eluting after $3MC_7$ when this pattern deteriorates. Many of the intermediate sampling isotope signatures also show a parallel trend, but later results show more variability. For example, the compound $3MC_7$ shows a large range in $\delta^{13}C$ values (-25.4‰ to -29.0‰) over the 14 hour study.

Enrichment in $\delta^{13}C$ values is measured in 21 of the remaining 25 compounds after 14 hours of weathering (Figure 3.16b). Four compounds, $CYC_6$, $1t2DMCYC_5$, $25DMC_6$ and $3MC_7$ (although variable throughout the study) show no change in isotopic ratio compared to the $T_0$ headspace within experimental error for the initial and final compound runs. The overall mean $^{13}C$ enrichment in the Alberta study is 1.5 ‰ with 17 of the 25 compounds showing $^{13}C$ enrichments of greater than 1‰.

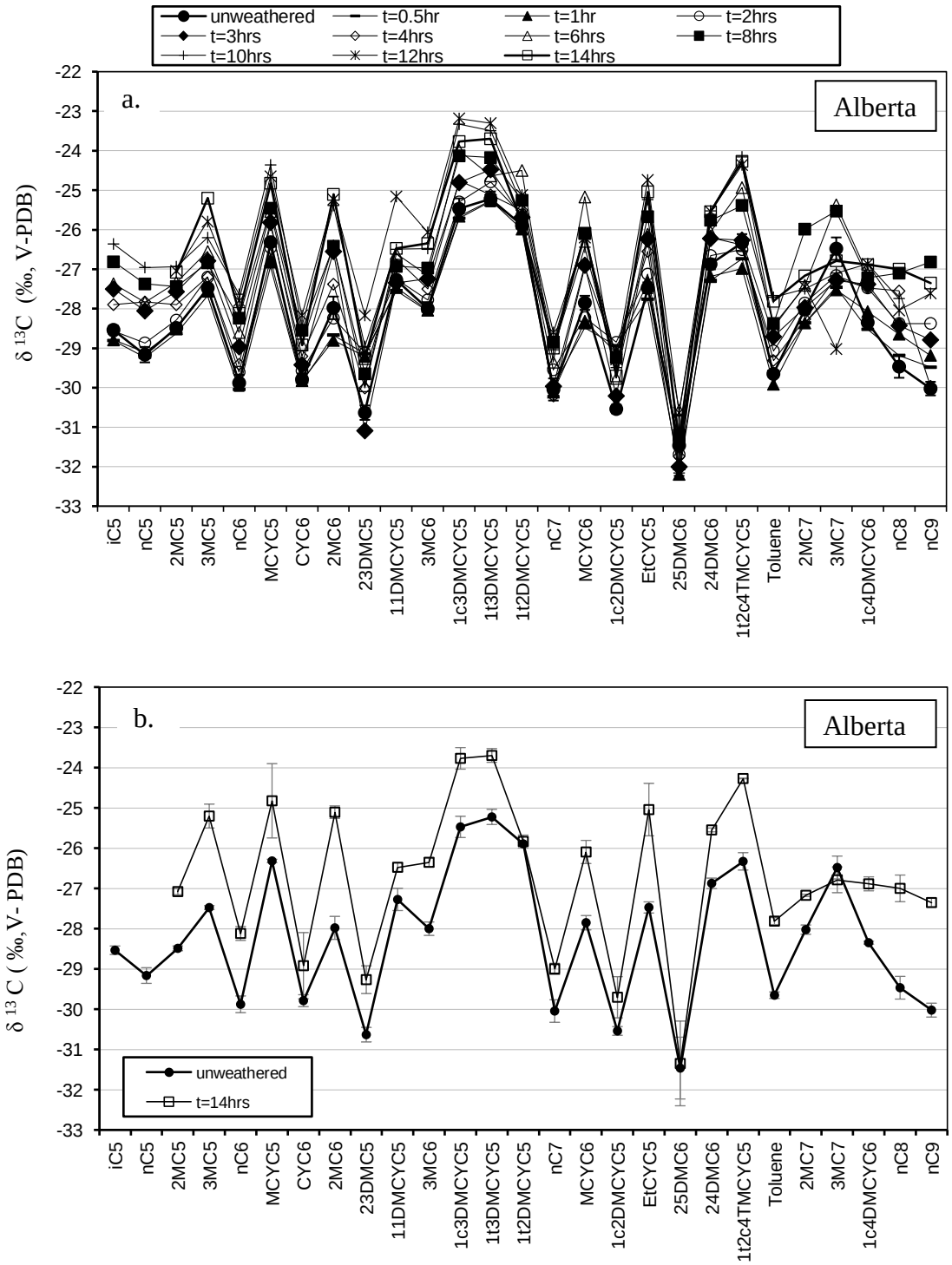



*Figure 3.16. $\delta^{13}C$ values for gasoline-range compounds in Alberta oil measured over a 14 hour weathering period. a.) 10 sampling intervals b.) comparison of unweathered and final 14 hour periods only.*

The final $\delta^{13}C$ differences between unweathered and final isotope ratios ($\Delta\delta^{13}C$) are given in the differential isotopogram Figure 3.17. Unweathered $\delta^{13}C$ values in the figure are assigned a baseline value of zero. Positive values indicate $^{13}C$ enrichment, negative values a $^{13}C$ depletion relative to the unweathered oil. As previously stated, Figure 3.17 shows that 21 of the 25 headspace compounds show enrichment in the heavier $^{13}C$ isotope. Compounds $2MC_6$ and $nC_9$ showed the largest enrichment, with $EtCYC_5$ potentially as large within experimental error.

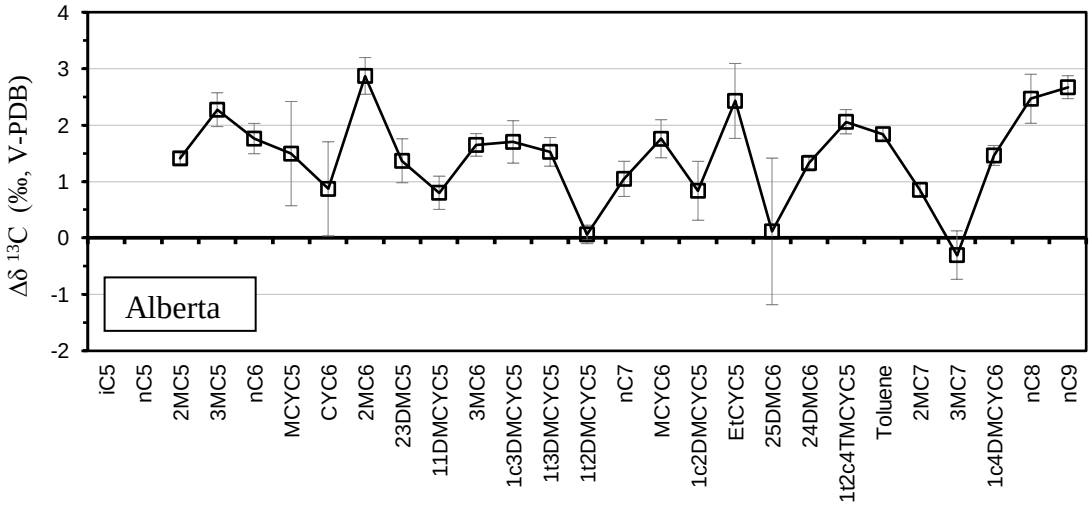



*Figure 3.17. Change in headspace $\delta^{13}C$ values relative to unweathered Alberta oil after14 hours of weathering. Unweathered values have a baseline value of 0. Positive values represent enrichment in $^{13}C$.*

Although not clearly seen in Figure 3.16a, the isotopic ratio shifts are not consistent throughout the weathering regime. Figures 3.18a-e display the changes in carbon isotope ratios between unweathered and each of the sampling events over the 14 hours for the various molecular chemical classes. Enrichment in $^{13}C$ is seen in various compounds from all of the representative chemical classes.

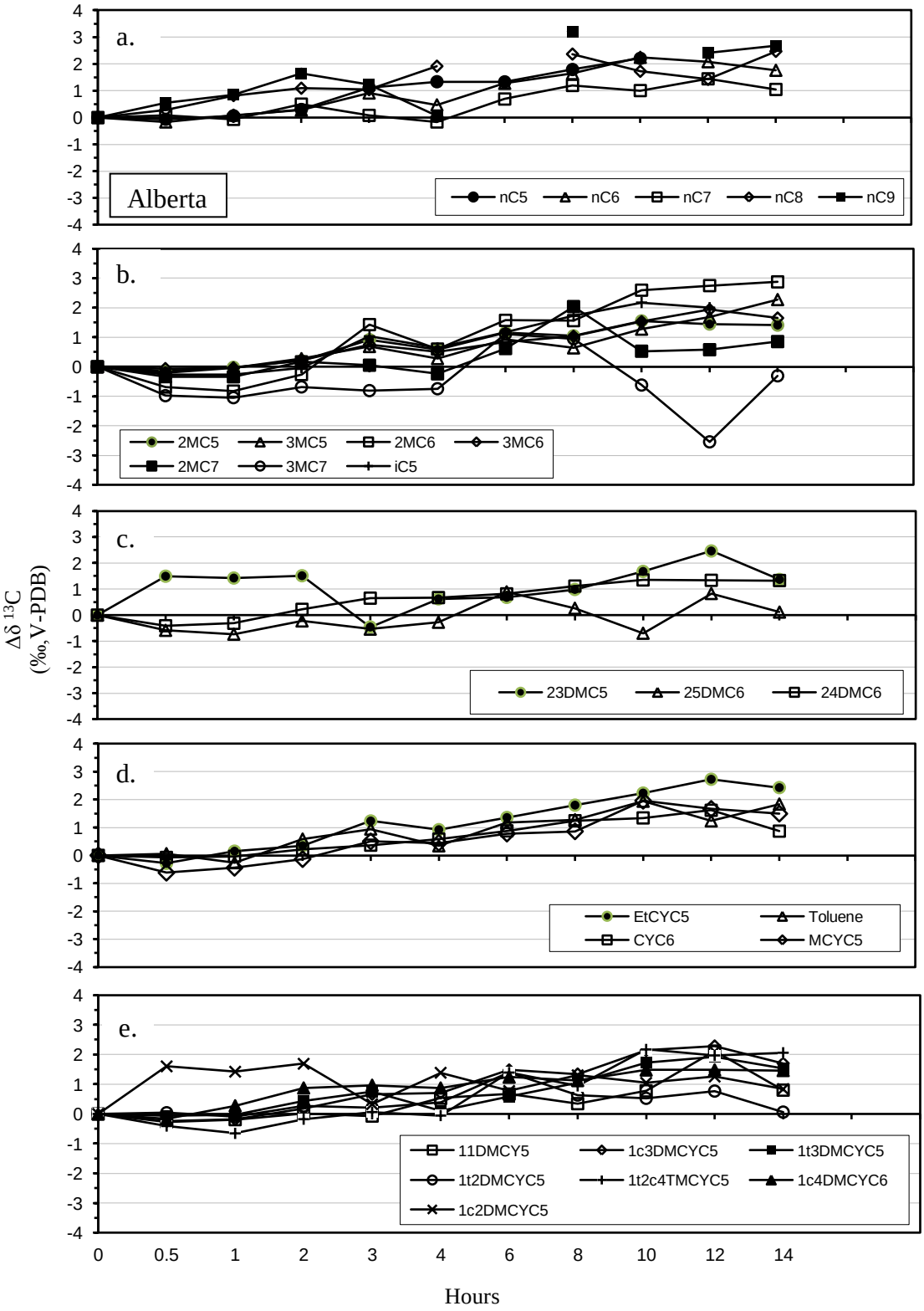



*Figure 3.18. Change in $\delta^{13}C$ values after 14 hours of weathering relative to unweathered Alberta oil. a.) n-alkanes; b.) branched alkanes; c.) multibranched alkanes; d.) cyclic/aromatic; e.) cyclic alkanes.*

All of the measured compounds in all classes listed show a clear enrichment in $^{13}C$ at hour 6. The n-alkanes continue this trend until the final 14 hour measurements (Figure 3.18a). The branched alkanes show a similar trend in $^{13}C$ enrichment, with the exception of $3MC_7$ (Figure 3.18b) and $25DMC_6$ (Figure 3.18c). Cyclic and aromatic compounds also continued the post 6 hour trend, with the exception of only two compounds; $CYC_6$ and $1t2DMCYC_5$ (Figure 3.18d through e). Although $CYC_6$ shows a $^{13}C$ enrichment relative to the unweathered measurement (Figure 3.18d), this compound has a large standard deviation (±0.8‰) and is therefore not considered isotopically different from the unweathered compound.

Both n-alkanes $nC_8$ and $nC_9$ showed an isotopic enrichment after the first 0.5 hours of weathering and although showing variability at hour 4, show the highest final enrichment in $^{13}C$ of the measured n-alkanes.

Various branched and iso-alkanes show some $^{13}C$ enrichment after 3 hours of weathering (Figure 3.18b). The remaining compounds $2MC_7$ and $3MC_7$ show $^{13}C$ enrichment after 6 hours. The variability in the values for $3MC_7$, especially after 8 hours (Figure 3.18b), was not due to low molecular concentrations in the samples, and is attributed to co-elution with neighboring compound peaks during IRMS analysis. Although the compound $2MC_6$ at 2.9 ±0.2‰ shows the largest $^{13}C$ enrichment in the Alberta trials, $EtCYC_5$ with less precision may have been similar at 2.4 ±0.7 ‰.

Branched alkanes $23DMC_5$ and $25DMC_6$ show inconsistent $\delta^{13}C$ changes as seen in Figure 3.18c. Compound $24DMC_6$ shows enrichment after 3 hours of weathering and continues this trend to the final sampling.

Aromatic (toluene) and cyclic headspace compounds (Figure 3.18d) show the most consistent enrichment in $^{13}C$ over the course of the Alberta trials. Compounds in this

class show some enrichment at after 3 hours of weathering and remain enriched until the final sampling. $EtCYC_5$ shows the highest degree of enrichment with a shift of 2.4 ±0.7‰ relative to unweathered oil headspace (Figure 3.17, 3.18d).

The branched cyclic alkane $1c2DMCYC_5$ (GC peak 26) shows a substantial enrichment during the first few sampling events (Figure 3.178e) but is isotopically similar to the unweathered compound at the final sampling. This could be attributed to peak co-elution associated with a highly abundant concentration of $MCYC_6$ (GC peak 25) in the unweathered oil.

Overall the n-alkanes show the most consistent enrichment in headspace $^{13}C$, all showing a 1‰ or greater enrichment after 14 hours. The compound $2MC_6$ shows the most $^{13}C$ enrichment (2.9 ±0.2‰) in the Alberta trials; $3MC_7$ shows the least change (0.3 ±0.3‰) from the unweathered headspace.

### *3.2.2.2 Lacula Crude Oil*

All of the measured compounds in the initial Lacula headspace were still present in sufficient quantities to produce reliable IRMS measurements after 20 hours. Even the most volatile fractions, $iC_5$ and $nC_5$, were still present in abundant quantities, even with a 16 mls/min injector split flow dilution.

It is noted that during the Lacula oil weathering experiments, a persistent waxy film formed on the surface of the experimental sample mixtures. The film was observed on all samples prior to $T_8$. After 8 hours, "islands" of thickened waxy film existed on the surface.

The isotopogram for the 27 compounds in the Lacula study are shown in Figure 3.19a. Initial versus final 20 hour isotopic signatures are shown in Figure 3.19b, with only 9 of the 14 sampling intervals displayed for a less congested and more readable figure. The isotopic ratio changes for all weathering intervals are included in subsequent graphs, Figures 3.21a-e.

Figure 3.19a shows that the change in isotopic ratios of certain compounds is inconsistent over the course of the Lacula study. Compounds such as $nC_5$, $nC_6$, $MCYC_6$, $3MC_7$, and especially $1c2DMCYC_5$, do show some exaggerated $\delta^{13}C$ values during the intermediate sampling periods. The variability could be attributed to GC peak co-elution associated with the consistently high molecular abundances of adjoining compounds. In particular, $MCYC_6$ (peak 25), a compound in high relative abundance in all three study oils has the potential to co-elute with $1c2DMCYC_5$ (peak 26). For example on Figure 3.19a the compound $1c2DMCYC_5$ shows a significant depletion in $^{13}C$ relative to the unweathered oil at various intermediate sampling periods.

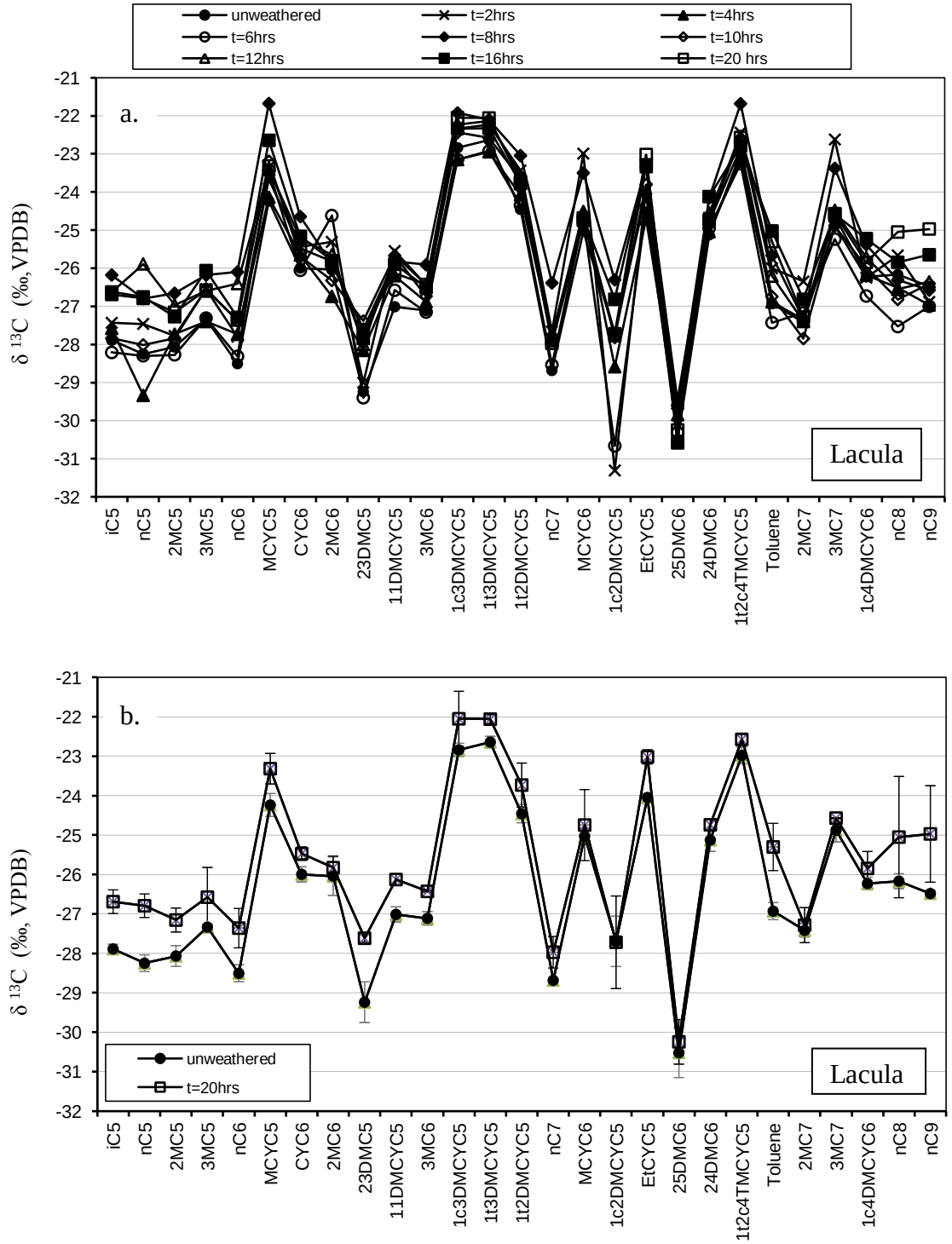



*Figure 3.19. $\delta^{13}C$ values for gasoline-range compounds in Lacula oil over a 20 hour weathering period. a.) 8 sampling intervals; b.) unweathered and final 20 hour periods only.*

Review of the un-normalized data showed that a significant $\delta^{13}C$ offset has been added to the raw IRMS measurements obtained, suggesting that co-elution may have occurred in the standard oil run used for normalization and an unreliable offset value being applied to the associated value for this compound during early IRMS runs.

The final 20 hour isotopic signature (Figure 3.19b) closely parallels the unweathered trace for many of the compounds. The $\delta^{13}C$ values for 15 of the 27 compounds show $^{13}C$ enrichment at $T_{20}$ within experimental precision (Figure 3.19b and 3.20). The largest degree of $^{13}C$ enrichment is observed in the compounds toluene (1.6 ±0.6‰) and $23MC_5$ (1.6 ±0.1‰). The overall compound mean $^{13}C$ enrichment relative to the unweathered headspace for the Lacula oil was 0.8‰.

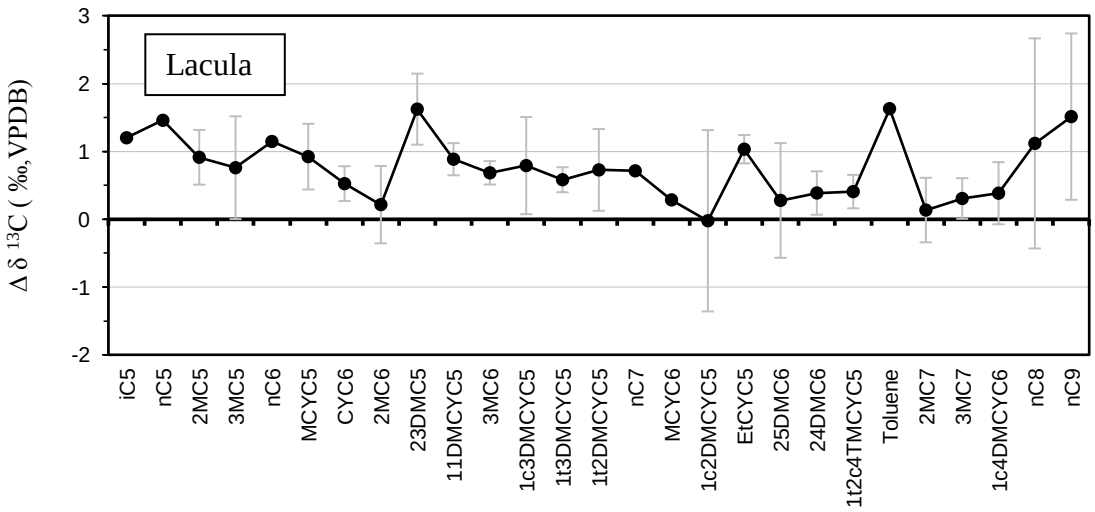



*Figure 3.20. Change in gasoline-range $\delta^{13}C$ values relative to unweathered Lacula oil after20 hours of weathering. Unweathered values have a baseline value of 0. Positive values represent enrichment in $^{13}C$.*

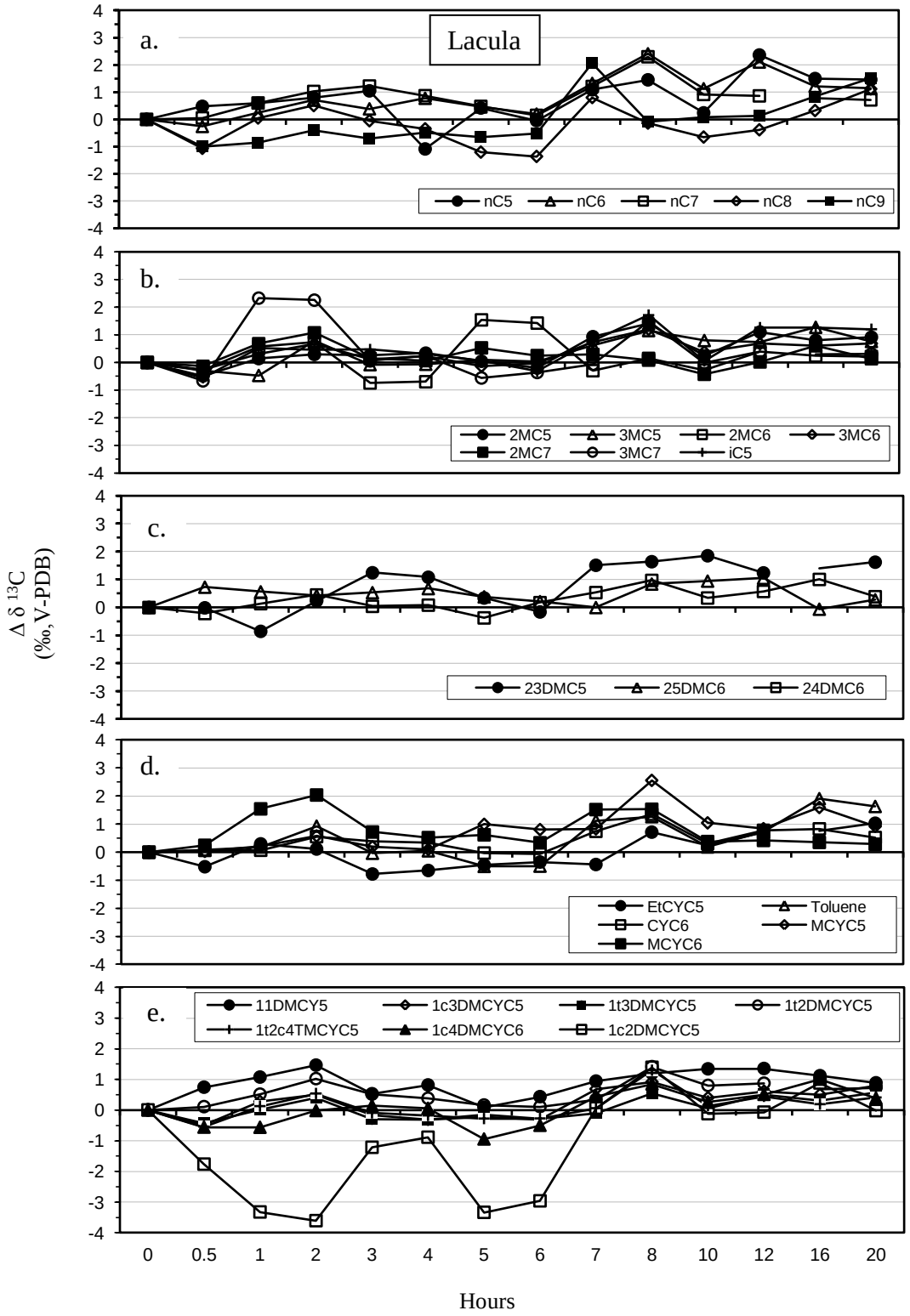



*Figure 3.21. Change in gasoline-range $\delta^{13}C$ values relative to unweathered Lacula oil during 20 hours of weathering. a.) n-alkanes; b.) branched alkanes; c.) multi-branched alkanes; d.) cyclic/aromatic; e.) cyclic alkanes.*

Changes in isotopic ratios over time relative to the unweathered oil for the various compound classes are given in Figures 3.21a-e. The diagrams more clearly show the variability in various compound isotope ratios, particularly in the first 7 hours of weathering. Numerous compounds show $^{13}C$ depletion after the 7 hour measurements. This trend is seen in all of the classes with the exception of the n-alkane $nC_8$ (Figure 3.21a).

The n-alkanes $nC_5$, $nC_6$, $nC_7$ and $nC_8$ show early enrichments but between the $T_4$ and $T_7$ hour samplings the trend reverses (Figure 3.21a). Compound $nC_9$ shows a consistent depletion in $^{13}C$ until $T_7$ .

Branched alkanes also do not show a clear pattern of isotopic enrichment until the later periods of analyses (Figure 3.21b,c). Compounds $2MC_6$, $3MC_7$ and $23DMC_5$ are variable until the $T_7$. Variability is attributed to co-elution since the compounds were present in sufficient quantities for reliable IRMS measurements.

Although somewhat variable during earlier analyses, compound $23DMC_5$ is shown to be the most enriched compound in the study with a 1.6 ±0.1‰ change relative to the unweathered compound.

Cyclic compounds (Figure 3.21d-e) illustrate the sudden shift in isotope ratios at the $T_7$ sampling. $MCYC_6$ shows early $^{13}C$ enrichment between $T_1$ and $T_3$ hours, but reverses this trend up until the $T_6$ hour measurements. There is potential for this compound to co-elute with $1c2DMCYC_5$ which exhibits sudden significant $^{13}C$ depletions during the same sampling periods (Figure 3.21e). Compound $EtCYC_5$ remained neutral or depleted in $^{13}C$ until the $T_8$, after which all compounds included in this chemical class show some degree of enrichment up to the final $T_{20}$ (3.21d).

Branched cyclic compounds (Figure 3.21e) did not exhibit a clear isotopic trend during the first 7 hour sampling periods. Variations in both early $^{13}C$ enrichments and subsequent $^{13}C$ depletions are shown in all compounds included in this grouping. Figure 3.20e shows a $^{13}C$ depletion of approximately 3‰ for $1c2DMCYC_5$ four times during the first 6 hours of weathering. These values are not deemed diagnostically reliable as previously mentioned, $1c2DMCYC_5$ can co-elute with $MCYC_6$. Throughout the Lacula analyses, $MCYC_6$ consistently showed an approximate 10 fold molecular abundance relative to $1c2DMCYC_5$. In addition, during the sampling periods prior to hour 8, molecular quantities of $1c2DMCYC_6$ were close to IRMS lower threshold of diagnostic reliability. A large differential in molecular quantities can result in the insufficient portioning of adjacent hydrocarbon components related to co-elution.

Overall, the branched alkane $23DMC_5$ shows the most $^{13}C$ enrichment with a 1.6 ±0.1‰ shift relative to unweathered measurements. Toluene also shows a similar amount of change but has a higher standard deviation (1.6 ± 0.6‰). The compound $1c2DMCYC_5$ has the lowest degree change (0.0 ± 1.2‰), but there is a significant standard deviation associated with the final $\delta^{13}C$ value.

### *3.2.2.2 Louisiana Crude Oil*

As seen in the abundance diagram for the Louisiana oil (Figure 3.13) $iC_5$ and $nC_5$ were not in sufficient abundance for reliable IRMS measurement after only 2 hours of weathering. Compounds $2MC_5$ and $3MC_5$ were nearing lower IRMS threshold limits for reliable measurement after only 3 hours.

The isotopograms, Figure 3.22a and b, show the $\delta^{13}C$ signatures for all weathering intervals. Isotope ratios for 21 of the original 23 compounds are measurable at $T_3$. The final isotope signature curve (Figure 3.22b) does not parallel the unweathered signature as consistently as seen in the two previous study oils (Figures 3.16b and 3.19b)

Enrichment in $^{13}C$ was observed in 12 of the 21 remaining compounds after 3 hours of weathering. Eight compounds showed a final $\delta^{13}C$ value unchanged from the initial head space, within experimental precision. Compound $1t3DMCYC_5$ showed a $^{13}C$ depletion of -0.6 ±0.1‰. The difference isotopogram Figure 3.23 shows that toluene and $3MC_7$ display the most $\delta^{13}C$ change relative to the unweathered oil, with $^{13}C$ enrichments of 2.8 ±0.2‰ and 2.8 ±0.3‰ respectively. Toluene also showed elevated $^{13}C$ enrichment in the other two study oils. The overall un-weighted average $^{13}C$ enrichment for the Louisiana oil headspace compounds over the 3 hour study was approximately 0.8‰.

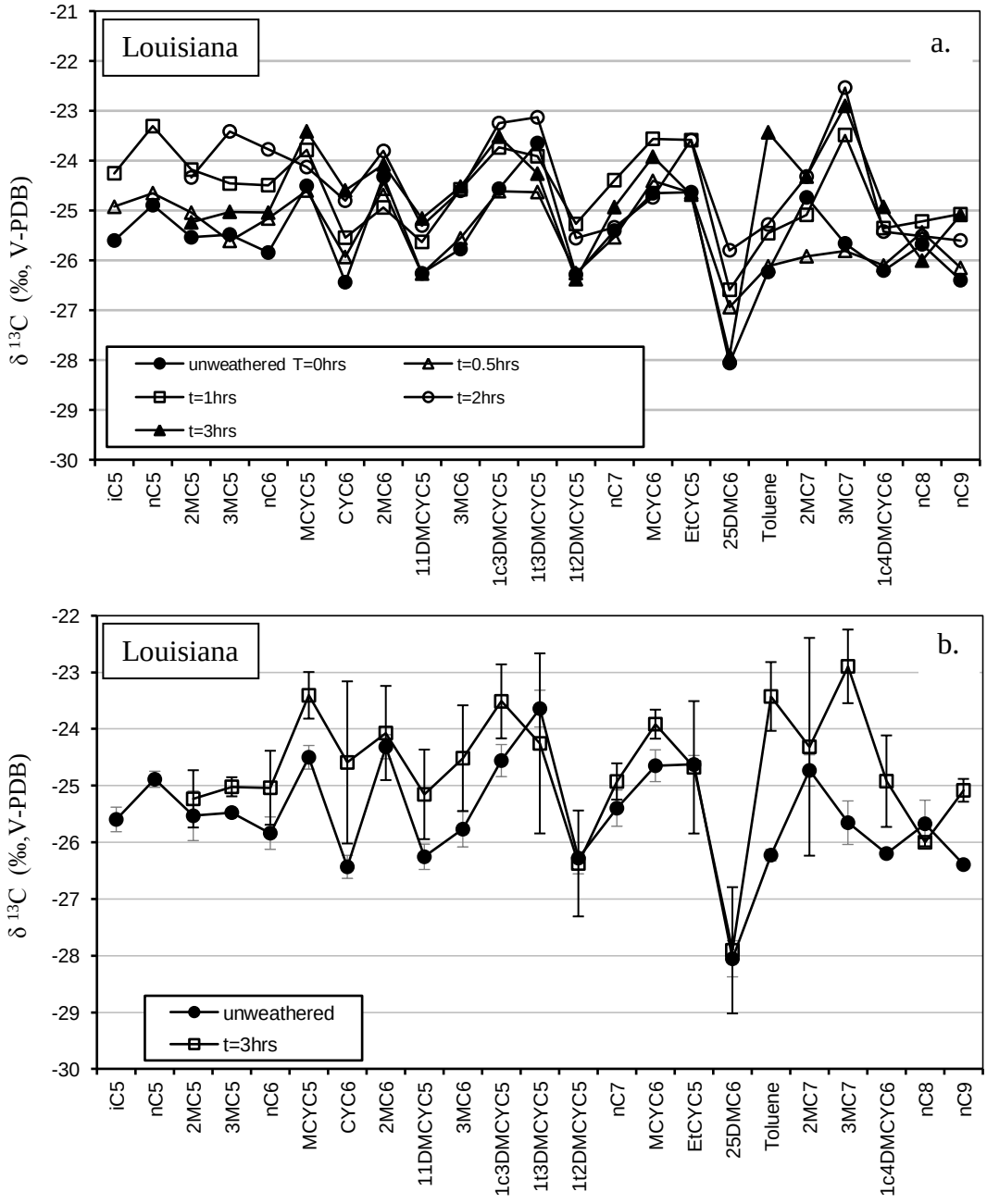



*Figure 3.22. $\delta^{13}C$ values for gasoline-range compounds in Louisiana oil over a 3 hour weathering period. a.) 4 sampling intervals b.) unweathered and final 3 hour periods only.*

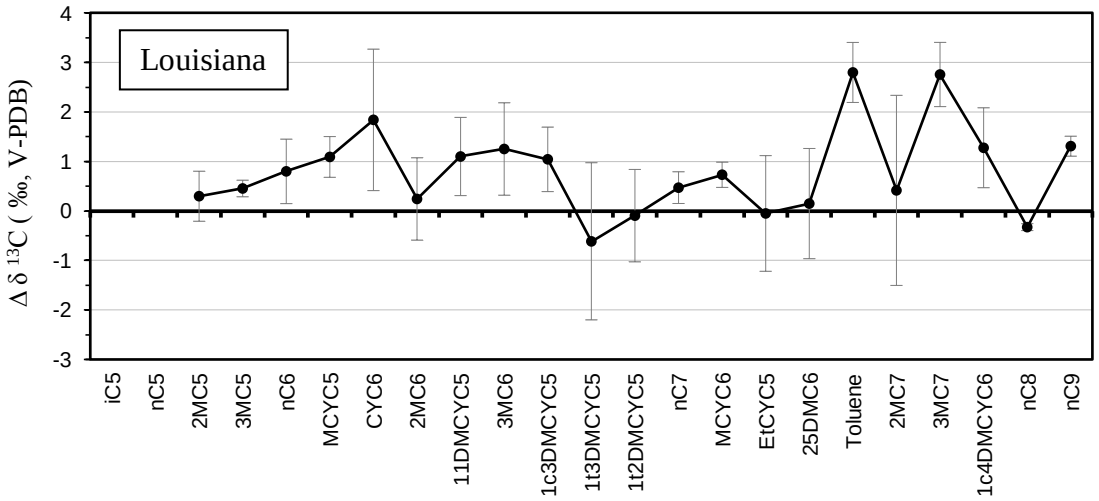



*Figure 3.23. Change in gasoline-range $\delta^{13}C$ values after 3 hours of weathering relative to unweathered Louisiana oil. Unweathered values have a baseline value of 0. Positive values represent enrichment in $^{13}C$.*

Figures 3.24a-d. show the final change in $\delta^{13}C$ values relative to the unweathered Louisiana oil. As seen in the previous oils, many compounds at some common interval show significant $^{13}C$ enrichment; in this case at the 1 hour sampling. Based on results from the previous oils, timing of this event appears to be related to the rate of evaporation, occurring later with the slower evaporating oils.

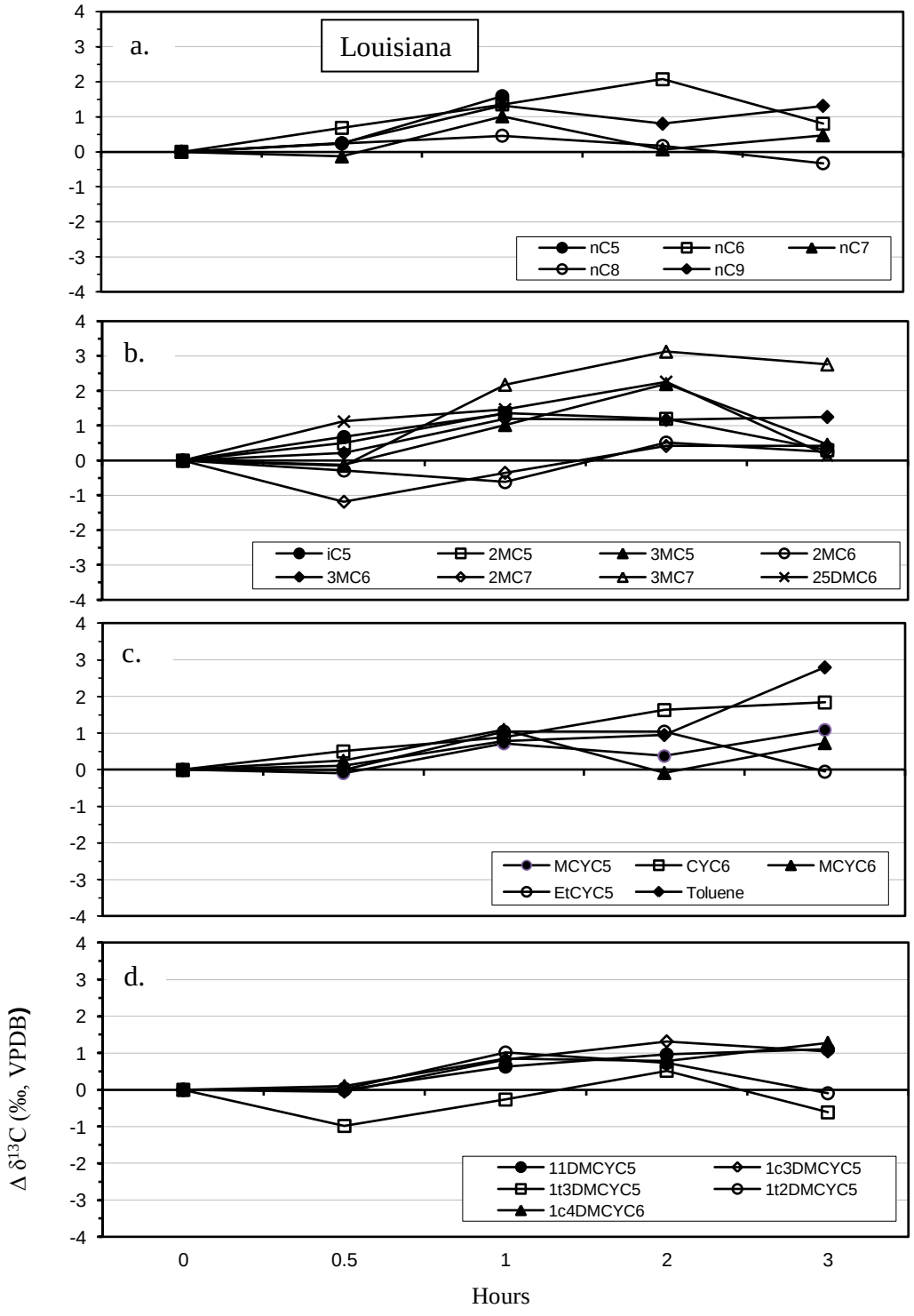



*Figure 3.24. Change in gasoline-range $\delta^{13}C$ values relative to unweathered Louisiana oil. after 3 hours of weathering a.) n-alkanes b.) branched alkanes; c.) cyclic/aromatic; d.) multi-branched cyclic*

All of the measured n-alkanes show some $^{13}C$ enrichment after the first hour of sampling (Figure 3.24a). Although not represented in the final sampling events, $nC_5$ shows a $^{13}C$ enrichment of 1.6‰ at $T_1$. Compounds $nC_6$ and $nC_9$ continued to show enrichment until the final analysis ($T_3$), with $nC_9$ showing the largest enrichment of the n-alkanes at 1.3 ±0.3‰. Both $nC_7$ and $nC_8$ are more variable, showing final $\delta^{13}C$ values unchanged from the initial headspace.

Except for an initial $^{13}C$ depletion exhibited by $2MC_6$ and $2MC_7$ the branched alkanes (Figure 3.24b) all show a trend towards enrichment at $T_1$. The $T_3$ results show little change (0.2 ±0.3‰) from the initial headspace for $2MC_6$ and of 0.4 ±0.5‰ for $2MC_7$. The most $^{13}C$ enrichment was shown in the branched alkane $3MC_7$ (2.8 ±0.3‰).

The trend in the cyclic and aromatic classes shown in Figure 3.23c, mimics that observed in the n-alkanes. The compounds all show $^{13}C$ enrichment at the 1 hour sample with increased compound variability in the later samplings. The compound $CYC_6$ shows a continuous trend in $^{13}C$ enrichment with a final value of 1.8 ±0.1‰. Despite showing enrichment of approximately 1‰ to 2‰ in the Lacula and Alberta studies respectively, at final analysis, the compound $EtCYC_5$ remains unchanged at 0 ±0.1‰. Toluene displays the most $^{13}C$ enrichment with 2.8 ±0.2‰. Branched cyclic compounds in Figure 3.24d all show $^{13}C$ enrichment relative to the initial headspace at the 2 hour sampling period but are more variable again at 3 hours. Reasons for the depleted $^{13}C$ values in $1t3DMCYC_5$ and $1t3DMCYC_5$ are undetermined, but could be related to borderline IRMS abundance voltages exhibited as a result of the requirement to blend multiple runs to obtain a complete set of isotopic values.

Various $\delta^{13}C$ measurements have comparatively large errors in certain oils (e.g. $nC_8$ and $nC_9$ in Lacula; $2MC_7$ in Louisiana; $CYC_6$ and $EtCYC_5$ in Louisiana). Although the

reasons for the larger uncertainties in the Louisiana oil are unknown, a review of the raw data for $nC_8$ and $nC_9$ in the Lacula oil runs shows that the standard deviations are calculated from only 2 of typically triplicate IRMS runs for the final (i.e. $T_{20}$) analyses, due to analytical difficulties. The 2 samples were analyzed 2 days apart with the second sample $\delta^{13}C$ approximately 2‰ heavier than the first.

Based on earlier work by Harris et al., (1999), equilibrium between the liquid and vapour phase in this study is assumed during SPME sampling. This earlier work however, used Chester and Alberta oils for the equilibrium time experiments (see Section 2.3.3). Both of these oils differ in physiochemical characteristics from the waxy Lacula oil. Due to the crusty wax layer, diffusion of the volatiles may be inhibited and equilibrium times prolonged. It is observed that abundances of these higher molecular weight compounds in the second analyses were approximately 1.5 times the first, even though the injector split ratios were identical. Furthermore, increased handling of the stored sample jars prior to the second IRMS run may have further fractured hardened surface layers, allowing additional evaporation.

#### *3.2.2.3 Final Weathered Isotopograms*

Final time series $\delta^{13}C$ data for the carbon isotope ratio signatures for all measureable compounds in all 3 study oils are displayed in Figure 3.25. Various compound data points are missing from the isotopogram due to either insufficient molecular abundances or unreliable isotope measurements. Only those compounds reliably diagnostic and common to all 3 oils and with continuous data throughout the time series will be compared in the final discussion and statistical discrimination between oils.

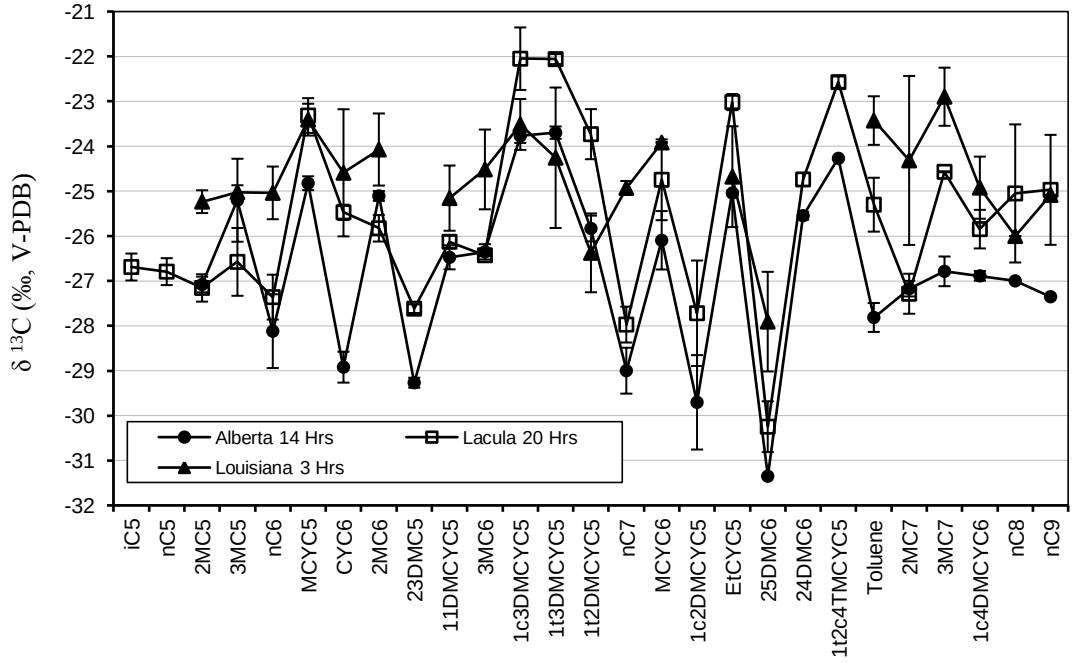



*Figure 3.25. $\delta^{13}C$ values for resolvable gasoline-range compounds in the 3 weathered study oils.*

Reliably measureable carbon isotope ratios for the unweathered oils include 27 gasoline-range compounds for the Alberta and Lacula oils and 23 for the Louisiana oil.

$\delta^{13}C$ values for 6 compounds ($2MC_6$, $23DMC_5$, $1c2DMCYC_5$, $24DMC_6$, $1t2c4TMCYC_5$ and $3MC_7$) are inconsistent throughout the weathering process, in at least one oil at various sampling periods (see Figures 3.18 b,c,d; 3.21 b,c,e). The compounds $23DMC_5$, $1c2DMCYC_5$, $24DMC_6$, $1t2c4TMCYC_5$ are not reliably measureable even at the onset of the unweathered Louisiana oil trials. To facilitate oil comparisons, using compounds consistently measureable in all periods of the study in all oils, these 6 compounds will not be used in the final statistical analyses.

As previously mentioned , to obtain reliable carbon isotope ratio measurements, good peak resolution (e.g., baseline separation) of the individual gasoline-range compounds is

required (Ricci et al., 1994). All of these 6 excluded compounds are susceptible to peak co-elution due to adjacent compound peaks having similar retention times on the GC column (see Figure 2.9). This is particularly true when a compound is in high abundance relative to its adjacent peak as in the case of $MCYC_6$ and $1c2DMCYC_5$. All of the study oils had high concentrations of $MCYC_6$ in the measured headspaces (see Figures 3.6, 3.9, 3.12). Gas chromatography can affect the measured carbon isotope composition of the individual hydrocarbons due to the partitioning that occurs during repeated sorption and desorption between the column's stationary and mobile phases. The heavier $^{13}C$ compound components elute towards the front of the peak and the $^{13}C$ depleted components elute towards the tail (Hayes et al., 1990). Analysis of the entire peak is required; peak co-elution and the resulting lack of baseline peak resolution limits the IRMS software's ability to accurately calculate isotope ratios (Mathews and Hayes1978, Hayes et al., 1990; Ricci et al., 1994). A previous CF-IRMS study at SEOES using a shorter (60m) GC column was able to identify 16 compounds that produced a reliably/diagnostic molecular or isotopic signature (Harris et al., 1999). This present study, using a longer *Petrocol* column designed for petroleum separation, was able to separate more compounds than the 21 used for oil to oil comparisons, however not consistently throughout the entire weathering phase of the study for all 3 study oils. The previous study did not involve any oil weathering, or the multiple injector split flow adjustments necessary to capture the full range of compounds due to successive change in molecular abundances. During the early periods of weathering it was sometimes difficult to adjust split flows in order to capture diminishing lighter fractions without the over abundance of higher molecular weight fractions saturating IRMS amplifiers or effecting resolution through bleeding (overlapping) of adjacent compound peaks.

The compounds $iC_5$ and $nC_5$ are only included in final comparisons in order to describe trends in data, as their concentrations were insufficient for IRMS measurements during the final samplings in both Alberta and Louisiana oils due to their high volatility. These two compounds are referred to in the Discussion section when comparing the overall isotopic behaviors of compounds based on chemical structure and carbon number.

The resulting differential $\delta^{13}C$ data ($\delta^{13}T_0$- $\delta^{13}T_f$) associated with the remaining 19 compounds is presented and reviewed in the Discussion section to assist with comparisons between study oils and the results of related investigations by other researchers.

# CHAPTER 4. DISCUSSION

The following provides and discusses the evidence that supports the ability of Compound Specific Isotope Correlation (CSIC) to reliably discriminate between different crude oils, despite extensive evaporative weathering. The SPME-CF-IRMS measurement technique has sufficient sensitivity and resolution to track the changes in both the molecular abundances and the carbon isotope ratios of gasoline-range compounds of the 3 study oils which have been subjected to simulated sea surface evaporation.

Various physicochemical characteristics of each oil (Table 2.1) and experimental conditions are considered in discussing the molecular abundance loss rates and subsequent temporal availability of gasoline-range compounds using this technique.

The process of evaporation of crude oil at sea is not the direct subject of this thesis, and is not treated in depth. However, the experiments are designed to replicate the molecular and stable carbon isotope signatures and their respective fractionations in the gasoline-range compounds within and between the studied oils undergoing evaporative weathering. A brief overview of the evaporative rates of oils spilled at sea is included in the Introduction (Section 1.2.2), and although experiments are designed to roughly simulate sea surface conditions, results and observations are solely laboratory test based. Emulsion formation and the effect of wax content in oils are discussed in general terms due to the influence of these processes on the evaporation rates of the study oils.

The measurement setup of the present study, found that 19 gasoline-range compounds, common to all of the 3 study oils, could be used for further comparative interpretation. The trends found here that show increasing $^{13}C$ enrichment of the gasoline-range compounds relative to increasing degrees of evaporative weathering are comparable to

the results of similar investigations. Molecular abundance and isotope ($\delta^{13}C$) data are treated using Hierarchical Cluster Analysis (HCA) to classify and discriminate between the original (fresh) and weathered oils.

## 4.1 EFFECTS OF SIMULATED WEATHERING

### 4.1.1 Evaporation Rates: Changes in Relative Molecular Abundances

Evaporation rates of the volatile fractions in crude oils depend on various factors, such as, vapour pressure, oil composition, environmental conditions and sea state (Bobra, 1992; Fingas et. al., 2003; El-Nemr, 2006). As with any other volatile liquid, with a specific gravity less than the water, when a crude oil is spilled on the ocean, it will disperse and start to evaporate. As previously mentioned, the amount of material mass lost through the evaporation of a bulk oil follows a logarithmic rather than linear relationship with time, since crude oil is a complex mixture of many thousands of compounds with varying vapour pressures. This logarithmic behavior has been reported by other authors, e.g., Okamoto et al., 2010, Okamoto, Watanabe, Hagimoto, Miwa, & Ohtani, 2009; Fallah & Stark, 1976; Fingas,1995, 1997, 1998, 2004; Goodwin, Mackay, & Shiu, 1976; Mackay & Matsugu, 1973; Payne & McNabb, 1984; Tkalin, 1986.

Vapour pressures for various compounds investigated in this study are given in Table 4.1.

*Table 4.1. Vapour pressures for various gasoline-range hydrocarbons (20 $^{o}$C).*

| Compound | Vapour Pressure kPa | Compound | Vapour Pressure kPa |
|---|---|---|---|
| $iC_5$ | 92.6 | $nC_7$ | 6.11 |
| $nC_5$ | 68.4 | $MCYC_6$ | 5.73 |
| $2MC_5$ | 28.2 | $EtCYC_5$ | 5.06 |
| $3MC_5$ | 25.14 | $25DMC_6$ | 4.05 |
| $nC_6$ | 20.2 | $24DMC_6$ | 4.04 |
| $MCYC_5$ | 18.28 | Toluene | 3.8 |
| $CYC_6$ | 13.0 | $3MC_7$ | 2.6 |
| $2MC_6$ | 8.78 | $nC_8$ | 1.88 |
| $23DMC_5$ | 9.18 | $nC_9$ | 0.6 |
| $3MC_6$ | 8.21 | | |

Typically, the lighter fractions with the highest vapour pressures should evaporate most rapidly, with evaporation rates of the remaining lower vapour pressure fractions generally slowing with time. As a result, the overall vapour pressure of a multi-component fuel mixture exponentially decreases with time as the weight loss fraction increases, as reported by authors, e.g., Okamoto et al., 2010, Okamoto et al., 2009.

Plots of abundance fractions versus time (Figures 4.1 through 4.3) show that evaporation rates for the individual compounds within the 3 oils, in all but a few instances, e.g., cyclic compounds in Lacula, are proportional to their respective vapour pressures, i.e., lighter molecules with higher vapour pressures evaporate faster.

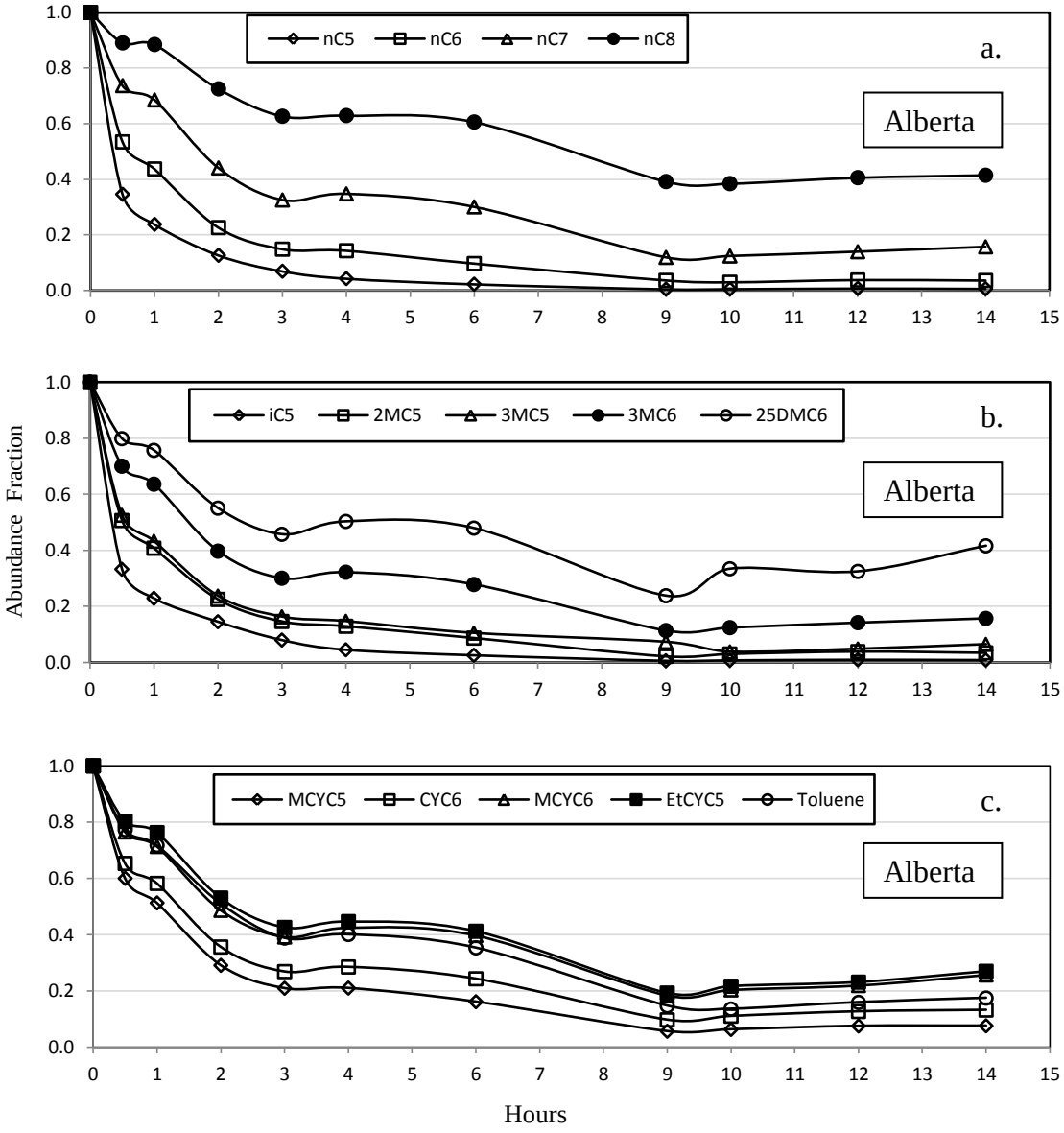



*Figure 4.1. Rate of evaporation for various compounds in the Alberta oil. a.) n-alkanes; b.) branched alkanes; c.) cyclic alkanes/aromatic.*

Abundance fractions, as previously explained, are the abundances (normalized to $nC_9$), of a compound remaining relative to its initial ($T_0$) abundance. Unweathered ($T_0$) abundance fractions of all compounds begin as 1 (i.e., 100%), with the fraction decreasing as evaporation progresses. Results presented as abundance fractions allow all

compound $T_0$ results to be plotted against a common reference point thereby making direct comparison of the individual evaporative rate curves.

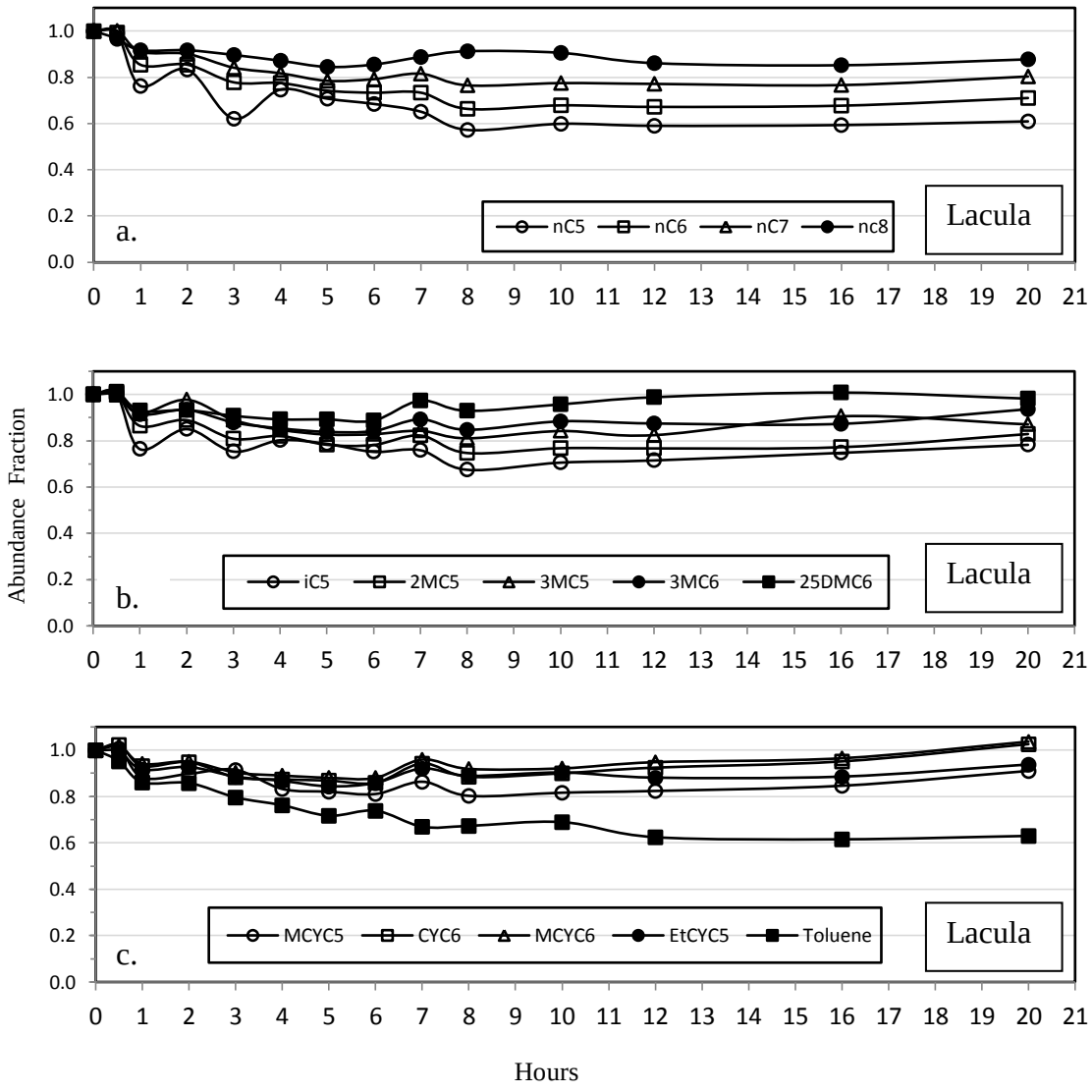



*Figure 4.2. Rate of evaporation for various compounds in the Lacula oil. a.) n-alkanes; b.) branched alkanes; c.) cyclic alkanes/aromatic.*

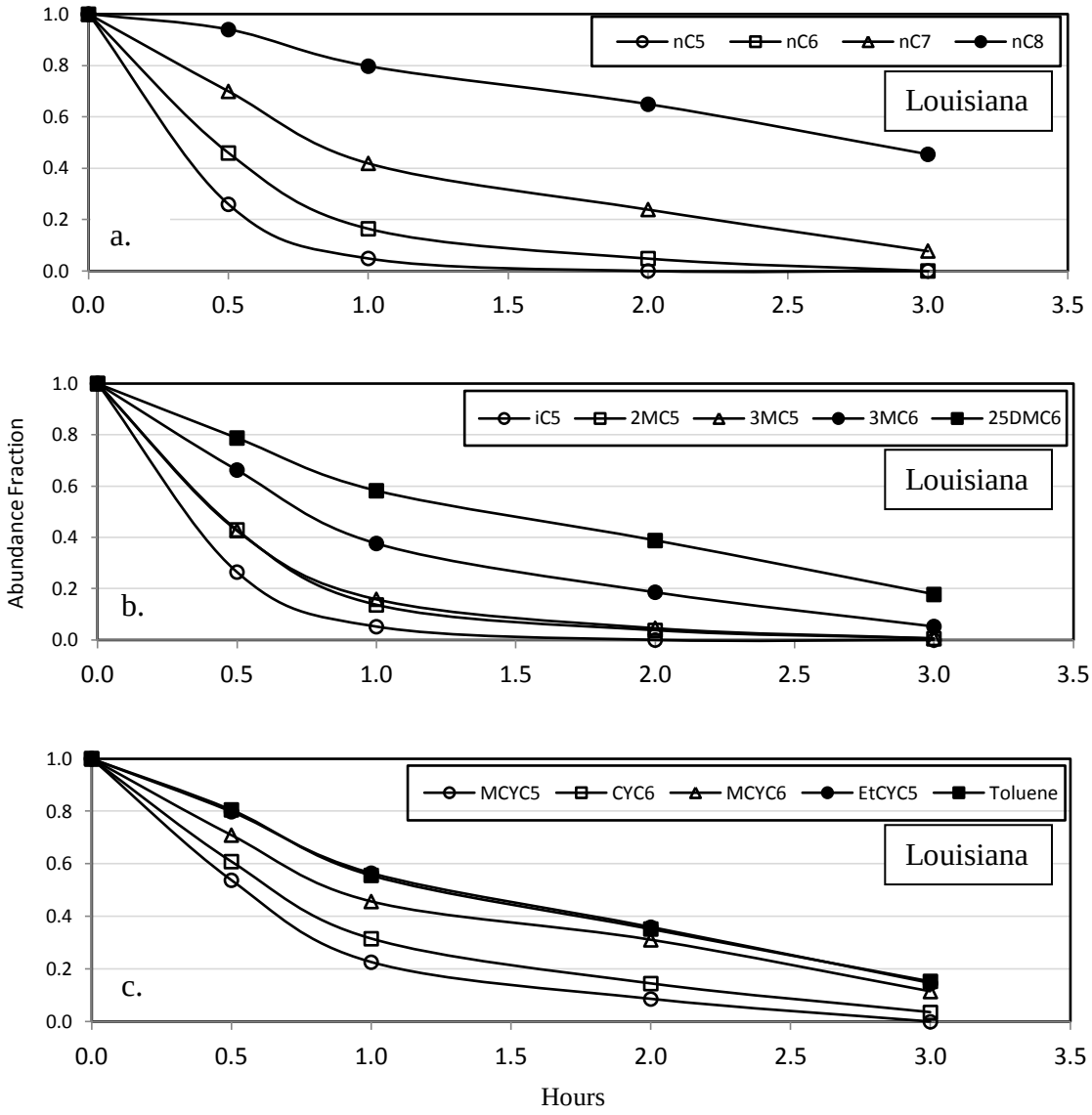



*Figure 4.3. Rate of evaporation for various compounds in the Louisiana oil. a.) n-alkanes; b.) branched alkanes; c.) cyclic alkanes/aromatic.*

The cycloalkanes in the Lacula oil (Figure 4.2c), as well as the aromatic toluene, do vary slightly from expected vapour pressure predictions. However this oil shows little overall change in all compound abundances over the duration of the experiment. Toluene has solvent properties and may have diffused through the waxy surface layers of the Lacula oil prior to those cyclic compounds with higher vapour pressures. Stiver et.al.

(1989) reports that for very viscous or waxy oils, evaporation will not only be slower but the relative evaporation rate of individual components can be altered.

Although the relative evaporation rates of the individual compounds, within each oil, follow expected patterns according to vapour pressures, the overall rate of evaporative loss for the measured compounds is different for each of the 3 study oils.

Laboratory evaporation results for bulk oils can often vary greatly from that of oil spills in the natural environment (Dodd, 1975). Even in the laboratory, differing experimental conditions and oil specific characteristics can determine the evaporative process. To illustrate this, the loss rates observed in this study are compared to bulk evaporative loss rates predicted by the suppliers of the oil, Emergencies Science Division (ESD) of Environment Canada. Predicted evaporative rate loss curves for the 3 study oils are given in Figures 4.4 and are determined using the following ESD equations:

**Alberta**: % Evaporated = (3.24 + (0.054*T) * Ln(t) (4.1)

**Lacula**: % Evaporated = (2.17 + (0.045*T) * Ln(t) (4.2)

**Louisian** % Evaporated = (2.39 + (0.045*T) * Ln(t) (4.3)

Where T is the temperature in degrees $^{o}C$

and t is the evaporation time in minutes.

(after Emergencies Science Division of Environment Canada; Jokuty et. al., 1999a).

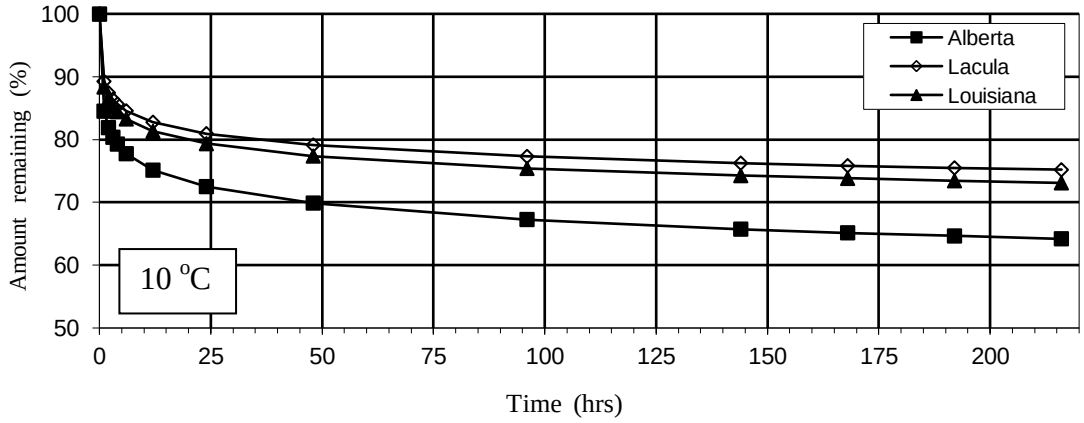



*Figure 4.4. Predicted evaporation rate curves for the three study oils at 10 °C. (Emergency Sciences Division, Environment Canada, 1999).*

Figure 4.4 shows that the ESD evaporative method predicts that the Alberta oil evaporates most rapidly, followed by Louisiana, and finally the Lacula oil. General evaporation loss trends in this present study, based on relative abundance changes and the loss of compounds to the IRMS quantification limits, differed from those predicted by the Environment Canada ESD equations (Figure 4.4). Study results show that gasoline-range fractions in the Louisiana oil evaporated most rapidly (Figure 3.12), followed by the Alberta oil (Figure 3.6) and finally the Lacula oil (Figure 3.9). Louisiana oil exhibits the most rapid loss of the lowest molecular weight compounds ($iC_5$ and $nC_5$), with concentrations insufficient for measurement after only 2 hours of weathering. These same compounds are measurably present at 12 hours of weathering in the Alberta oil, while the Lacula oil continues to have measureable concentrations of these same compounds after 20 hours of weathering.

Comparison of evaporative losses is based on the abundance losses of the gasoline-range fractions measured to the corresponding bulk losses shown in the first 25 hour section of the ESD evaporation curves (Figure 4.4). During this period the more volatile

gasoline-range fractions, that can constitute 20-40% of a crude oil, are rapidly lost (Bobra, 1992; McDonald et al., 1984).

All compound losses in this study are assumed to be attributed solely to evaporation as experimental conditions exclude other causes of bulk oil losses, such as biodegradation and/or dispersion. ESD evaporation experiments are based on a simple pan evaporative technique with progressive weight loss systematically monitored by a computer assisted electronic balance as outlined in the Appendix of Methods, Pan Evaporation of Oils in the Catalogue of Crude Oil and Oil Properties (Jokuty et. al., 1999a). Weight losses of the bulk weathered oil samples are not systematically measured in this present study and as explained in section 3.2.1, abundance losses are calculated using the abundance ratio of a compound relative to $nC_9$ (i.e., $nC_9$ normalized).

Chromatograms of the unweathered oil samples (Figure 3.1) show that the Louisiana oil has roughly 40% of the abundance of $iC_5$ and $nC_5$ compared to the other two study oils, not supporting that these Louisiana compounds evaporated to undetectable concentrations 8-times and 10-times faster than the Alberta and Lacula oils respectively. Unlike the ESD static pan evaporation technique, the present study involves the addition of oils added onto a saltwater medium and exposure to continuous mechanical wave energy. The differences in weathering methods may explain the observed changes resulting in emulsion and waxy film formation on the Louisiana and Lacula oils, and the differences in evaporation trends compared to ESD rate predictions. As gasoline-range compounds do evaporate rapidly from a spill, any factors associated with the slowing of the evaporative process in a natural setting increase the potential availability of these volatile fractions for CSIC.

Although terrestrial spill contamination is not the focus of this thesis, oils spilled on the ocean surface often reach shorelines and may undergo physical changes that decrease their rate of weathering. Owens et al. (2008) evaluated the results of studies (e.g., Harper et al., 1995;Owens and Lee, 2003; Short et al., 2003) that investigated the factors associated with short and long term persistence of oils spilled on coarse sediment beaches; concluding that small amounts of oil can persist for weeks or months under various environmental conditions, in the pore spaces between coarse sediment particles.

The delay or prolonging of typical weathering however, does require specific circumstances in climactic conditions. Investigations by Harper and Kory (1995), have shown that various oil types penetrate shoreline sediments after a spill and remain at depth for extended periods potentially inhibiting evaporative losses of volatile fractions.

Owens (1985) earlier defined the wide range of parameters that determine residence time of spilled oil on low-energy shoreline as follows:

- the volume of oil that reaches the shoreline;
- the physicochemical properties of the stranded oil;
- mechanical wave energy levels at the shoreline;
- the distribution of the oil with respect to littoral processes;
- rates of short-term sediment redistribution dynamics.

Furthermore petroleum products spilled , or leaked, into soils can be less effected by typical weathering, whereby gasoline-range fractions may persist longer than those spilled directly onto ocean surfaces. Various studies investigating the use of the CSIC technique using to characterize petroleum spills into soils and groundwater have been reviewed by Wang and Stout (2007).

#### *4.1.1.1 Surface Emulsions*

As previously stated in section 3.2.1.3, surface emulsions are observed on the Louisiana oil samples at $T_{0.5}$, $T_1$ and $T_2$, with emulsion thicknesses on the triplicate $T_{0.5}$ samples being up to five times the original 4.0 mm thickness of the oil initially added to the saltwater surface, (i.e., 1.8, 1.9 and 2.0 cm). Although emulsion thicknesses gradually decreased, thicknesses at $T_2$ are still twice that of the original oil applied (Figure 4.5).

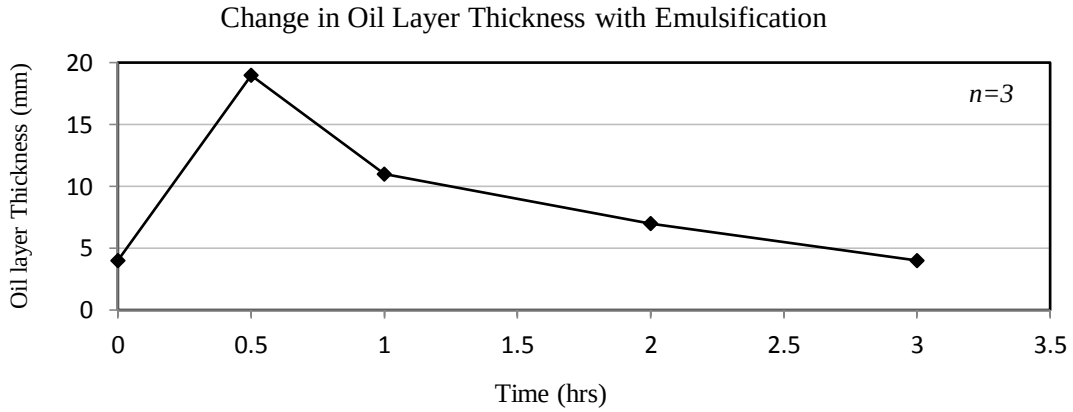



*Figure 4.5. Average change in oil thickness with increased weathering time. Surface emulsion is observed at the $T_{0.5}$ sampling. No emulsion was observed at the $T_f$ (3 hours).*

In addition to the oil characteristics necessary for emulsions described in the Introduction (Section 1.2.2), Fingas et. al. (2002) describes four states, or types, of emulsions including: stable emulsions, meso-stable emulsions, unstable emulsions (or simply water and oil mixtures). Unstable emulsions are those that decompose to water and oil rapidly after mixing, generally within a few minutes to hours (Fingas et. al., 2000).

All surface emulsions dissipated within 15 minutes after being removed from the mechanical wave energy in the environmental chamber, therefore the Louisiana emulsions are considered unstable.

The formation of a typical water-in-oil emulsion in the Louisiana oil is somewhat inconsistent with its undetectable asphaltene content, as listed in the ESD specifications (Table, 2.1). Unweathered Louisiana has a resin content of 4% by weight. Results from Bobra (1992) describe that even in the absence of asphaltenes, resins alone can act as effective emulsifiers although the emulsions formed are generally less stable than with both asphaltenes and resins present.

Since reduced viscosity can also promote emulsion formation in lower energy sea surfaces (Fingas et. al., 2000), and both Louisiana and Alberta have similar viscosities (Table 2.1), it is unclear as to why the Alberta oil did not form an emulsion under identical weathering conditions. Alberta is considered to have high emulsion forming properties and has been used in many oil spill emulsion investigations (Bobra, 1992; Fingas et. al., 2003). Aromatic solvents were more abundant in the Alberta oil so may have required more weathering to reduce BTEX low enough to allow stabilization of asphaltenes and resins (and more wave energy), to promote emulsification.

A review of the ESD Catalogue of Crude Oil and Oil Product Properties lists interfacial tension (mN/m) as a measurement of a spill spreading rate and also the likeliness an oil will form an emulsion. Interfacial tension is the force of attraction of molecules at the oil-water interface (Fingas et. al,. 1979). Louisiana has an unweathered interfacial tension slightly less than the Alberta oil, 19.6, versus 23.1 mN/m. This lower surface tension could allow an unstable mixture of oil in water or even air-in-water to form as a result of the simulated wave energy alone. This would explain the rapid decomposition of the surface mixture soon after the simulated wave energy was removed. Generally, even a temporary unstable emulsion of water-in-oil can retard evaporation (Fingas et. al., 1995a; Aranberri et al., 2002). An air-in-oil mixture would explain the

much more rapid evaporation, with the small air bubbles increasing surface area and accelerating the evaporation rate. Observations of the decomposing emulsions did show small oil bubbles bursting, but it is undetermined as to whether they contained water and/or air. Since the oils are weathered at one temperature only, it is unknown as to what degree temperature effected emulsion formation in these oils. Since the sealed sample jars are transported to the laboratory for analyses, warmer laboratory temperatures may influence the decomposition of the emulsions. The absence of an emulsion at $T_f$ is most likely the end point of the destabilization of an initially formed emulsion, followed by increased viscosity due to volatile losses and subsequent reduced air-oil-water interaction.

#### *4.1.1.2 Wax Content*

The slower rate of evaporation observed in the Lacula oil (Figure 3.10; 3.12), compared to both Louisiana and Alberta, is attributed to its relatively high wax content (Table 2.1). Lacula has a 13% by weight wax content, over twice as much as the Alberta oil and 3 times that of Louisiana. Oils with more than 5% wax content are considered high wax oils, although some oils (e.g., Azeri crude) contain as much as 23% wax (Chapman, 1983). Petroleum waxes are complex mixtures of high molecular weight alkanes (paraffins and isoparaffins: paraffin wax) in the $C_{18}$ to $C_{36}$ range but may also include napthenic hydrocarbons in the $C_{30}$-$C_{60}$ range. The pour point, which is the lowest temperature at which an oil will flow (under standard test conditions), is generally associated with high-wax oils (Chapman, 1983). Lacula has a pour point of 18 $^{o}$C. Alberta and Louisiana have pour points much lower at -27 and -28 $^{o}$C respectively (Table 2.1). Much of the evaporation rate research prior to a study on waxy oils performed by

Ross and Mackay (1988) made the assumption that a spilled oil layer was well mixed, with no diffusive resistance to volatilization in the oil phase. Their experiments determined that the 'crusty' film layer that forms on waxy oils essentially traps the volatile hydrocarbons and significantly retards evaporation. All oil spill evaporation models at that time appreciably overestimated the evaporation rates of volatile compounds in waxy oils. Ross and Mackay (1988) also quantified "crust resistance" for the more volatile components in waxy oils. Less volatile components of waxy oils evaporate much more slowly and therefore have more time to diffuse through the oil layer so crust resistance was considered less important. The study concluded that the major characteristics of waxy oils when spilled on water are that they are slow or non-spreading, have anomalous emulsification and reduced evaporation rates (Ross and Mackay, 1988). Others, including Bobra (1992) also confirmed that evaporation was inhibited by the formation of waxy surface crusts.

At the 10 $^{o}$C weathering temperature used in this study (8 $^{o}$C below the Lacula pour point; Table 2.1), any resulting surface film can act as a semi-permeable layer to the volatilizing gasoline range fractions. As shown in Figures 3.11 relative abundance losses are less than seen in the Alberta or Louisiana oils and appear to stabilize after 8 hours of evaporation. A persistent waxy film was first noticed at the 6 hour sampling, although was most likely present to a lesser degree earlier in the time series. Slower, yet progressive evaporation of the more volatile components ($< C_6$) during the first 6 hours may increase both surface wax formation and the resistance in the liquid phase diffusivity.

Development of the waxy film could explain why many of the compounds show little change in relative abundances after $T_8$ (Figure 3.12). A more impermeable crust is

favored as an explanation, however the lack of change in relative abundance ratios is not an indicator that evaporation had ceased or that molecular abundances are not changing, rather it indicates no relative changes were occurring. Although beyond the scope of this thesis, more complex diffusion processes may be in effect wherein compounds are diminishing more slowly and even at similar rates as $nC_9$ through the waxy crust, resulting in an unchanging abundance ratio. Regardless, molecular abundances measured by IRMS show much higher concentrations of the target fractions remaining in Lacula than in both other oils at $T_f$.

Lacula compounds show only very slight decreases (1-5%) in abundance in the first 0.5 hour (Figure 3.10), unlike the Alberta and Louisiana oils where losses in some compounds (e.g. $iC_5$, $nC_5$) were as high as 74% (Figures 3.7 and 3.13). More significant changes are seen at $T_1$, wherein $iC_5$ and $nC_5$ show 24% decreases in abundance. The slowed evaporation in the initial 0.5 hour may be due to the fact that the Lacula oil was evaporated at 8 $^oC$ below the pour point temperature of 18 $^oC$ (see Table 2.1). Oils spilled into the sea at temperatures below their pour point tend to become semi-solid. As an oil cools, it will reach a temperature, the so-called 'cloud point', at which the wax components begin to form crystalline structures, eventually changing from liquid to semi-solid at the pour point (ITOPF, 2002).

Early evaporative losses could have been inhibited in the first 0.5 hour by the sudden decreased temperatures and resulting highly viscous waxy oil. As weathering progressed, the wave energy produced by the shaker table had more time to mechanically alter the surface layers or fracture any initial film that developed, allowing more evaporation to occur at $T_1$. In the case of a persistent surface film, it is also possible that additional time

was required for any significant amounts of the volatile fractions to the diffuse through relatively thick oil layer.

### 4.1.2 Carbon Isotope Ratio Changes

There are mass dependant kinetic carbon isotope effects during evaporation of oils. This is a result of the two stable carbon isotopes ($^{12}C$ and $^{13}C$) not evaporating at the same rate, i.e., having different vapour pressures. When evaporation occurs in a non-equilibrium system, as in this study, where the evaporation is unidirectional and vapours are removed and isolated, the remaining liquid oil is isotopically fractionated from the vapour. Typically for hydrocarbons, the lighter isotopologue (relatively more $^{12}C$-enriched), has a higher vapour pressure and hence evaporates faster than the heavier isotopologue (relatively more $^{13}C$-enriched). The initial vapour phase is depleted in the $^{13}C$ isotopologue, with the residual liquid oil phase becoming increasingly enriched in $^{13}C$. As evaporation continues, the vapour phase gradually becomes more $^{13}C$-enriched due to the progressive $^{13}C$-enrichment of the residual liquid oil phase.

The expression used to describe this kinetic isotope partitioning as a function of the fraction of a compound remaining, where two phases do not equilibrate or re-exchange, is the Rayleigh Distillation Equation (Broecker and Oversby, 1971)

$$R/R_o = f^{(\alpha - 1)} \qquad (4.1)$$

where R is the $^{13}C/^{12}C$ ratio of the remaining liquid,

$R_o$ is the $^{13}C/^{12}C$ ratio of the initial liquid,

$f$ is the fraction of the liquid remaining and

$\alpha$ is the fractionation factor = $R_{oil}/R_{vapour}$

The isotope *fractionation factor* (α) is the amount of isotope partitioning that occurs as the oil transitions from liquid to vapour phase. It is described mathematically by the comparison of the two carbon isotope ratios before and after the physical-chemical transition process (Eq. 4.2). In general the carbon fractionation factors for the gasoline-range compounds are very small, being very close to 1, i.e, 1.0001-1.03.

$$\text{Fractionation factor } \alpha_{\text{oil-Vapour}} = R_{\text{oil}} / R_{\text{Vapour}} \qquad (4.2)$$

Figure 4.6 presents a generalized illustration of the Rayleigh process. The curves show the relationship between the isotopic composition of a compound in the liquid and vapour phases as evaporation progresses.

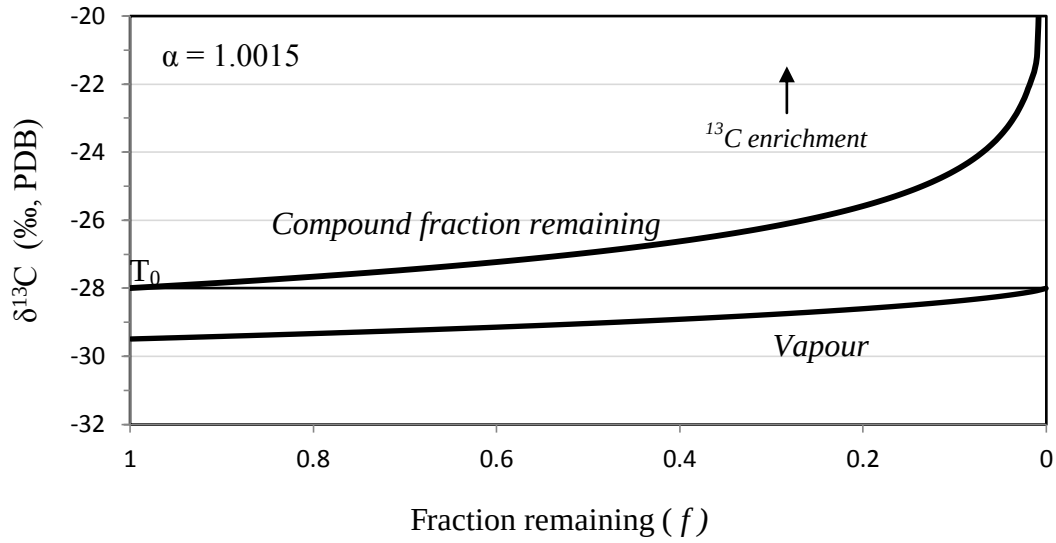



*Figure 4.6. Theoretical example of the continuous enrichment of the $^{13}C$ isotope of a compound in the liquid oil by the Rayleigh process as a function of the fraction removed. The lower curve represents the average cumulative $\delta^{13}C$ composition of the vapour product.*

In this study, the application of the Rayleigh function is not possible because the fraction ( *f* ) of the original liquid oil remaining could not be determined.

Time series measurements from the 3 study oils (Figures 3.18, 3.21, 3.24) illustrate a trend in $^{13}C$-enrichment in the oils as evaporation progressed. Figures 4.7 through 4.9 more clearly display the gradual $^{13}C$-enrichment of various individual compounds in the oils with diminishing abundances, as would be predicted with a Rayleigh distillation process. Results for the Lacula oil with comparatively much less abundance change (Figure 3.21), exhibits a less consistent pattern of $\delta^{13}C$ change (Figures 4.9b, d, f).

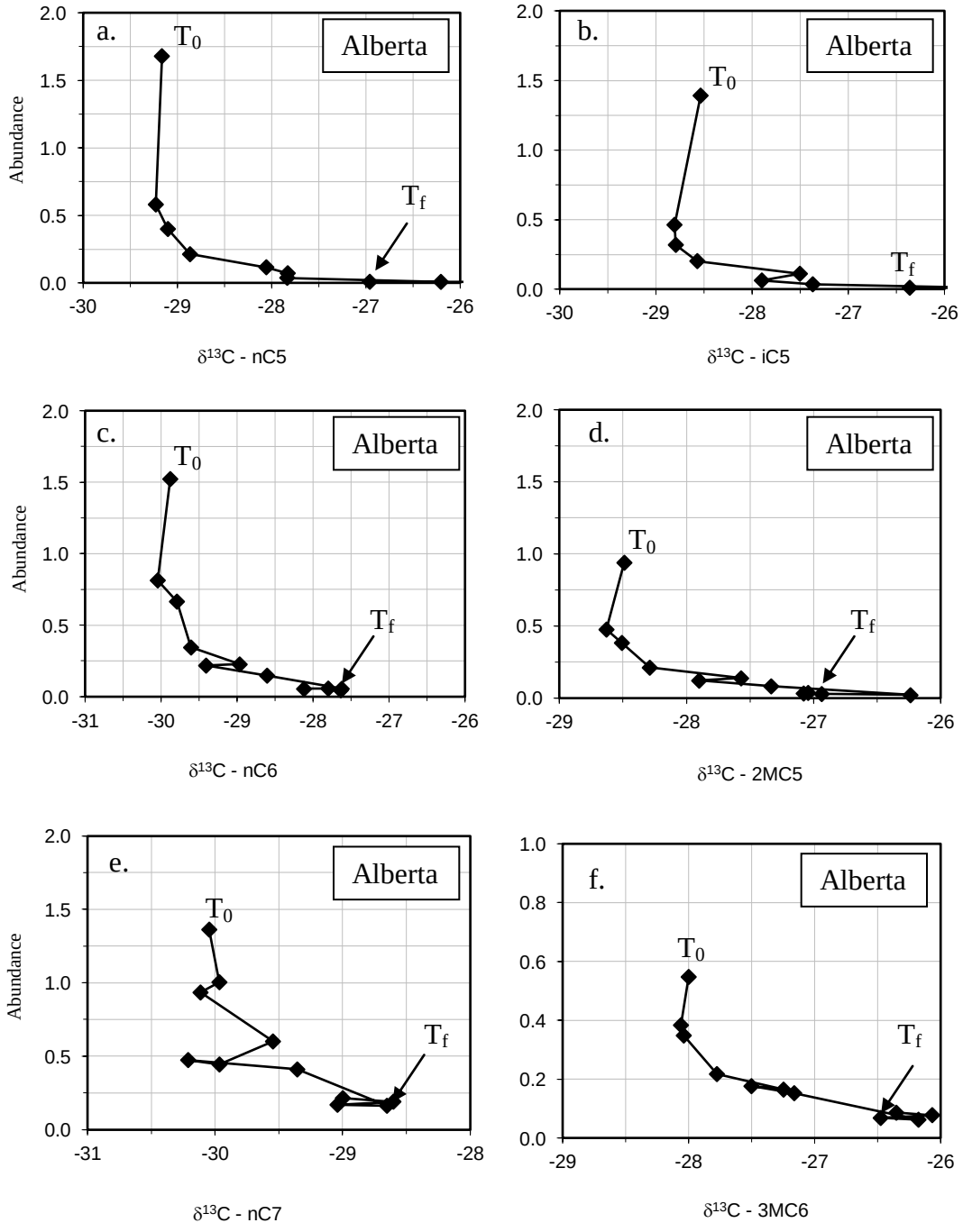



*Figure 4.7. Change in $\delta^{13}C$ with abundance decrease in various n-, and iso-alkanes in Alberta oil. $T_0$: unweathered; $T_f$: final sample.*

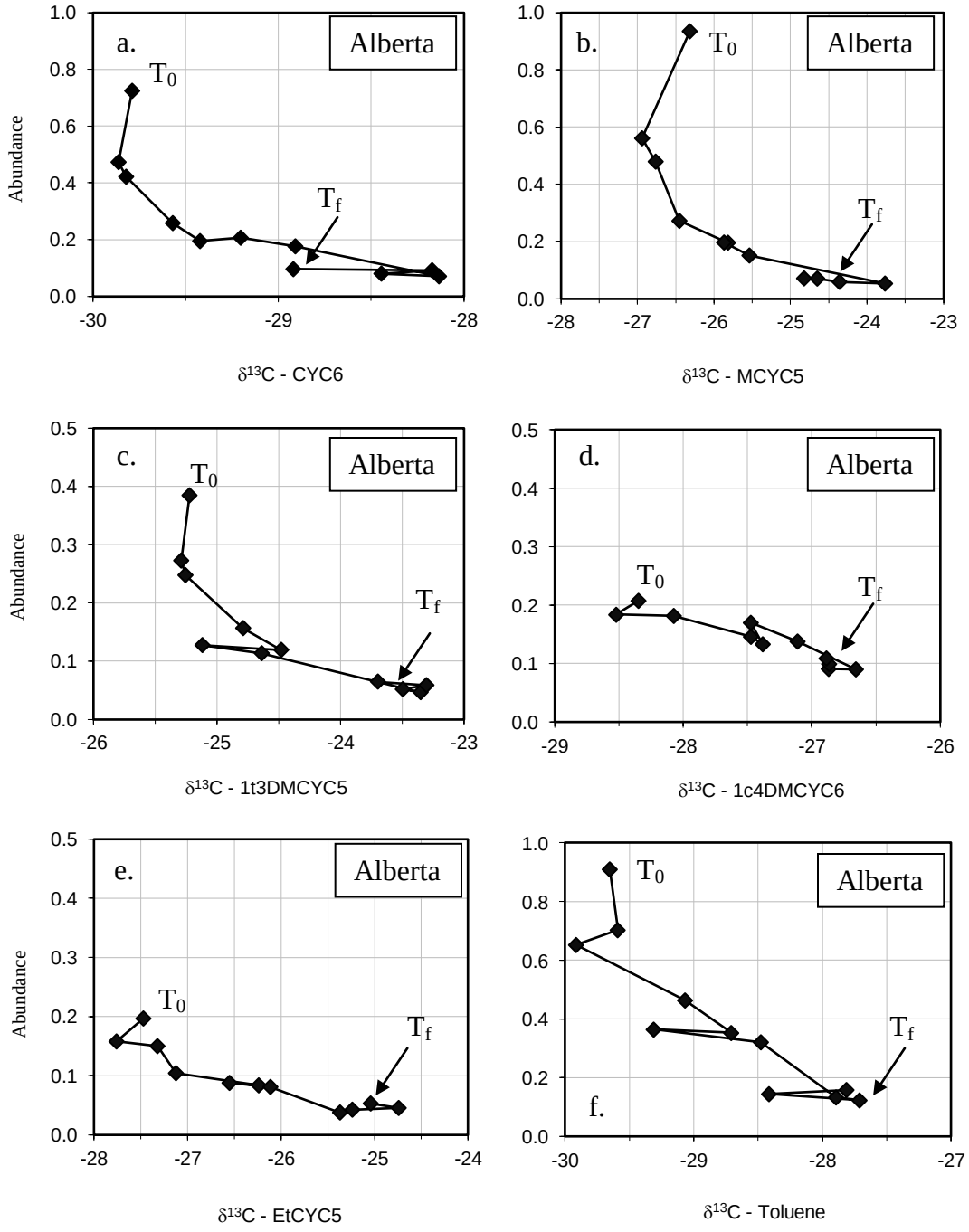



*Figure 4.8. Change in $\delta^{13}C$ with abundance decrease in various cyclo-alkanes and an aromatic (toluene) in Alberta oil samples.*

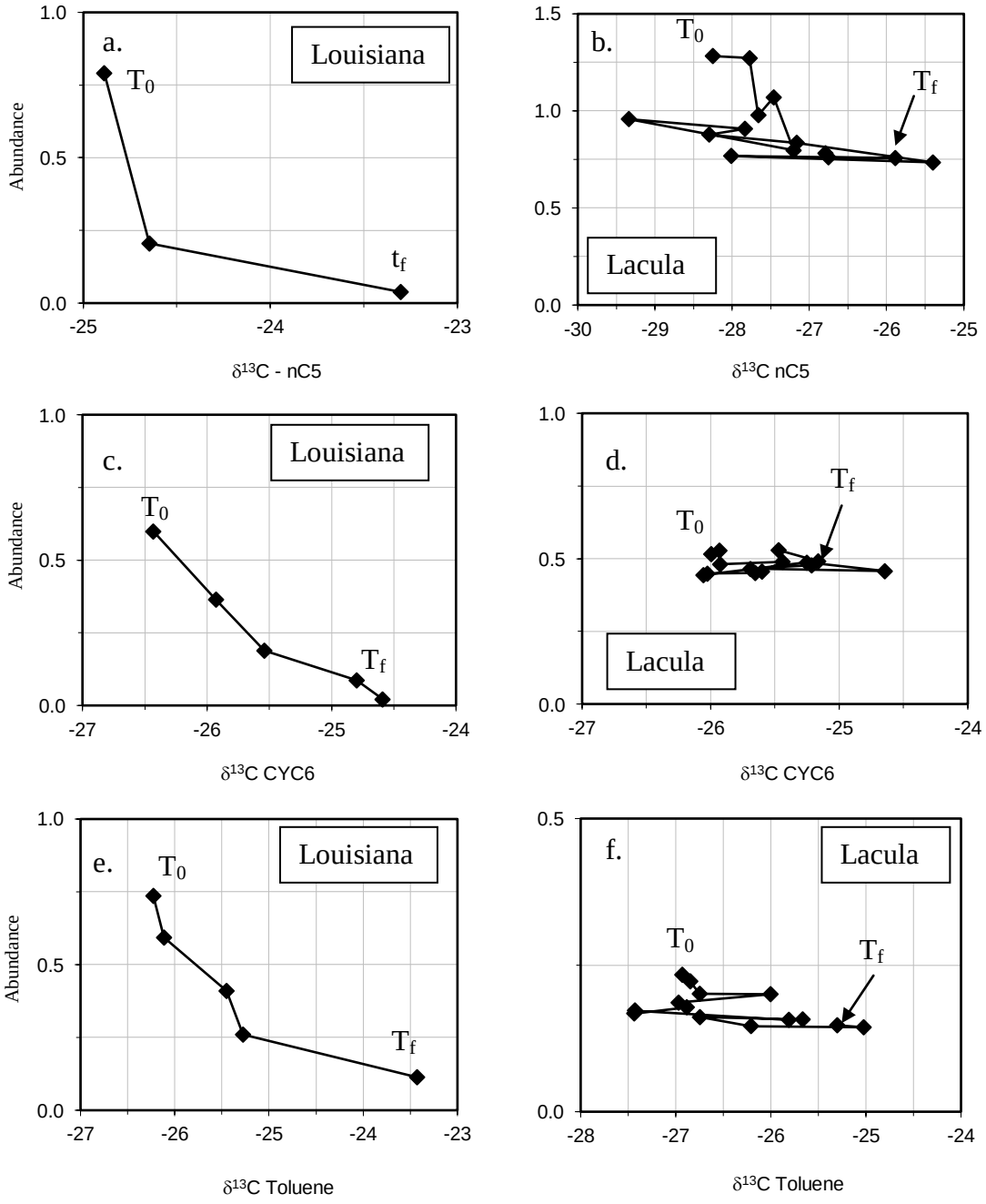



*Figure 4.9. Change in $\delta^{13}C$ with abundance decrease in an n-alkanes, a cyclic alkane and an aromatic (toluene) in Louisana and Lacula oil samples.*

Figures 4.7 through 4.9, also show that in some instances the final time intervals do not have the heaviest $\delta^{13}C$ values as would be expected as a consequence of the liquid becoming progressively depleted in $^{12}C$ (e.g., Figures 3.18a, 3.21b, d and 4.9 b, d, f). The explanation for this is uncertain, however as the amount of material decreases at the end of the experiments, the analytical error can increase due to factors such as incomplete combustion, water contamination and poor peak resolution, etc., as discussed in Sections 2.4.3 and 3.1. As another potential source of the inconsistent pattern of $^{13}C$ enrichment, it is also important to note that cumulative evaporation measurements do not occur from a single reservoir of oil. Each individual sample jar is autonomous and may have slightly different evaporative rates (and degrees of fractionation). This may be more relevant to the more waxy Lacula oil, which shows the most inconsistent pattern of $\delta^{13}C$ change, due to potential for variability in waxy film formation between different experimental jars.

Information from Figures 3.17, 3.20 and 3.23 has been condensed into 'difference isotopograms' Figures 4.10a-c (after Whiticar and Snowdon, 1999), showing the amount of change in compound $\delta^{13}C$ values ($\Delta\delta^{13}C$) between the unweathered and $T_f$ for the 19 common compounds. Data comprising Figure 4.10 are grouped into the different chemical classes and presented in Table 4.2. All errors associated with the $\Delta\delta^{13}C$ values are calculated using Eq. 2.2. presented in Section 2.5.1.

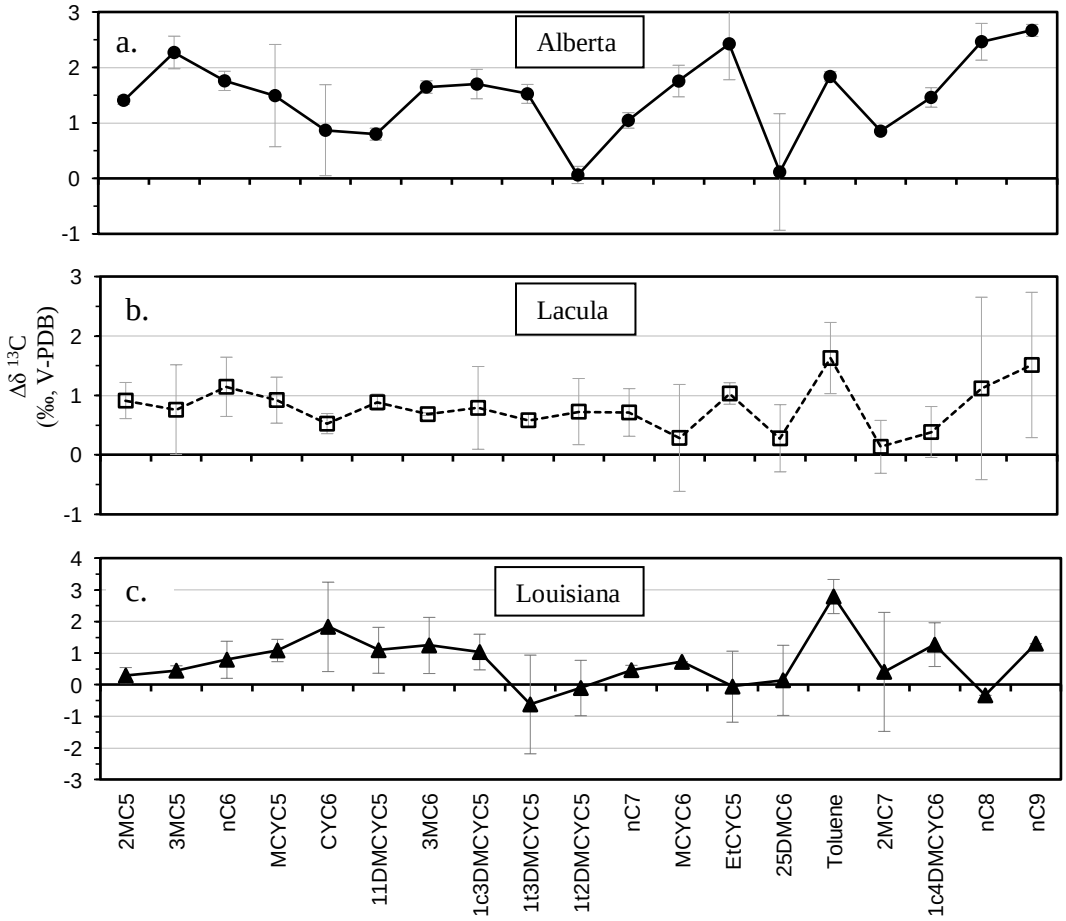



*Figure 4.10. Difference isotopograms showing change in $\delta^{13}C$ values ($\Delta\delta^{13}C$) relative to unweathered oils ($T_0$; x axis) after final sampling($T_f$ ). a.) Alberta; b.) Lacula; c.) Louisiana. Positive values represent $^{13}C$ enrichment.*

Table 4.2 shows that overall for the 19 compounds compared in the 3 oils, a total of 42 out of 57 or 74% of the compounds show some degree of $^{13}C$ enrichment for $T_f$ relative to $T_0$. Approximately 21% have no change in $\delta^{13}C$ after weathering within experimental precision. Three compounds in the Louisiana oil (nC8, 1t3DMCYC$_5$ and 1t2DMCYC$_5$) show a $^{13}C$ depletion for $T_f$ relative to $T_0$ , although these 'reversals' are small ($\leq$ 0.6‰) and uncertainties are relatively large (± 0.9-1.6‰). Approximately 54% (31/57) of the compounds show $^{13}C$ enrichment $\leq$ 0.5‰ within experimental uncertainty.

*Table 4.2. $\Delta\ \delta^{13}C$ ($\delta^{13}C_{Weathered} - \delta^{13}C_{Unweathered}$) measured after final weathering($T_f$) of the study oils. Compounds showing enrichment within experimental precision)in $^{13}C$ for $T_f$ relative to $T_0$ are shown in bold.*

| **Compound Class** | **$\Delta\ \delta^{13}C$ (‰)** | | |
|---|---|---|---|
| **n-alkanes** | **Alberta** | **Lacula** | **Louisiana** |
| **$nC_6$** | **1.8 ± 0.3** | **1.1 ± 0.5** | **0.8 ± 0.7** |
| **$nC_7$** | **1.0 ± 0.3** | **0.7 ± 0.4** | **0.5 ± 0.3** |
| $nC_8$ | **2.5 ± 0.4** | 1.1 ± 1.5 | -0.3 ± * |
| **$nC_9$** | **2.7 ± 0.2** | **1.5 ± 1.2** | **1.3 ± *** |
| **Branched alkanes** | | | |
| $2MC_5$ | **1.4 ± 0.1** | **0.9 ± 0.4** | 0.3 ± 0.5 |
| $3MC_5$ | **2.3 ± 0.3** | 0.8 ± 0.8 | **0.5 ± 0.2** |
| **$3MC_6$** | **1.6 ± 0.2** | **0.7 ± 0.2** | **1.3 ± 0.9** |
| $2MC_7$ | **0.9 ± 0.1** | **0.1 ± 0.5** | 0.4 ± 1.9 |
| $25DMC_6$ | 0.1 ± 1.3 | 0.3 ± 0.8 | 0.1 ± 1.1 |
| **Cyclic alkanes** | | | |
| **$MCYC_5$** | **1.5 ± 0.9** | **0.9 ± 0.5** | **1.1 ± 0.4** |
| **$CYC_6$** | **0.9 ± 0.8** | **0.5 ± 0.3** | **1.8 ± 1.4** |
| $MCYC_6$ | **1.8 ± 0.3** | 0.3 ± 0.9 | **0.7 ± *** |
| **$11DMCYC_5$** | **0.8 ± 0.3** | **0.9 ± 0.2** | **1.1 ± 0.8** |
| **$1c3DMCYC_5$** | **1.7 ± 0.4** | **0.8 ± 0.7** | **1.0 ± 0.7** |
| $1t3DMCYC_5$ | **1.5 ± 0.3** | **0.6 ± 0.2** | -0.6 ± 1.6 |
| $1t2DMCYC_5$ | 0.1 ± 0.2 | **0.7 ± 0.6** | -0.1 ± 0.9 |
| $EtCYC_5$ | **2.4 ± 0.7** | **1.0 ± 0.2** | 0.0 ± 1.2 |
| $1c4DMCYC_6$ | **1.5 ± 0.2** | 0.4 ± 0.5 | **1.3 ± 0.8** |
| **Aromatics** | | | |
| **Toluene** | **1.8 ± 0.1** | **1.6 ± 0.6** | **2.8 ± 0.6** |

*Single measurements only were obtained for these compounds in the final samplings, therefore no standard deviations are available.

Alberta has the most $^{13}C$-enriched compounds with 89% (17/19); followed by 74% (14/19) in the Lacula oil and 63% (12/18) in Louisiana. Only 9 of the 19 compounds are enriched in $^{13}C$ in all three oils ($nC_6$, $nC_7$, $nC_9$, $3MC_6$, $CYC_6$, $MCYC_5$, $11DMCYC_5$, $1c3DMCYC_5$ and toluene). Of these 9 compounds, only toluene exhibits $\Delta\delta^{13}C$ values greater than 1‰ in all 3 oils within measurement precision (1.8 ± 0.1‰, 1.6 ± 0.6‰ and 2.8 ±0.6‰ for Alberta, Lacula and Louisiana oils respectively). $25DMC_6$ is the only

compound with an absolute value of $\leq 0.3$‰ in all 3 oils, although this value is below the analytical uncertainties of over > 0.8 ‰ for the three oils. The compounds $nC_8$, $1t3DMCYC_5$ and $1t2DMCYC_5$ show a $^{13}C$ depletion of -0 .3‰ (1analysis only), -0.6 ±1.6‰ and -0.1 ± 0.9‰ respectively, although the analytical uncertainty of the dialkyl-alkanes is over > ±0.9‰.

Overall there is a trend in $^{13}C$ enrichment for all compounds as evaporative weathering progresses. The data does not however display any consistent amount of $^{13}C$ enrichment in any of the individual compounds of specific chemical class or carbon number (see Section 3.2.2; Figure 4.10; Table 4.2). Based on weighted bulk averages for $T_0$ and $T_f$ $\delta^{13}C$ values from Table 4.2, the mean amount of $\delta^{13}C$ enrichment for compounds within an oil at $T_f$ are:

Alberta: 1.3‰ ($T_{f=14hrs}$)

Lacula: 0.9‰ ($T_{f=20hrs}$)

Louisiana: 0.4‰ ($T_{f=3hrs}$)

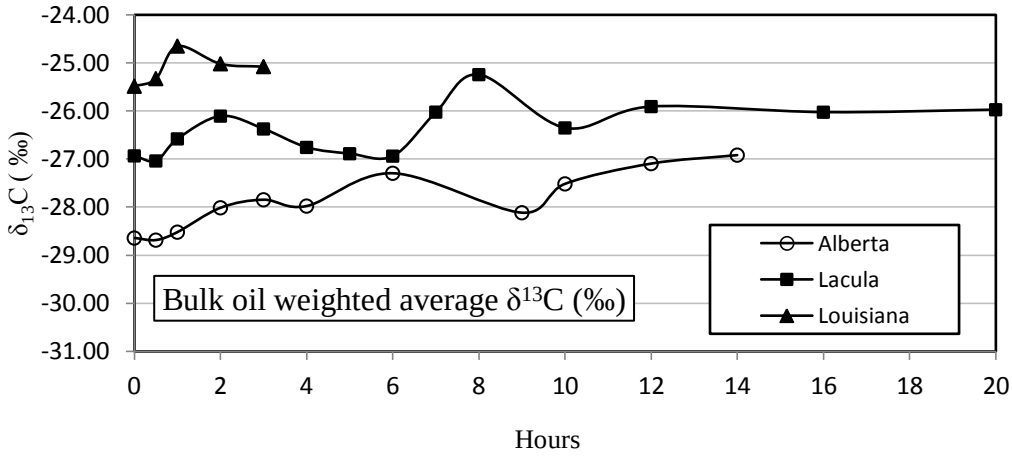



*Figure 4.11. Bulk weighted averages in $\delta^{13}C$ for gasoline-range hydrocarbon compounds in the 3 study oils.*

The weighted average $\Delta\delta^{13}C$ for the entire suite of compounds in all 3 oils, comparing $T_0$ to $T_f$, is approximately 1.0‰.

The $\Delta\delta^{13}C$ range in all compounds is up to 2.8‰ (toluene in Louisiana). Toluene showed consistently larger amounts of positive $\Delta\delta^{13}C$ in all 3 oils. The reason for larger $\Delta\delta^{13}C_{toluene}$ may be attributed to toluene's solvent properties and its high aqueous solubility (490-627 ppm) relative to non-aromatic compounds (e.g., the immiscibility of $nC_7$ in water) which may affect the magnitude of any fractionation measured. The $^{13}C$ substituted toluene may situated deeper in the liquid oil phase (and water phase) leading to preferential and more rapid evaporation of $^{12}C$ substituted compounds.

***Previous gasoline-range carbon isotope investigations***

There are few comparable studies that investigate the effects of evaporation on compound specific, gasoline-range stable carbon isotope composition of petroleums. Investigators, e.g., Li et al.,(2009); Smallwood et al., (2002); Mansuy et al., (1997); Fingas, (1997); Fingas, (1995a), generally focus on heavier chemical fractions of crude oil since typically there is a rapid loss of hydrocarbons below $C_{12}$ in the first 24 hours after a spill. Li et al., (2009) concluded that short term weathering (i.e., 72 hours) has no effect on the $\delta^{13}C$ values of individual n-alkanes in the heavier non-gasoline range ($C_{12}$-$C_{33}$). In general, in temperate conditions, oil compounds with boiling points $\leq 200\ ^oC$ (see Table 2.3) evaporate within the first 24 hours (Fingas, 1997).

However, despite the typically rapid loss of these volatile constituents, gasoline-range fractions from ocean surface oil slicks have been successfully collected using HSPME (Abrams et al., 2010). They used various sample methods, including sorbent materials and water sample containers, for the collection of ocean surface gasoline-range

hydrocarbons at a natural oil seep area off the coast of California (Trilogy Seep). They did not report any isotope measurements. One of the Abrams et al. (2010) methods is very similar to this study, and used a commercial 1 liter plastic collection container (*Disrupter*) with a teflon syringe septum and an air-tight lid to collect a water sample for later HSPME analysis of volatile hydrocarbons. Surface samples over fresh seeps, collected using the sorbent materials (*Gore Sorber Slick Sampler*), also stored in sealed containers and analyzed using HSPME, found detectable concentrations of gasoline-range n-alkanes $C_4$ and larger. HSPME analysis of the *Disrupter* samples, containing surface oil and water mixtures, resulted in undetectable concentrations of these fractions. Abrams et al. (2010) report that the hydrophobic sorbent materials cumulatively collected a higher concentration of the desired fractions available for HSPME.

CSIC evaporation studies reviewed, where gasoline-range fractions are available for CF-IRMS analysis, focus on residuals of gasoline-range fractions typically measured in pure gasolines ($C_4$-$C_{10}$) or oil condensates ($C_4$-$C_{20}$) to study carbon isotope changes (e.g., Sherwood et al., 2002, Harrington et al., 1999; Bjorøy et al.,1994).

Smallwood et al. (2002) using CF-IRMS, performed evaporation experiments on three gasoline samples, evaporating them for a total of one week (168 hours) at room temperature. After 168 hours the composition of the residual gasoline was very different from the fresh sample; Smallwood et al. (2002) reports that due to the absence of gasoline-range peaks and the residual hydrocarbon fractions being unresolvable, spill to source correlations using GC or GC-MS identification would be impossible. Only $C_{11}$ compounds were present in measurable concentrations after 120 hours. Sufficient concentrations of toluene, $2MC_7$, $3MC_7$, $nC_8$ and $nC_9$ were measureable in some samples

after 24 hours, with the results of the amount of $^{13}C$ enrichment observed compared to the present study presented in Table 4.3 and in the differential isotopogram Figure 4.12.

*Table 4.3. Comparison of the amount of $\Delta\delta^{13}C$ ‰ ($T_f$ relative to$T_0$) observed in compounds common to Smallwood et al. (2002) and the present CSIC study.*

| | **Gasoline (Smallwood et al., 2002)** | **Alberta** | **Lacula** | **Louisiana** |
|---|---|---|---|---|
| **Compound** | **$\Delta\delta^{13}C$ ‰** | | | |
| Toluene | 1.0 ± 0.6 | 1.8 ± 0.1 | 1.6 ± 0.6 | 2.8 ± 0.6 |
| $2MC_7$ | 0.8 ± 0.5 | 0.9 ± 0.1 | 0.1 ± 0.5 | 0.4 ± 1.9 |
| $nC_8$ | No change | 2.5 ± 0.4 | 1.1 ± 1.5 | -0.3 ± * |
| $nC_9$ | 1.1 ± 0.7 | 2.7 ± 0.2 | 1.5 ± 1.2 | 1.3 ±* |

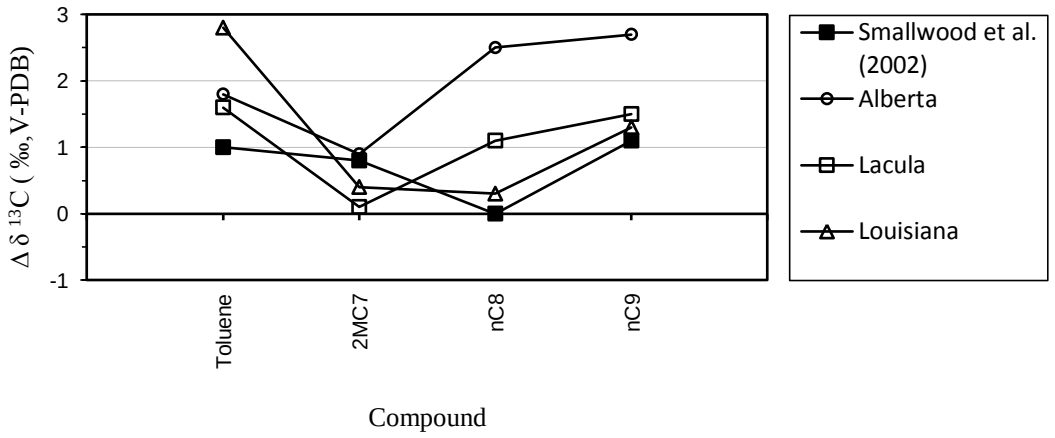



*Figure 4.12. Difference isotopogram comparing $\Delta\delta^{13}C$ values from Smallwood et al., (2002) to those same compounds of the present study (Table 4.2).*

Smallwood et al. (2002) injected neat gasoline samples so the $\delta^{13}C$ values represent the residual liquid. Although a shift in $\delta^{13}C$ values was measured in some compounds in Smallwood's study, at least 67% of components (> $C_8$) in the weathered residual retained carbon isotope signature that is similar (±0.5‰) to the fresh samples. In comparison, although 75% of the compounds show some degree of $^{13}C$ enrichment in this current

study, it is important to note that approximately 54% of the compounds have overall $\Delta\delta^{13}C$ values $\leq$ 0.5‰ (Table 4.2).

Smallwood et al. (2002) also investigated effects of water-washing on the carbon isotope composition of individual hydrocarbons of spilled gasoline in groundwater. A gasoline sample was mixed with groundwater and shaken then left in a sealed separating funnel for 1 week. Headspace samples were injected directly into the GC-IRMS; HSPME was not used. Only 7 of the 21 gasoline headspace compounds analyzed were found to have large variations in $\delta^{13}C$ (i.e., >1‰). Depletions of the $^{13}C$ isotope were observed in $nC_6$, $nC_7$, and $nC_9$, with $\Delta\delta^{13}C$ of -0.8‰, -1.16‰ and -1.42‰ respectively. Toluene also showed only a small depletion (-0.3‰). The results are consistent with the general isotope effects that predict that the $^{13}C$-richer isotopologue of a compound would be more concentrated in the liquid phase, the $^{12}C$ isotopologue in the vapour phase.

Figures 3.18, 3.21 and 3.24 in the Results Section do show $^{13}C$ depletions in some compounds particularly in the slower evaporating Lacula oil (Figure 3.21). For example, the compound $nC_9$ shows a depleted $^{13}C$ value in the Lacula oil continuously up to $T_6$ (Figure 3.21a). This may be due to $nC_9$ diffusing very slowly through the waxy oil, however this does not explain similar examples of $^{13}C$ depletions in the other study oils (e.g., Figures 3.18b and c; 3.24b and d).

Typically, in hydrocarbon compounds, the heavier $^{13}C$ containing molecule generally favors the liquid phase, as occurs in water (Faure, 1986). The groundwater used in the mixture was not treated with biocide, however based on conditions required for hydrocarbon biodegradation described in section 1.2.2.3, it is unlikely that significant biodegradation occurred after only 1 week.

Investigations by Harrington et al. (1999) reported that carbon isotope fractionation does occur in aromatics (benzene, ethylbenzene and toluene) during vapourization, with the initial vapour phase being enriched in the $^{13}C$ isotope, rather than $^{12}C$, as would normally be expected. High precision experiments (±0.05‰) performed over a temperature range of 5 to 70 $^{o}C$ resulted in enrichment of toluene in the vapour phase of about 0.25‰ at 10 $^{o}C$, with no trend in $\Delta\delta^{13}C_{liquid\text{-}vapour}$ versus temperature. The analyzed vapour in Harrington et al. (1999) was the initial vapour produced in a sealed headspace above pure liquids. This reported preference for the accumulation of the heavier isotopologues in the vapour phase in aromatic compounds is termed an *inverse isotope effect* (Balabane and Latolle, 1985). The atypical behavior of the heavier isotope containing molecules favoring the vapour phase in this case is suggested by the author to be attributable to the more complex chemical nature of aromatic compounds compared to simple inorganic compounds, which have been reported to show higher vapour pressures for the $^{13}C$ substituted aromatic compounds (Baertschi et al., 1953).

An inverse isotope effect would result in the oil phase becoming less $^{13}C$-enriched as evaporation progressed, which is not observed in this study. Toluene shows a consistent $^{13}C$ enrichment in all 3 oils, as evidenced in Figures 3.18d, 3.21d, 3.24c, 4.8 f and 4.9 e, f, indicating preferential evaporation of the $^{12}C$-substituted molecules.

Progressive evaporation experiments conducted by Sin and Lee (2010), using pure (≥ 99%) reagent grade toluene, reported that the remaining solvent showed progressive $^{13}C$ enrichment with up to 2‰ change in $\delta^{13}C$ observed during the whole course of evaporation (2 hours), also indicating preferential evaporation of the more abundant $^{12}C$-containing molecules. Masterson et al. (2001) and Carpentier et.al. (1996) also reported isotopic enrichment of $^{12}C$-subsituted toluene in the vapour phase relative to the

residual oil during evaporative fractionation experiments. As previously discussed, Smallwood et al.(2002) also found no evidence of preferential evaporation of the heavier $^{13}C$- substituted toluene in headspace samples after water-washing, and also found $^{13}C$ enrichment in gasolines after 24 hours of evaporation. The findings of this present study also do not support an inverse carbon isotope effect as $\delta^{13}C$ values for toluene gradually become heavier in the oil with progressive evaporation. Although beyond the scope of this investigation, there may be differences in isotope effects between pure compounds and gasolines or crude oils.

Bjorøy et al. (1994) investigated the variation in the carbon isotopic composition of individual $C_4$–$C_{20}$ compounds in condensates, using CF-IRMS. Condensates are also comprised of gasoline-range hydrocarbons. Condensates are natural versions of gasolines and lighter fuel types, generally composed of lighter hydrocarbon fractions ($C_2$-$C_{20}$) and generally have lower specific gravities (0.5 to 0.8; API: 50-120$^o$) than most crude oils. At the higher temperatures of deeper petroleum reservoirs, condensates occur in the gas phase. However as the pressure is reduced and temperature decreases as the gas travels up a well pipe or is exposed at the surface, these gaseous species condense to liquid. In the Bjorøy et al. (1994) study, small amounts of condensate (0.5g) were placed in an open beaker and left in an oven at 30 $^o$C. Samples of the liquid phase were analyzed for carbon isotope ratios at the start of the experiment and after 2, 4, 8, 24 and 48 hours.

A comparison of the enriched $\Delta\delta^{13}C$ values for 16 gasoline-range compounds in 2 condensates analyzed by Bjorøy et al. (1994), common to those measured in the current study, are presented in Table 4.4 and in the difference isotopogram Figure 4.13.

*Table 4.4. Comparison of the amount of $^{13}C$ enrichment ($\Delta\delta^{13}C$) observed in compounds common to Bjorøy et al. (1994) and the present CSIC study.*

.

| | **Condensate #1** Bjorøy et al. (1994) | **Condensate #2** Bjorøy et al. (1994) | **Alberta** | **Lacula** | **Louisiana** |
|---|---|---|---|---|---|
| **Compound Class** | **$\Delta\delta^{13}C$ ‰** | | | | |
| **Alkanes** | | | | | |
| $nC_6$ | 0.3 ± 0.3 | 0.8 ± 0.3 | 1.8 ± 0.3 | 1.1 ± 0.5 | 0.8 ± 0.7 |
| $nC_7$ | 0.1 ± 0.3 | 0.5 ± 0.3 | 1.0 ± 0.3 | 0.7 ± 0.4 | 0.5 ± 0.3 |
| $nC_8$ | 0.3 ± 0.3 | 0.5 ± 0.1 | 2.5 ± 0.4 | 1.1 ± 1.5 | -0.3 ±* |
| $nC_9$ | 0.2 ± 0.3 | 0.3 ± 0.4 | 2.7 ± 0.2 | 1.5 ± 1.2 | 1.3 ±* |
| **Branched alkanes** | | | | | |
| $iC_5$ | 1.0 ± 0.5 | 0.5 ± 0.6 | 1.5 ± 0.3 | 0.4 ± * | 1.4 ± 0.5 |
| $2MC_5$ | 0.7 ± 0.6 | -0.2 ± 0.6 | 1.4 ± 0.1 | 0.9 ± 0.4 | 0.3 ± 0.5 |
| $3MC_5$ | 0.0 ± 0.6 | 1.1 ± 0.6 | 2.3 ± 0.3 | 0.8 ± 0.8 | 0.5 ± 0.2 |
| $3MC_6$ | 0.9 ± 0.5 | -0.2 ± 0.5 | 1.6 ± 0.2 | 0.7 ± 0.2 | 1.3 ± 0.9 |
| $2MC_7$ | 0.8 ± 0.4 | -0.6 ± 0.5 | 0.9 ± 0.1 | 0.1 ± 0.5 | 0.4 ± 1.9 |
| **Cyclic alkanes** | | | | | |
| $CYC_6$ | 0.5 ± 0.5 | 0.9 ± 0.5 | 0.9 ± 0.8 | 0.5 ± 0.3 | 1.8 ± 1.4 |
| $MCYC_5$ | 1.0 ± 0.4 | 0.3 ± 0.5 | 1.5 ± 0.9 | 0.9 ± 0.5 | 1.1 ± 0.4 |
| $MCYC_6$ | 1.2 ± 0.5 | 0.3 ± 0.5 | 1.8 ± 0.3 | 0.3 ± 0.9 | 0.7 ± * |
| $1c3DMCYC_5$ | 2.2 ± 0.4 | n/a | 1.7 ± 0.4 | 0.8 ± 0.7 | 1.0 ± 0.7 |
| $1t3DMCYC_5$ | 0.2 ± 0.6 | n/a | 1.5 ± 0.3 | 0.6 ± 0.2 | -0.6 ±1.6 |
| $1t2DMCYC_5$ | 1.2 ± 0.4 | n/a | 0.1 ± 0.2 | 0.7 ± 0.6 | -0.1 ± 0.9 |
| **Aromatics** | | | | | |
| Toluene | n/a | 0.4 ± 0.6 | 1.8 ± 0.1 | 1.6 ± 0.6 | 2.8 ± 0.6 |

Similarly to the current study, all hydrocarbon compounds ≤ $C_4$ in the Bjorøy et al. (1994) study were found to have evaporated completely by the initial 2 hour sampling. All those ≤ pentane were removed in less than 4 hours; < hexane in 8 hours; < octane in 24 hours. There was almost no change in the $C_{10}$+ hydrocarbon concentration over the 48 hour time frame of these experiments. Although the longevity of compounds ≥$C_5$ in the Louisiana is undetermined, the Alberta and Lacula oils still had measureable amounts of

$\geq C_5$ after 14 and 20 hours respectively, which is attributed to the more complex mixtures of hydrocarbons and physical characteristics of the crude oils compared to condensates.

Also similar to the present study, there appeared to be inconsistent trends in the degree of $^{13}C$ enrichment in most compounds with evaporation time. Bjorøy et al. (1994) found that only minor changes in the isotopic composition of the n-alkanes with increasing evaporation is observed (< 1‰). In one of the two condensates the residual n-alkanes ($C_5$-$C_9$) showed ≤ 0.3‰ change in carbon isotope ratios for their respective availabilities up to 48 hours of evaporation. These same compounds in the current study show much more variability, with absolute values ranging from -0.3‰ ($nC_8$; Louisiana) to 2.7‰ ($nC_9$; Alberta) (Figure 4.13).

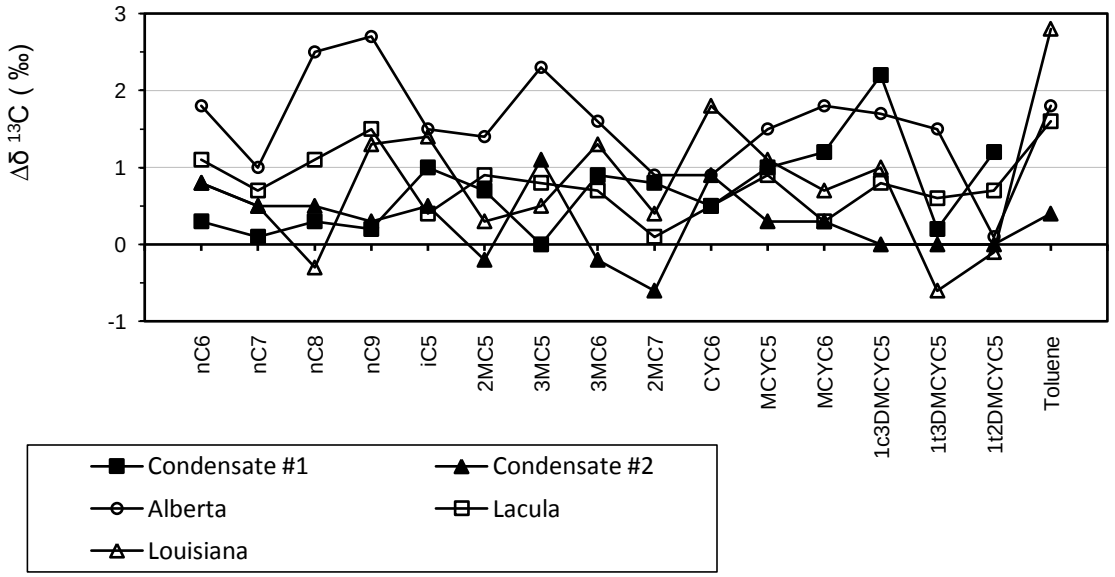



*Figure 4.13. Difference isotopogram comparing $\Delta\delta^{13}C$ values of 2 condensates (Bjorøy et al.,1994) to the present study (Table 4.4).*

Bjorøy et al.(1994) also found that earlier evaporation samples were sometimes more $^{13}C$ enriched than later samples, similar to findings in the present study, e.g., Figures 3.16a , 3.19a and 3.22a. For example, in one of the condensates, the $\delta^{13}C$ of $2MC_7$ showed an enrichment of the $^{13}C$ isotope of 1.2 ± 0.5‰ after 24 hours, wherein a 48 hour

sample the same compound showed an enrichment of 0.8 ± 0.4‰. Since all of the condensate samples were collected from a single reservoir, the anomalies seen in the present study may be due to analytical error.

Isoalkanes show a maximum $^{13}C$ enrichment in $\delta^{13}C$ of about 1‰ (0.7-1.1‰), comparatively much less variability than this same chemical class in this current study, showing ranges in $\Delta\delta^{13}C$ of 0.3‰ to 2.3‰ in $3MC_5$ (Alberta) (Figure 4.8).

The cycloalkanes available for comparison show $^{13}C$ enrichment in $\delta^{13}C$ between 0.5 and 1‰. $1c3DMCYC_5$ show an enrichment of approximately 2.2 ±0.4‰ at the final 4 hour sampling in one condensate. This value was the highest $^{13}C$ enrichment in $\delta^{13}C$ for the Bjorøy et al. (1994) study and larger than any recorded for this compound in any of the present 3 study crude oils.

Bjorøy et al. (1994) concluded that the experiments showed that, independent of the type of hydrocarbon compound, in general the $\delta^{13}C$ of the residues remaining after evaporation may become enriched in $^{13}C$ by about 0.5‰. The differences in $\Delta\delta^{13}C$ are considered to be mainly within the limits of reproducibility and that the $C_5$-$C_{20}$ hydrocarbons can be used with confidence for condensate correlation.

In the studies discussed, where irreversible evaporation is allowed to occur, results indicate a general enrichment of $^{13}C$ in the pool of remaining oil. The important observations are the amounts of fractionation reported in the studies, which are generally less than or equal to about 1‰ after as much as 48 hours of evaporation, compared to an average of roughly 1‰ in this present study (albeit with high variability). The highest weighted average $^{13}C$-enrichment observed for compound 13C enrichment was 1.7‰ in the Alberta oil, however individual values in 5 Alberta compounds show > 2‰ (as high

as 2.8‰ in toluene; Table 4.2). These larger amounts of $^{13}C$ enrichment are not observed in these same compounds in all 3 oils, with differences of ≥ 1‰ between the oils.

#### 4.1.2.1 Isotope Ratio Variability

As previously discussed, some $^{13}C$-enrichment isotope is observed in most of the compounds consistently measured in this study, with approximately 54% of the compounds having $\Delta\delta^{13}C$ values ≤ 0.5‰. Although the methodologies differ, other studies discussed also showed similar lack of change in $\delta^{13}C$ in numerous gasoline-range compounds over as much as 48 hours of evaporation. These results indicate that carbon isotope ratio changes of available gasoline-range compounds during the general processes of evaporation, whether measuring crude petroleums or pure liquids, result in overall average changes in $\delta^{13}C$ typically from 0‰ to about 2‰.

This is a relatively conservative amount of change in $\delta^{13}C$ when compared to the natural isotope variation of the different hydrocarbon compounds in oils which can be greater than 13‰ (O'Sullivan and Kalin, 2008). The hydrocarbon compound $nC_7$, in the unweathered oils, had the largest individual $\delta^{13}C$ range in this current study with 4.6‰.

Unweathered Alberta, Lacula and Louisiana oils exhibited an overall range in $\delta^{13}C$ values for all compounds of 6.3‰ (-31.5 to -25.2‰), 7.9‰ (-30.5 to -22.6‰) and 4.5‰ (-28.1 to -23.6‰) respectively. The total overall range in $\delta^{13}C$ for all compounds in the 3 unweathered oils was approximately 9‰, a range not inconsistent with findings in other gasoline-range isotope studies. Whiticar and Snowdon (1999) reported $\delta^{13}C$ ranges in some samples gasoline-range compounds to be greater than 20‰, but generally the average range within the 41 oils measured was about 12‰. The gasoline-range CF-IRMS

study by Smallwood et al. (2002) measuring 16 compounds in 19 gasoline samples showed a range in carbon isotopic ratios of approximately 13‰. Wang and Stout (2007) state the range in $\delta^{13}C$ values for hydrocarbon compounds in oils to be approximately 15‰.

Individual compound $\delta^{13}C$ ranges are generally somewhat narrower. Individual compounds in the unweathered study oils range from 4.6‰ ($nC_7$) to 0.4‰ ($1t2DMCYC_5$), with an overall average range of 2.6‰ for the 19 compounds. Final weathered study oil $\delta^{13}C$ values ranged from 4.4‰ (toluene), to as low as 0.2‰ ($3MC_5$), with an average range in final $\delta^{13}C$ of 1.9‰.

Much larger ranges for individual compounds have been reported. For example, O'Sullivan and Kalin (2008) measured 19 compounds in gasoline samples collected from 28 countries and five continents using compound specific CF-IRMS. The study found the largest $\delta^{13}C$ range in an individual compound to be as large as 13.4‰, with an overall range from all $\delta^{13}C$ measurements to be 17.4‰. In a study of 7 West Shetland area oils the $\delta^{13}C$ values for 15 individual gasoline-range compounds was between 3 and 6 ±0.5‰ (Rooney et al., 1998). Bjorøy et al. (1994) determined the $\delta^{13}C$ isotopic composition of individual gasoline-range compounds from wells in the same geographic region could vary by as much as 5‰.

## 4.2 DISCRIMATING BETWEEN OILS

Correlation of spilled crude oils to their source requires discriminative and/or chemical properties, that can fingerprint the heritage of the oil. To be effective, the properties must be either relatively resistant to the weathering process, or follow a predictable and diagnostic degradation path. To unambiguously distinguish released oils requires that the source(s) responsible for the oils must also be significantly distinctive chemically from any other potential source oils. The primary goal of this CSIC study is to determine if the carbon isotope ratio signatures of gasoline-range compounds are robust enough to be used as a reliable diagnostic tool for such release-source correlation. The rapid loss after only a few hours of many of the gasoline-range compounds in the environment, through evaporation and solubilization, indicate that a pure molecular abundance/composition approach using this oil fraction is less effective for oil-source correlation. The carbon isotope signatures in concert with the molecular abundances of the present CSIC study, offer an additional opportunity to use the gasoline-range compounds to fingerprint and correlate released oils to their sources.

### 4.2.1 Chemical Relationships Between Individual Compounds

In addition to the overall carbon isotope signatures of oils, the relationships between individual compounds with different chemical structure, e.g., $nC_7$ and toluene, can have diagnostic information. An effective approach to illustrate such relationships is with the use of property-property plots, commonly referred to as cross-plots.

Relationships of the overall distribution of gasoline-range $T_0$ and $T_f$ $\delta^{13}C$ values between the 3 combinations of the study oils are presented in cross-plots, Figure 4.14.

Plots 4.14a through d, illustrate that the distribution of carbon isotope ratio values and their linear relationships after weathering, with compounds in the Lacula and Louisiana oils are typically more $^{13}C$-enriched compared to those of the Alberta oil. Comparison of the Lacula to the Louisiana oil (Figures 4.14e and f) shows more scatter in $\delta^{13}C$ ranges between the 2 oils with numerous data points deviating from the 1:1 unity line. Each of the 3 oil-oil plots exhibits a distinctive data grouping before and after weathering, with $T_f$ values generally shifted towards the lower left of the plot, towards less negative values (i.e., $^{13}C$ enrichment). This general shift towards $\delta^{13}C$ enrichment is consistent with expected isotope ratio shifts resulting from kinetic isotope effects associated with the progressive unidirectional evaporation.

Figure 4.15 shows the cross-plots comparing gasoline-range $\delta^{13}C$ values before ($T_0$) and after weathering ($T_f$) for each individual oil. Data in all 3 oils display linear relationships between fresh and weathered results, indicating a moderate (Louisiana) to strong (Alberta, Lacula) oil-source correlation. The Lacula oil, which underwent the least amount of evaporation compared to the other 2 study oils, displays the strongest linear relationship. Based on comparing 19 pairs of compounds (n-2;17 degrees of freedom), and a critical r value of 0.456, all three linear relationships are statistically significant at the 95% confidence level.

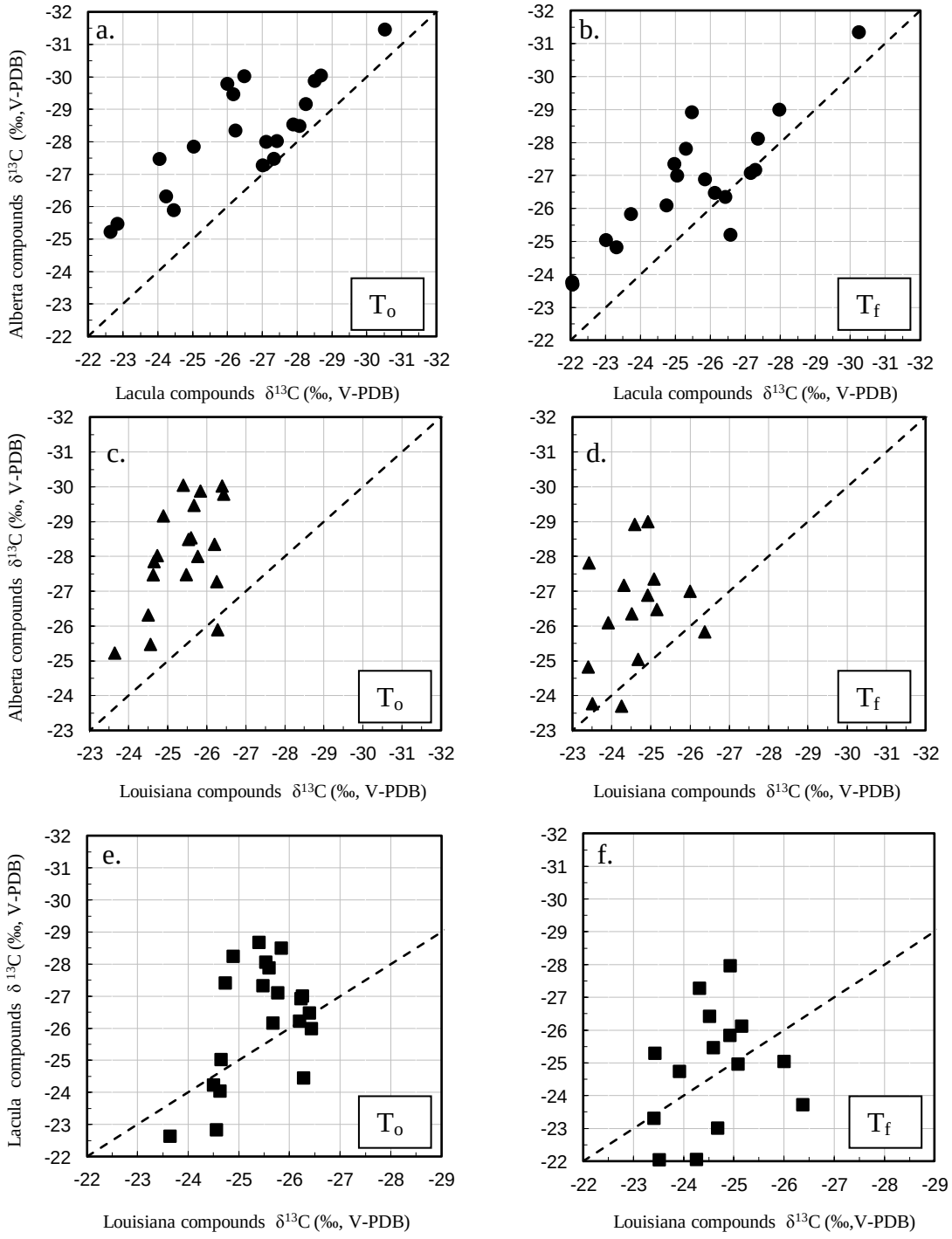



*Figure 4.14. Relationships between the $T_0$ and $T_f$ $\delta^{13}C$ values for gasoline-range compounds in a.,b.)Alberta and Lacula c.,d.) Alberta and Louisiana e.,f.) Lacula and Louisiana. A 1:1correspondence line is drawn for reference.*

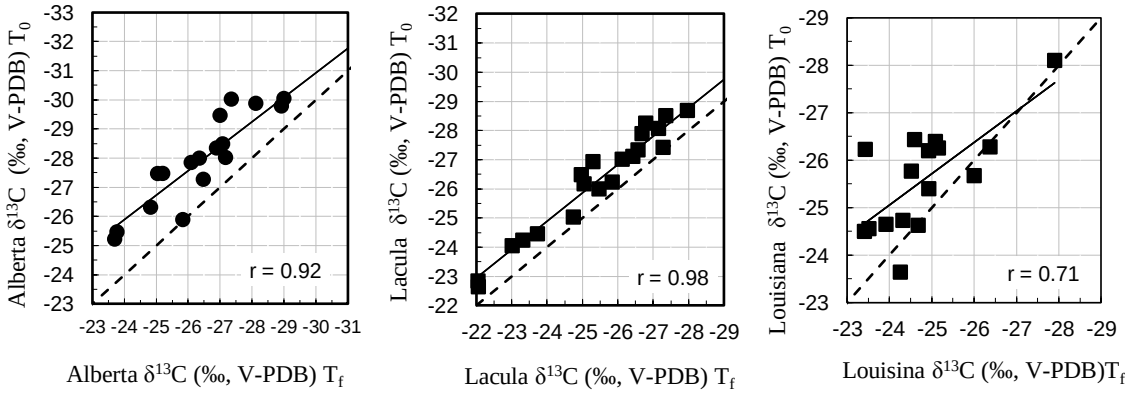



*Figure 4.15. Comparing $T_0$ and $T_f$ $\delta^{13}C$ values for all compounds in the 3 study oils. a.) Alberta; b.) Lacula and c.) Louisiana. A 1:1correspondence line is drawn for reference. The critical value for r(17) ≥ 0.46 at the 95% confidence level.*

In section 4.1.2 (Figures 4.7 through 4.9), the gradual change in $\delta^{13}C$ relative to abundance is plotted for various individual compounds. To investigate these relationships further, Figures 4.16 through 4.21 are presented to compare the isotopic behavior of compounds in the 3 oils to those of similar chemical structure or carbon number. Compounds $nC_5$ and $iC_5$ have limited diagnostic value for fugitive spill correlations in an ocean environment due to their typically rapid evaporation from a spill, however they do exhibit definite isotopic trends throughout the study so are included in the plots for comparison to other n-alkane and iso-alkane compounds.

In the Alberta oil, Figures 4.16 and 4.17, show that for many of the compounds the $^{13}C$ isotope compositions of residual compounds increased exponentially with increasing evaporation. The 5 and 6 carbon compounds exhibit the most rapid rate of $^{13}C$ enrichment as abundance fractions fall below 0.2, the 7 carbon compounds at higher abundances generally around 0.5. The 8 carbon compounds (e.g. $nC_8$, $25DMC_6$ and $1c4DMCYC_6$; Figure 4.16a and 4.17c.) show increased rates of $\delta^{13}C$ changes at higher abundances (i.e. approx. 0.6). Some higher molecular weight 8 carbon compounds in the Alberta oil (e.g.,

25DMC$_6$ , nC$_8$), show an anomalous increase in abundance fractions in the later stages of evaporation.

The Louisiana oil shows similar exponential trends in $\delta^{13}C$ changes with increased evaporation, with the 5 and 6 carbon compounds become increasingly more $^{13}C$-enriched at the lowest abundance fractions (Figure 4.18a and 4.19a), the 7 and 8 carbon compounds at higher abundance fractions (Figure 4.19b,c). Different from the Alberta results is that the Louisiana compounds generally exhibited increased rates of $^{13}C$ enrichment with higher abundance fractions remaining.

Due to the waxy surface crust formation on the Lacula oil, evaporation was limited to abundance fractions of no less than approximately 0.6 for even the lightest molecular weight compounds (i.e., iC$_5$, nC$_5$). Relationships between $\delta^{13}C$ and abundance are more variable than the other study oils, with numerous reversals during intermediate sampling for all of the compounds (Figures 3.21, 4.20 and 4.21). Except for nC$_5$, toluene exhibits the highest degree of evaporation, with a more consistent trend in $^{13}C$ enrichment compared to other compounds, speculated to be attributed to the solvent properties associated with this compound and its ability to more easily diffuse through the waxy surface crust. Many of the compounds in the Lacula oil did show some degree of $^{13}C$ enrichment at $T_f$, however based on the erratic isotope ratio results, it is difficult to speculate on any relationships between $^{13}C/^{12}C$ ratio changes and specific abundances.

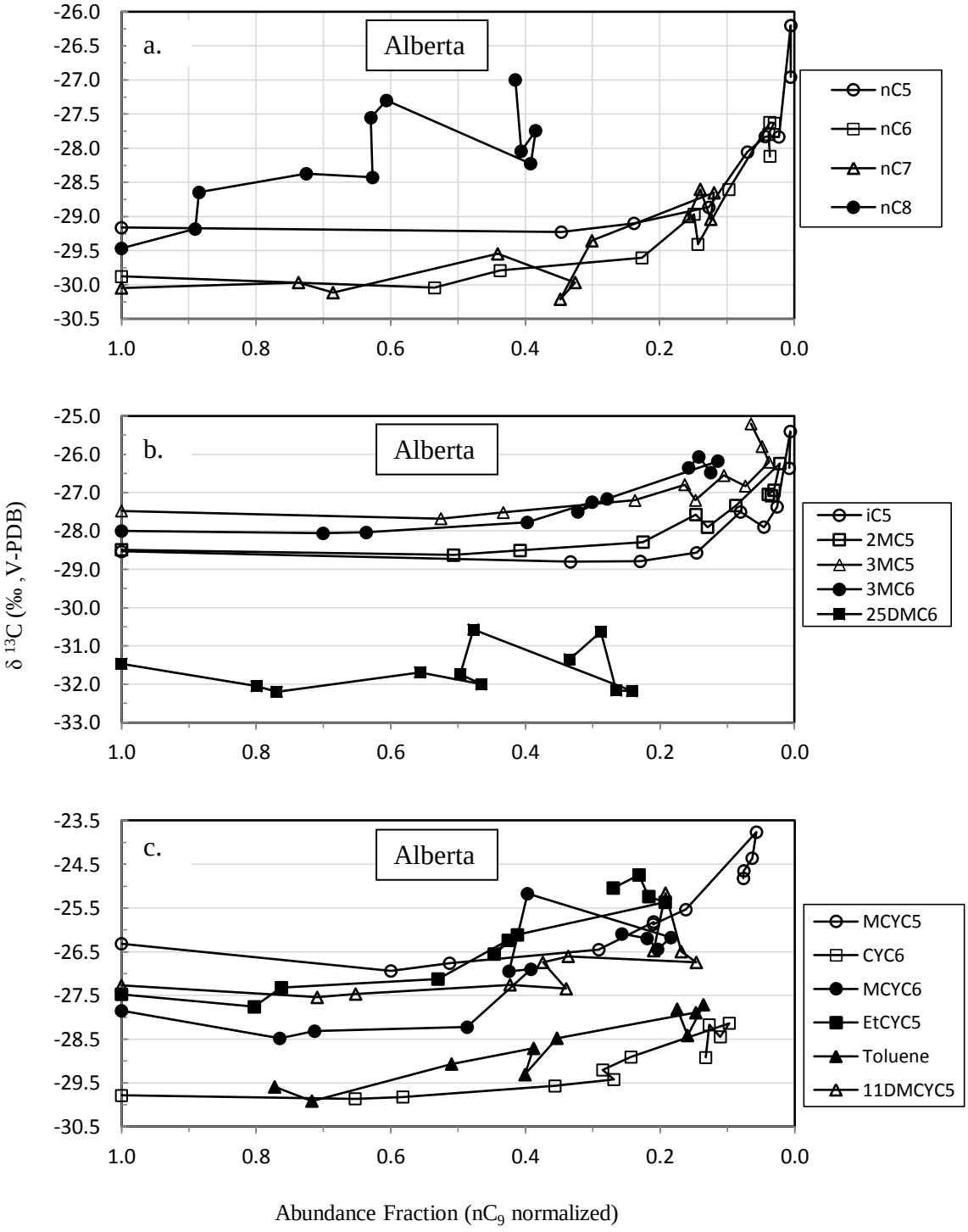



*Figure 4.16. Relationships of the abundance fraction remaining to $\delta^{13}C$ of gasoline-range compounds in the Alberta oil during evaporative weathering. a.) n-alkanes; b.) iso-alkanes and c.) cyclic/aromatic.*

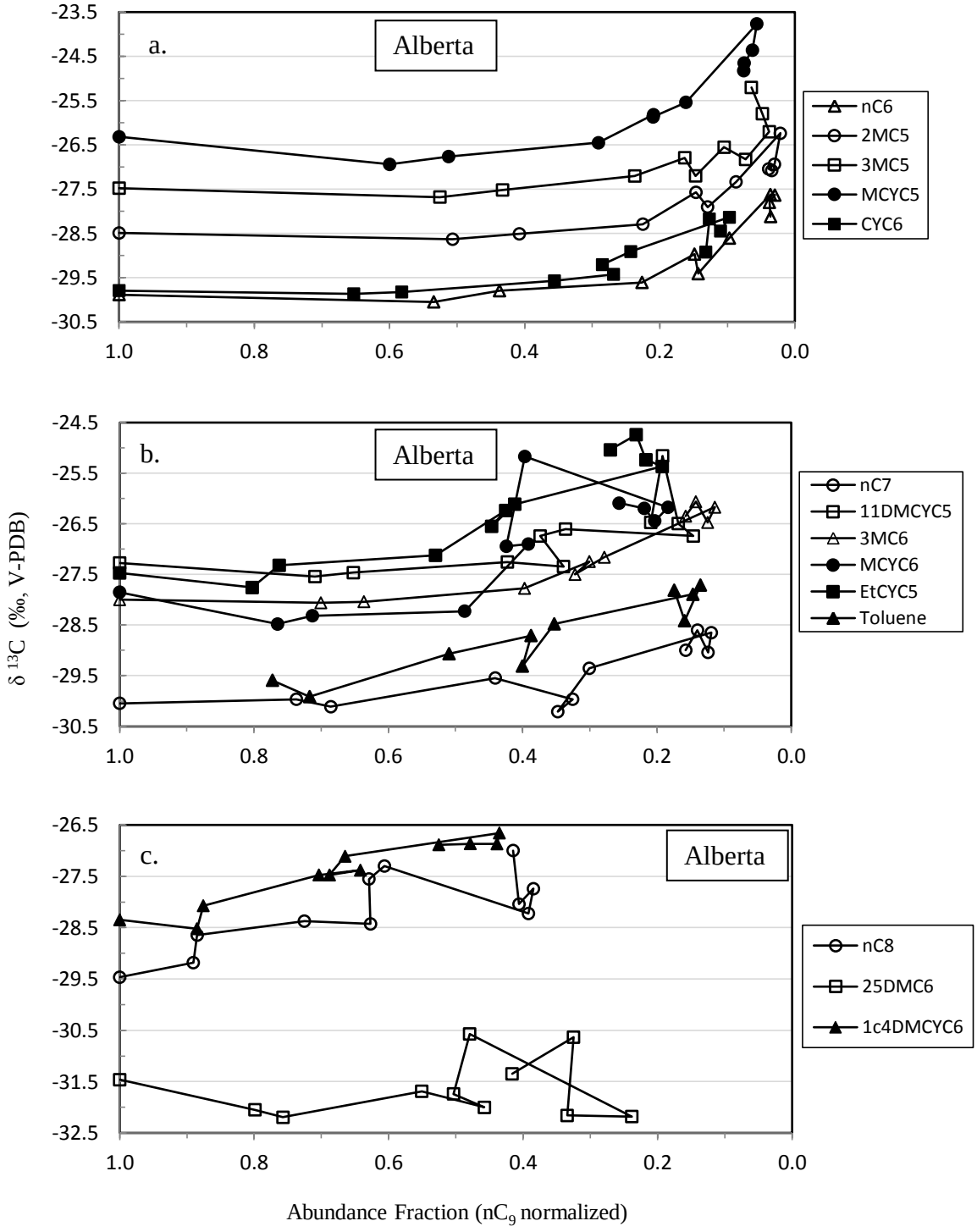



*Figure 4.17. Relationships of the abundance fraction remaining to $\delta^{13}C$ of gasoline-range compounds with same carbon number in the Alberta oil during evaporative weathering. a.) 6 carbons; b.) 7 carbons; and c.) 8 carbons.*

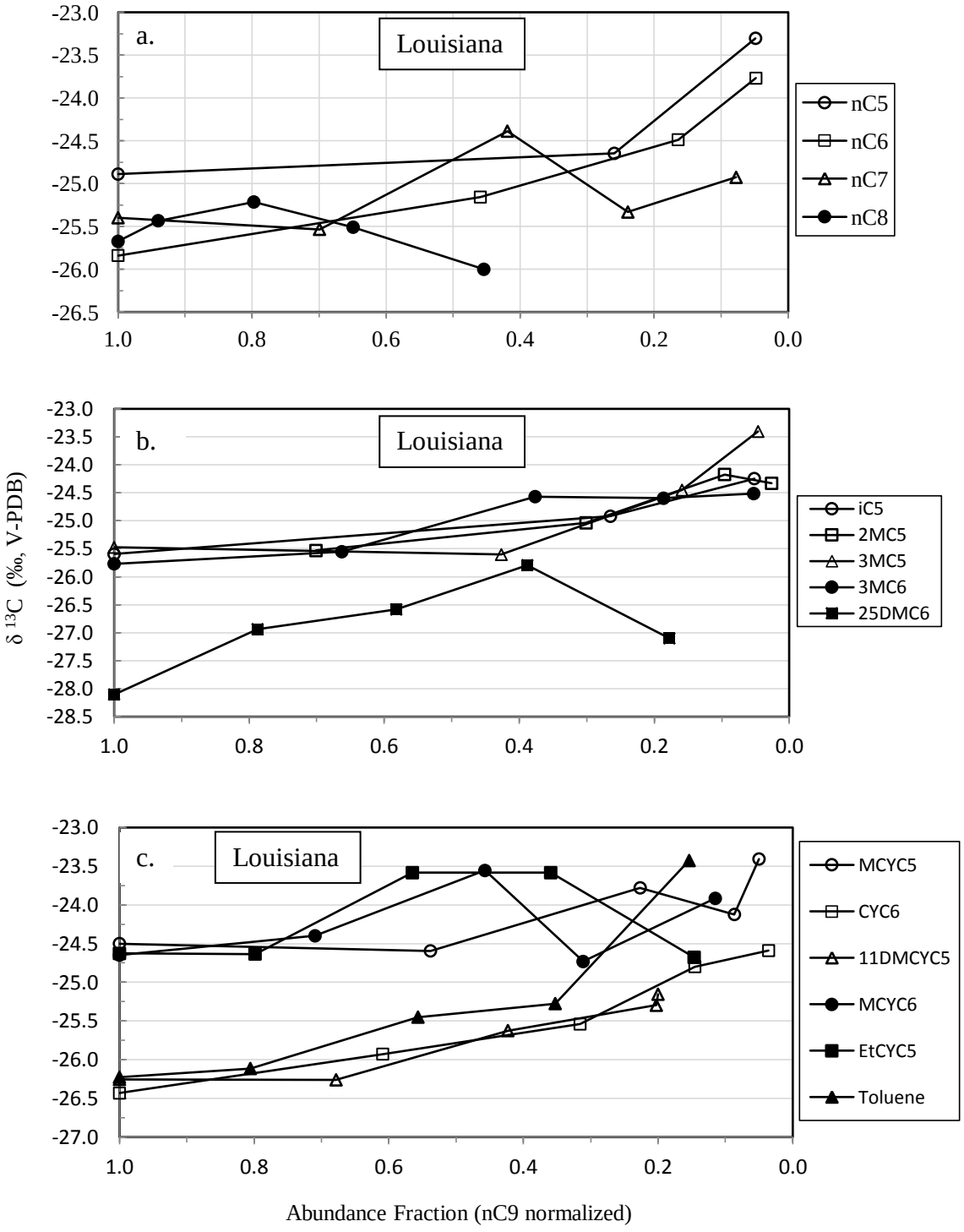



*Figure 4.18. Relationships of the abundance fraction remaining to $\delta^{13}C$ of gasoline-range-compounds in the Louisiana oil during evaporative weathering. a.) n-alkanes; b.) iso-alkanes and c.) cyclic/aromatic.*

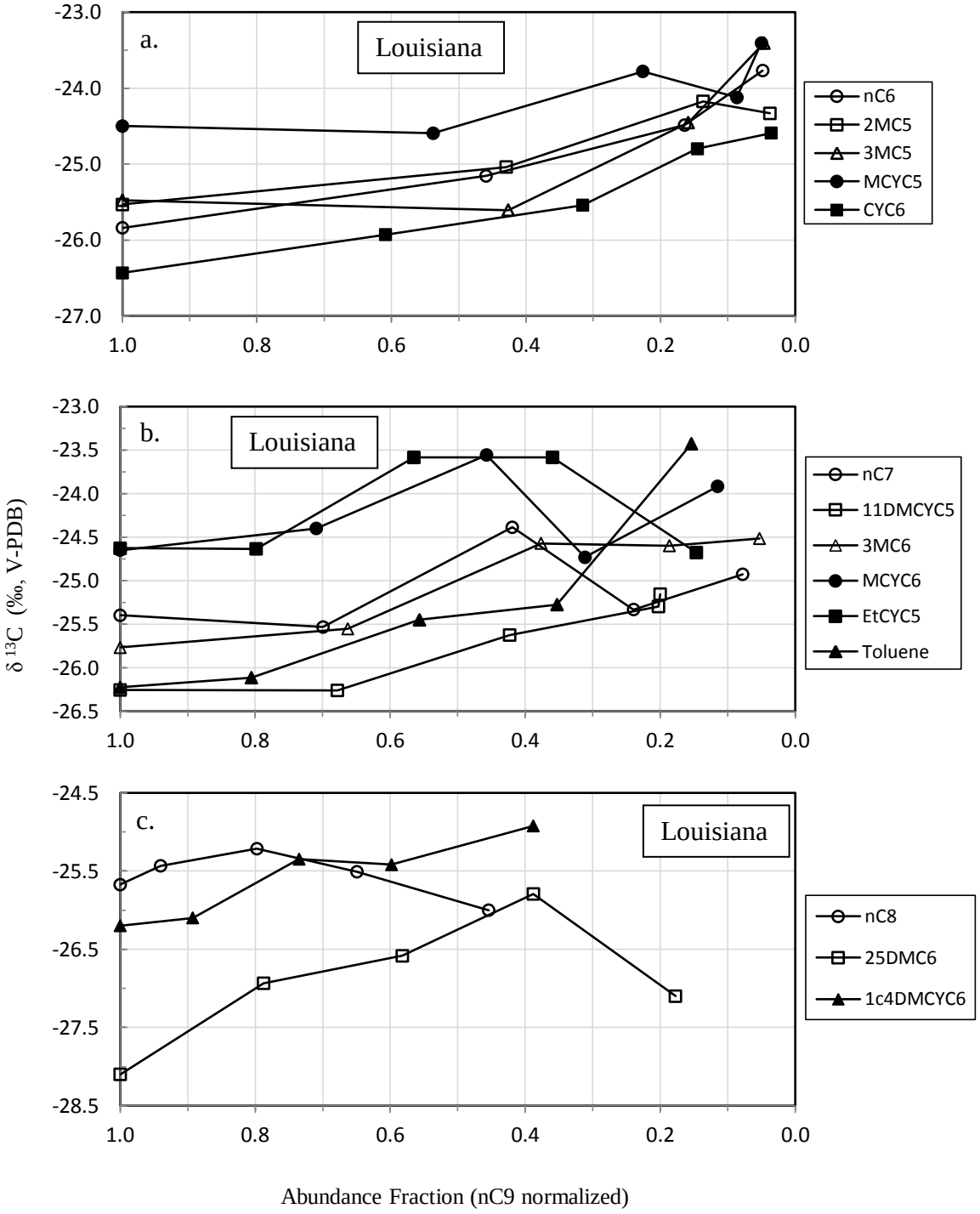



*Figure 4.19. Relationships of the abundance fraction remaining to $\delta^{13}C$ of gasoline-range compounds with same carbon number in the Louisiana oil during evaporative weathering. a.) 6 carbons; b.) 7 carbons; c.) 8 carbons.*

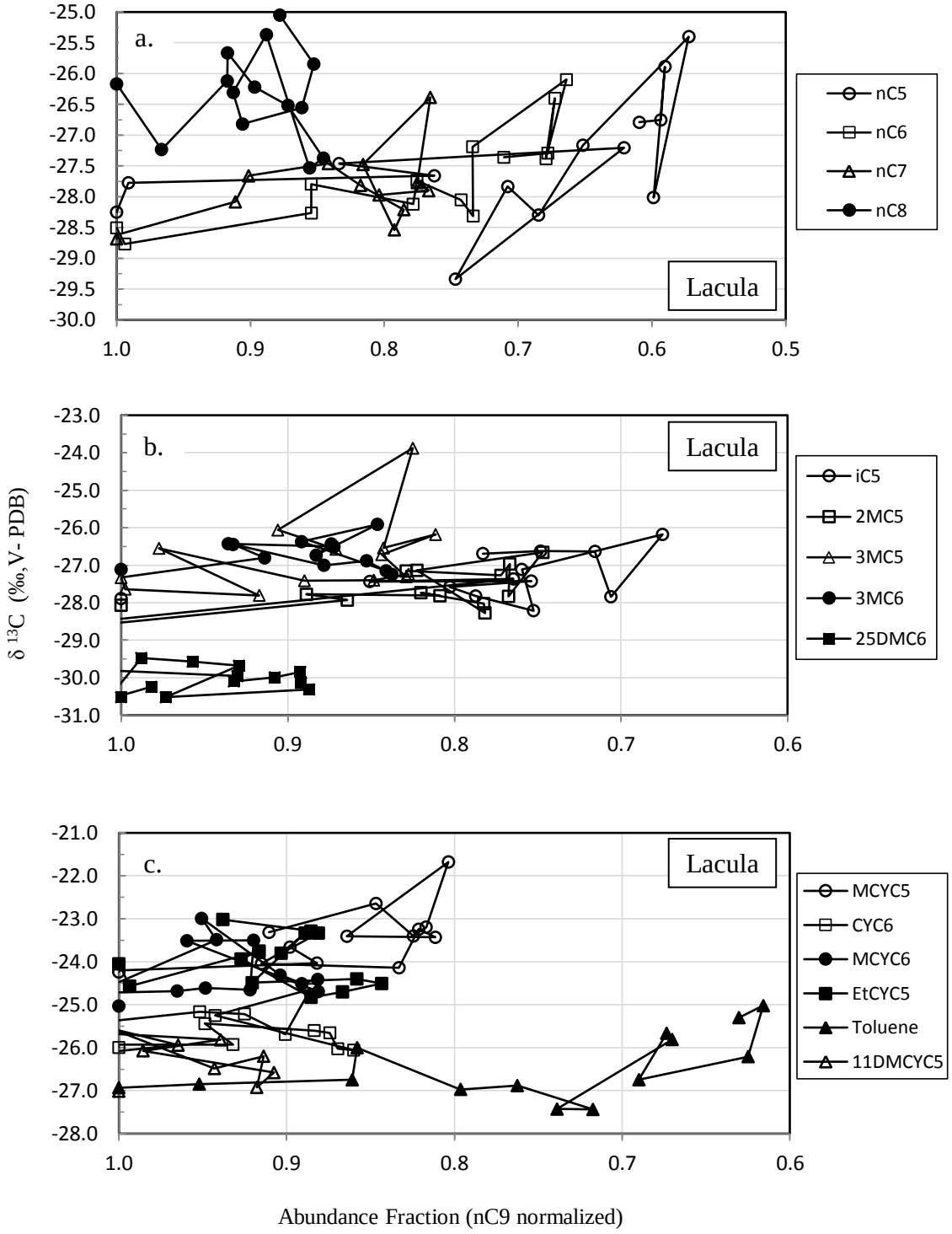



*Figure 4.20. Relationships of the abundance fraction remaining to $\delta^{13}C$ of gasoline-range compounds in the Lacula oil during evaporative weathering. a.) n- alkanes; b.) iso-alkanes and c.) cyclic/aromatic.*

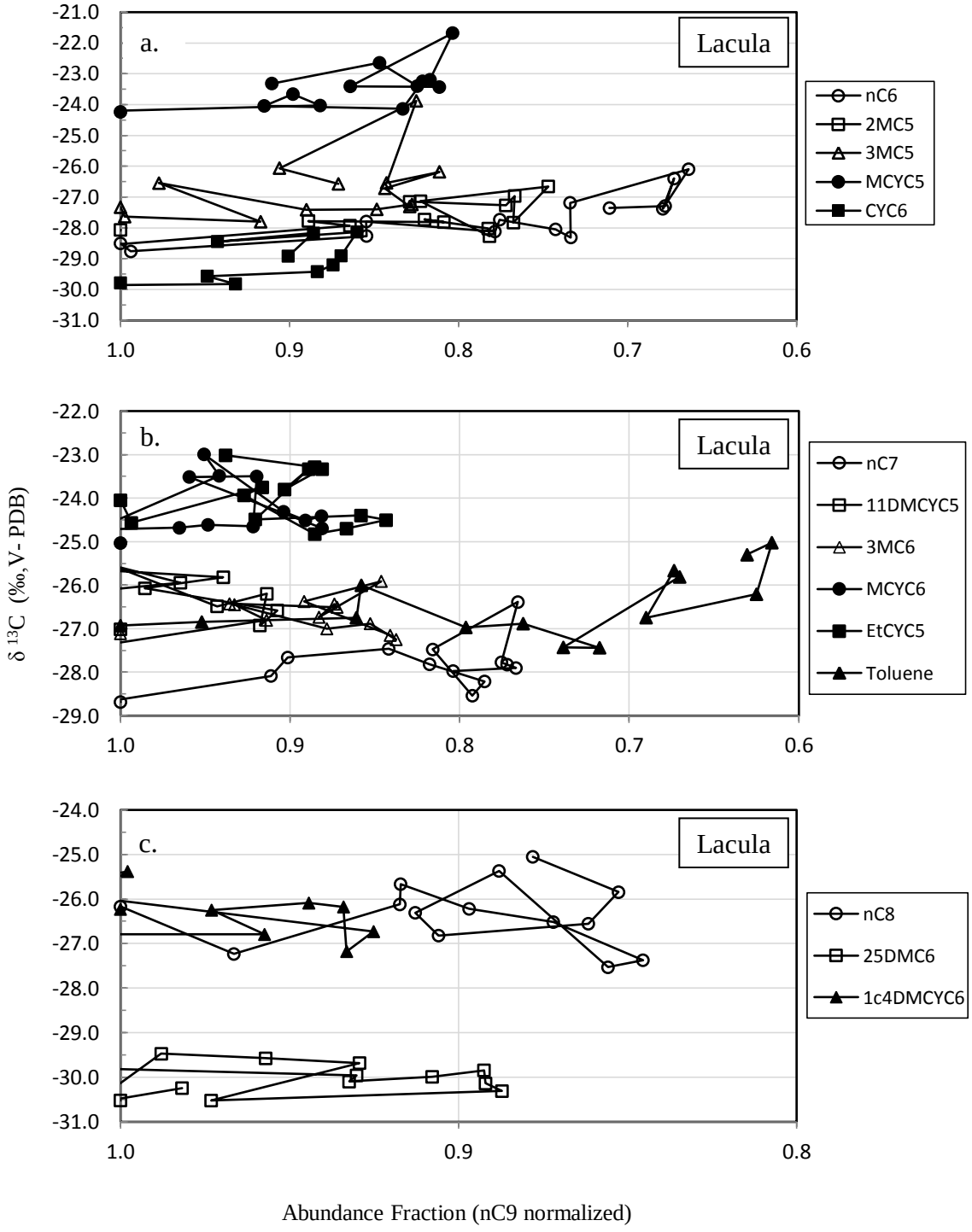



*Figure 4.21. Relationships of the abundance fraction remaining to $\delta^{13}C$ of gasoline-range compounds with same carbon number in the Lacula oil during evaporative weathering. a.) 6 carbons; b.) 7 carbons; c.) 8 carbons.*

Increases in compound $\delta^{13}C$ with diminishing abundances seen in the Alberta and Louisiana oils (Figures 4.16-4.21) are consistent with the trend illustrated in the *compound fraction remaining* curve shown on the Rayleigh process plot presented earlier in Figure 4.6.

The rates of change in $^{13}C$ enrichment (or depletion) expressed in a Rayleigh Distillation plot are determined primarily by the fractionation factor (α) for a particular molecule, as illustrated in Figure 4.22, using reasonable, illustrative choices for α values.

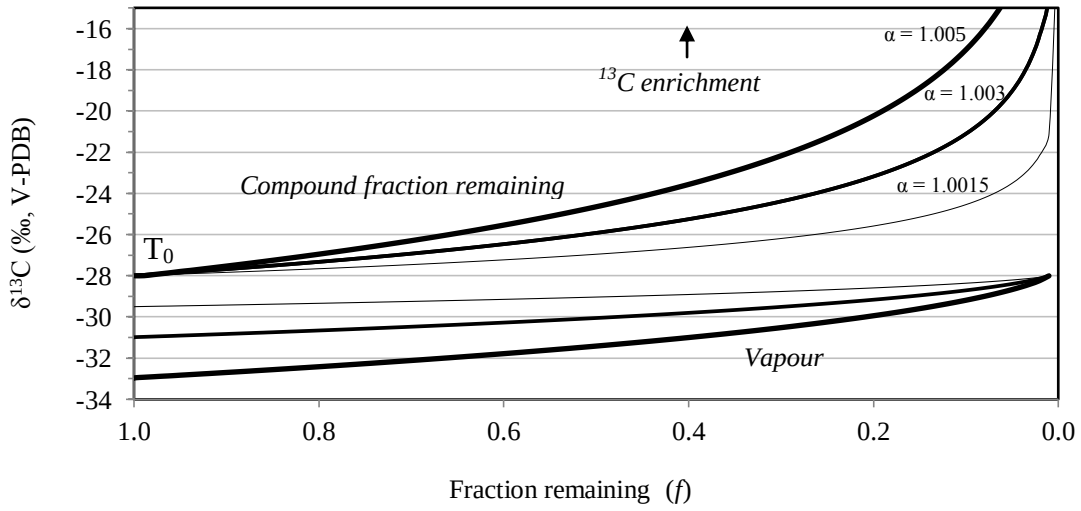



*Figure 4.22. The effects of different fractionation factors (α) on the rates of $^{13}C$ enrichment during the Rayleigh distillation process. The lower curve represents the average cumulative $\delta^{13}C$ composition of the vapour product.*

Similar to vapour pressures, each compound will have an individual fractionation factor (α) based on its molecular structure. Results for the Alberta and Louisiana oils (Figure 4.16-4.17) show that generally higher molecular weight compounds start to enrich in the $^{13}C$ substituted compounds at higher abundance fractions remaining, suggesting that the fractionation factors may increase with molecular weight. An example of how various compounds appear to follow this trend, $\delta^{13}C$ data for 4 Louisiana

compounds of increasing molecular weight ($nC_6$, toluene, $25DMC_6$ and $1c4DMCYC_6$) are plotted with Rayleigh curves calculated using a range of fractionation factors (Figure 4.23). These compounds were chosen as they exhibited a relatively consistent $^{13}C$ enrichment facilitating a smoother curve for comparisons to the Rayleigh plots.

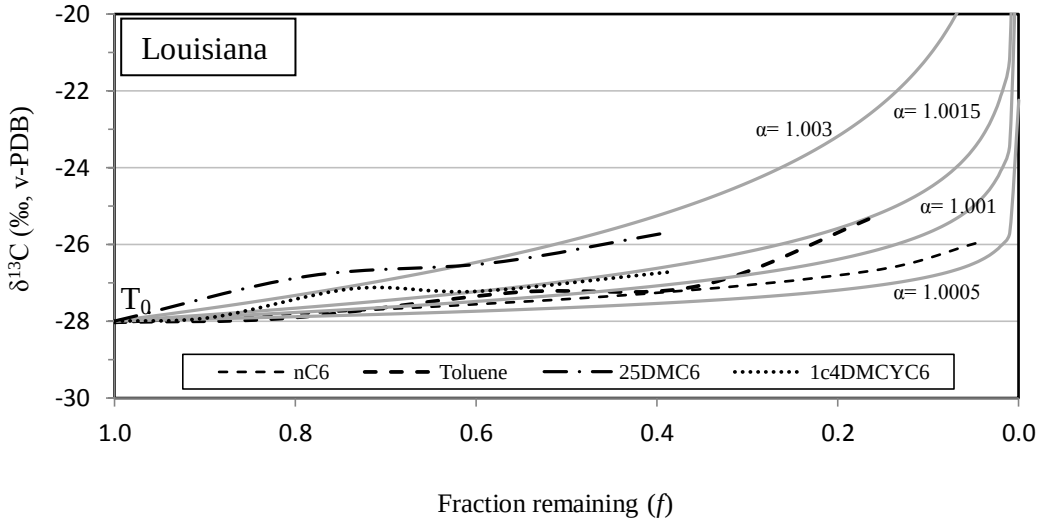



*Figure 4.23. Comparison of Louisiana compound $\delta^{13}C$ trends to Rayleigh curves using multiple fractionation factors (α). Values are normalized to $\delta^{13}C$ -28‰. The $T_f$ data portion of the $25DMC_6$ plot has been removed as it exhibits an anomalous depletion trend. (see Figure 4.19c).*

Figure 4.23 illustrates that the Louisiana oil compounds $\delta^{13}C$ trends approximate Rayleigh curves with fractionation factors between 1.0005 and 1.003. In this example, increased molecular weight is associated with higher fractionation factors, however data comparisons are difficult for many other compounds due to variability in data trends, particularly in the Lacula oil.

With larger fractionation factors, it would be expected that the larger molecular weight compounds would have proportionally larger amounts of $^{13}C$ enrichment at the end of the evaporation experiments compared to the lower molecular weight compounds. However based on the longevity of the experiments, as shown in the difference isotopogram

(Figure 4.10), the $\Delta\delta^{13}C$ results are inconsistent between the 3 oils, with no obvious relationship between the magnitude of fractionation and molecular weight in the 19 compounds compared. Table 4.2 shows that in the case of the Alberta oil, $nC_8$ and $nC_9$ have some of the largest values for $^{13}C$ enrichment (2.5 and 2.7‰ respectively) but these results are not consistent for all 3 oils.

Some of the larger molecules in both Alberta and Louisiana oils, e.g., $nC_7$, $MCYC_6$, $EtCYC_5$, $25DMC_6$, $nC_8$, initially display definite trends towards increasing $\delta^{13}C$ enrichment, however anomalous reversals deplete the $\delta^{13}C$ values prior to $T_f$ analyses, from which the overall amount of $\Delta\delta^{13}C$ is calculated. As all 3 study oils have significant amounts of $\geq nC_7$ compounds at $T_f$, extended evaporation trials would provide information regarding the magnitude of fractionation at minimum measureable abundances.

Again the explanation for the $\delta^{13}C$ reversals in the Alberta and Louisiana oils are unknown and potentially attributed to analytical uncertainty due to low abundances, as previously discussed in Sections 2.4.3, 3.1,and 4.1.2. It is possible that the reversals in the Louisiana oil may be an artifact of emulsification observed on the surface of the Louisiana experiments during the first 2 hours. Referring to Figure 4.5, the emulsion was thickest on the $T_{0.5}$, gradually destabilizing to thinner layers on $T_1$ and $T_2$ samples and absent after 3 hours ($T_f$). The plot of relationship of $\Delta\delta^{13}C$ to evaporation time (Figure 3.24) shows that most compounds in the Louisiana oil exhibit a distinct $\delta^{13}C$ enrichment at the $T_1$ sampling interval, during which destabilization of the emulsion is occurring. These patterns and subsequent reversals in $\delta^{13}C$ values are not observed in all compounds over this period however, so emulsion influences in the reversals are not sufficiently supported by the results.

Emulsion formation can introduce various factors which influence evaporation and potentially kinetic isotope effects. For example, surface emulsion did temporarily isolate the lower liquid oil layers, inhibiting the thorough mixing of the two isotopic species, which can lead to the oil becoming isotopically stratified. Evaporation at the unmixed surface layers would deplete the oil surface of the $^{12}C$ isotopologues without replacement from the larger body of oil, resulting in a premature and temporary $^{13}C$ enrichment of the residual surface layer until the emulsion subsides and mixing occurs. Also, the decreased thickness of the emulsified surface oil films at the oil-air interface (consisting essentially of water in oil micelles), could have disproportionately affected diffusion rates for less volatile compounds ($\geq C_7$) compared to those same compounds in the non-emulsified layer.

Numerous reversals in both $\delta\,^{13}C$ and abundance fractions are consistently observed in all Lacula compounds and are therefore speculated to be at least in some part, attributed to the potential differences in permeability of the formed waxy surface crust in each time series analyses involving individual experimental jars.

The casual relationships between the behaviors of the individual hydrocarbon species within each oil are further explored in the series of cross plots, Figures 4.24 through 4.26, comparing the changes in carbon isotope ratios between compounds with similar chemical structure or carbon number.

Although there is considerable scatter in some plots, 19 of 24 (79%) of comparisons between compounds in the Alberta and Lacula oils display strong linear relationships with correlation coefficients (r) larger than the critical values for 95% confidence levels (Alberta: r ($df$ : 9) = *0.602, $p$* < 0.05; Lacula: r ($df$ : 11) = *0.532, $p$< 0.05).* Linear relationships in the Louisiana oil plots are generally weak or absent in all but 4

comparisons, although the lack of correlation may be in part due to the small number of data and the variability observed during the rapid evaporation period. Only 2 of 12 (17%) compound comparisons (i.e., $C_6$-3$MC_5$ ( r = 0.94); $nC_7$-$MCYC_6$ (r =0.89)) display linear relationships at any level of statistical significance (the critical value for r (*df* 3), p < 0.1 = 0.805).

The strongest correlations observed consistently in all three oils for the 6 carbon compounds are those of $nC_6$-3$MC_5$ and $nC_6$-$CYC_6$ (Figure 4.24), compounds which generally show relatively less variability in $\delta^{13}C$ than other compounds throughout the experiments. Similarly the comparisons between $nC_7$-3$MC_6$ and show moderate to strong correlation in all 3 oils (Figure 4.25).

A good relationship between the aromatic toluene and $nC_7$ is observed in the Alberta oil only. Weak relationships in the Lacula and Louisiana oils are attributed to toluene showing a more consistent $^{13}C$ enrichment pattern relative to highly variable $nC_7$ data (and other 7 carbon compounds) in these oils (Figures 4.19b and 4.21b).

Comparisons between 8 carbon compounds, i.e., $nC_7$-$nC_8$ (Figure 4.25), $nC_8$-25$DMC_6$ (Figure 4.26), generally exhibit weaker linear relationships, 2 of the Louisiana oil plots ($nC_8$- $nC_9$ and $nC_8$-1c4$DMCYC_6$) display 0 correlation. This result is not unexpected considering the large ranges in the amounts of $^{13}C$ enrichments observed in $nC_8$. As previously discussed $nC_8$ and $nC_9$ displayed some of the largest $^{13}C$ enrichments in the Alberta oil (2.5 and 2.7‰ respectively), while showing a -0.3‰ depletion in the Louisiana oil (Table 4.2, Figure 4.10).

Overall the Alberta oil plots displayed the strongest linear relationships for the compounds compared. This oil also displayed the most consistent trends $^{13}C$ enrichment over time compared to the other oils. Physical changes, such as the emulsification and

wax formation, observed in the Lacula and Louisiana experiments, were absent in the Alberta oil.

Despite the variability in the Lacula isotope data, many compounds correlated well, however the larger sample size (n=14) strengthens linear regression calculations. Aspects of the correlation could simply be due to the fact that a similar degree of variability was observed in all of the compounds. Improvements in the consistency of the analytical results for compounds in the Lacula oil would be helpful for further interpretation of any relationships.

As previously discussed the Louisiana relationships are statistically less significant in most comparisons due to the small sample size (n=5) and variability in carbon isotope results.

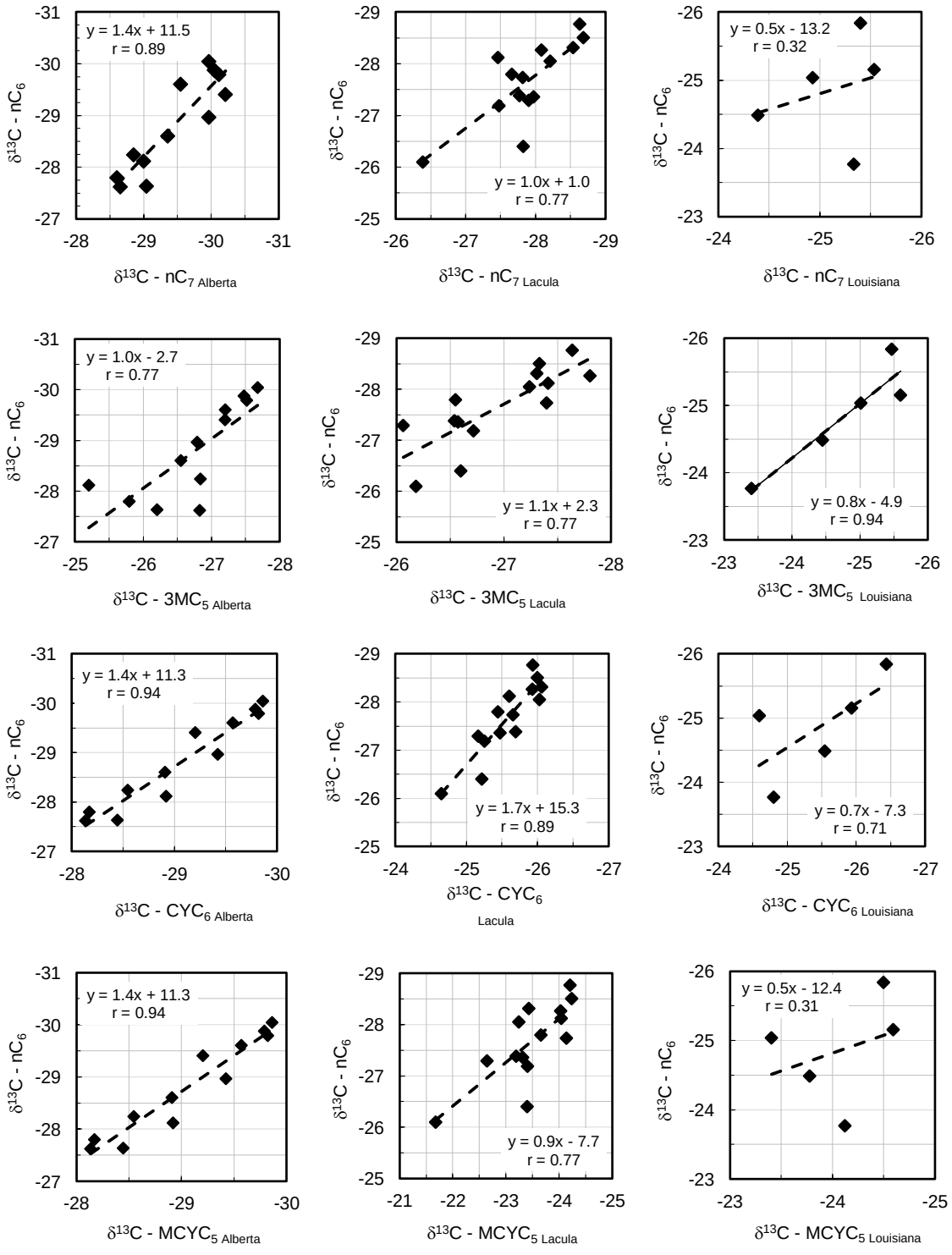



*Figure 4.24. Cross plots illustrating relationships of $\delta^{13}C$ (‰V-PDB) for individual compounds during evaporative weathering experiments. Alberta $T_f$ =14 hrs; Lacula $T_f$ =20hrs; Louisiana $T_f$ =3hrs.*

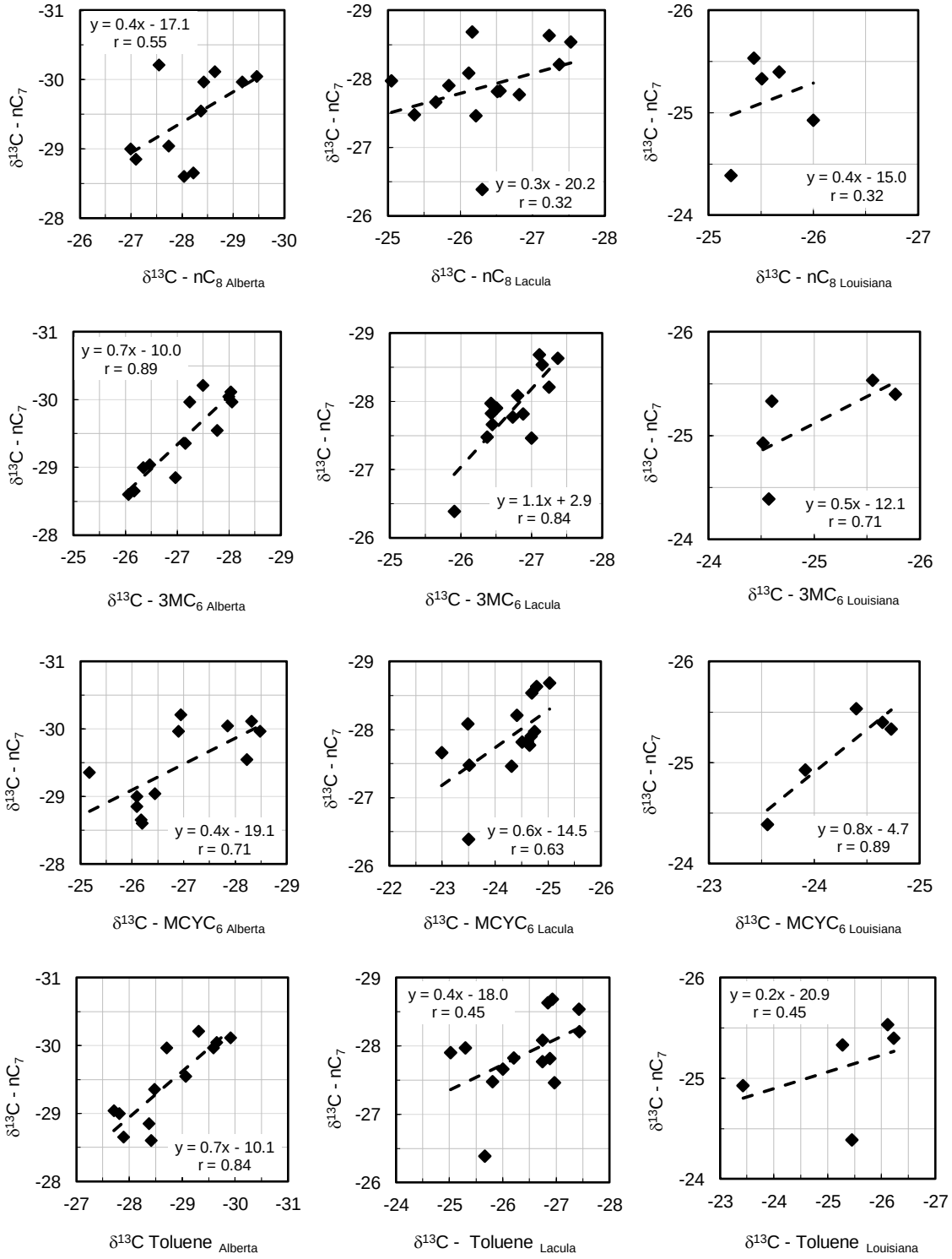



*Figure 4.25. Cross plots illustrating relationships of $\delta^{13}C$ (‰, V-PDB) for individual compounds during evaporative weathering experiments. Alberta $T_f$ =14 hrs; Lacula $T_f$ =20hrs; Louisiana $T_f$ =3hrs.*

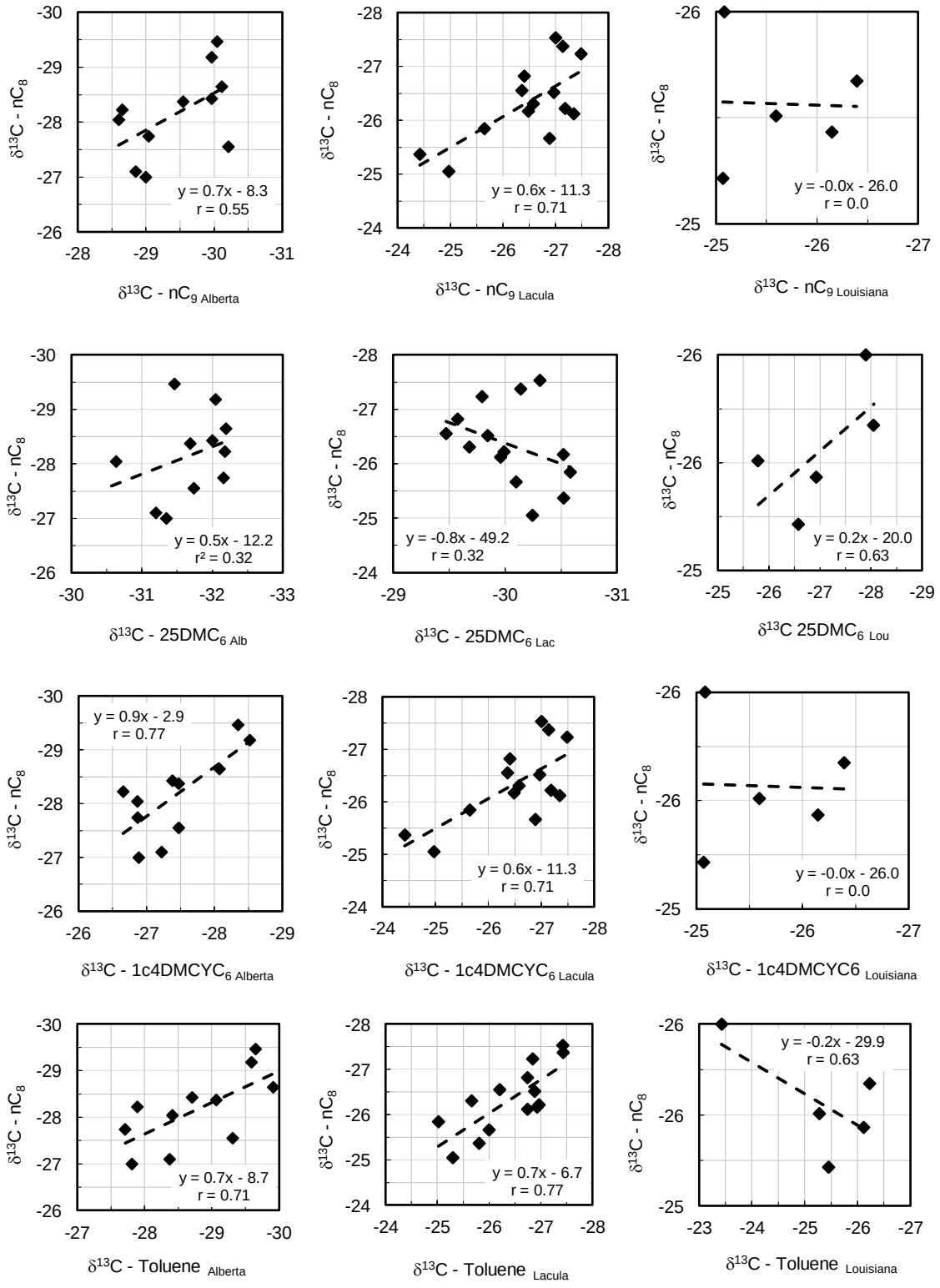



*Figure 4.26. Cross plots illustrating relationships of $\delta^{13}C$ (‰, V-PDB) for individual compounds during evaporative weathering experiments. Alberta $T_f$ =14hrs; Lacula $T_f$ =20hrs; Louisiana $T_f$ =3hrs.*

### 4.2.2 Hierarchical Cluster Analysis

The visual comparison of different oils using aids such as isotopograms is valuable but somewhat subjective, especially as the difference in range of $\delta^{13}C$ values for individual compounds between oils becomes narrower. The technique becomes more litigatively valuable as the range in $\delta^{13}C$ values for compounds between different oils is more dissimilar or when there is minimal change in $\delta^{13}C$ values when comparing weathered samples to a suspected source, as illustrated in the Lacula oil isotopogram below (Figure 4.27a). In comparison, the isotopogram for the 19 compounds in all 3 oils at $T_f$ (Figure 4.27b) have only 4 compounds with distinct $\delta^{13}C$ values, within experimental precision.

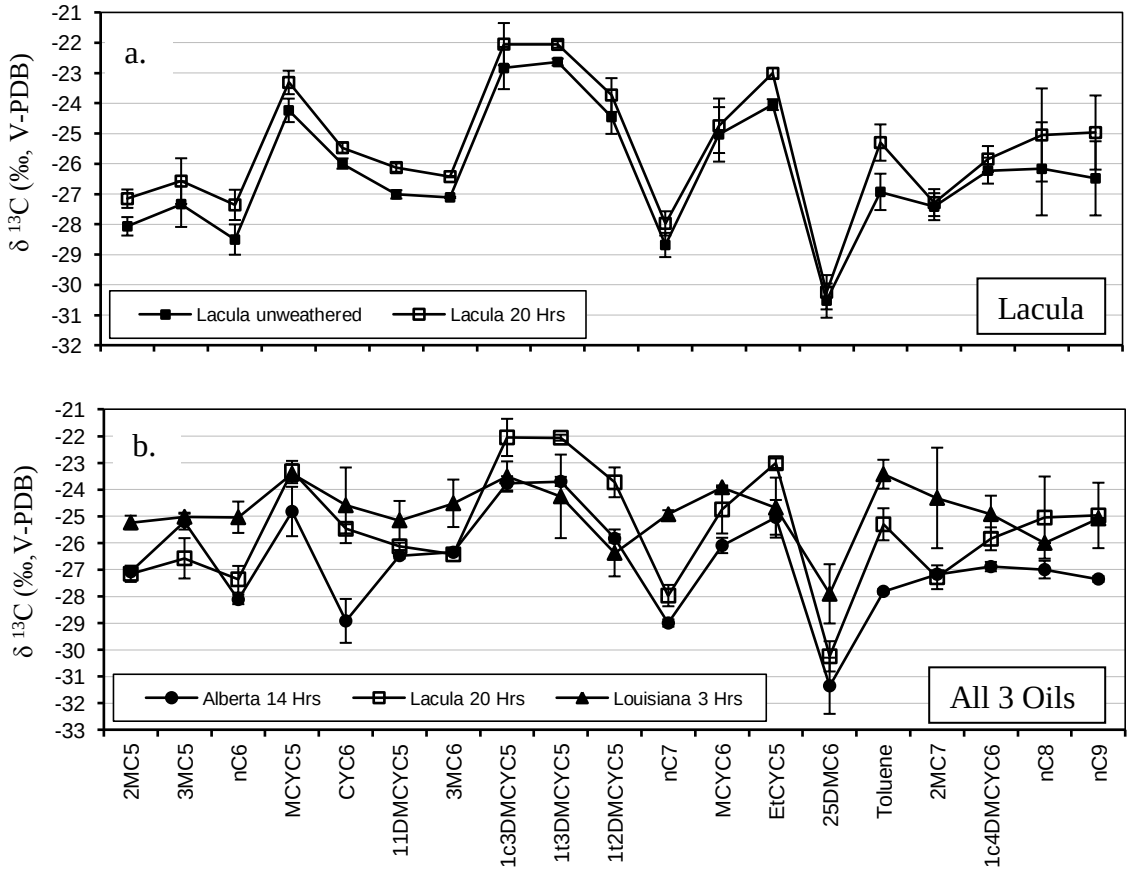



*Figure 4.27. Isotopograms illustrating the increasing subjectivity of the technique with varying isotopic ranges in oils. a.) single oil; b.) all 3 oils.*

Fugitive oil spill issues require more objective determinations, where a more rigorous treatment of the data using statistical methods is required. In their study of a series of selected oils from Western Canada, Whiticar and Snowdon (1999) determined that Hierarchical Cluster Analysis (HCA) was a successful method for oil-oil and oil-source correlations. HCA is the assignment of a set of observations into subsets (called *clusters*) so that observations in the same cluster are similar in some aspect. The members of a cluster are more like each other than they are like members of other clusters. Central to the goals of cluster analysis is the concept of degree of similarity (or dissimilarity) between the individual objects being clustered. The HCA method does not require any presupposition of how or with which criteria the values are clustered into the resulting groups. Statistics are based on cumulative variables called “cases”, which in this treatment, are all of the time series sampling intervals; consisting of associated abundance and isotope data.

HCA algorithms in this study use a "bottom-up" agglomerative approach and begin with each case as a separate cluster then finds the similarity or dissimilarity between every pair of cases in the entire data set and merges them into successively larger clusters through successive comparison. The HCA uses “average linkage between groups method” for the agglomerative clustering, computed using Squared Euclidean Distance. The method calculates distances between pairs of cases in different clusters, with the distance between two clusters being the average of the distances between all possible pairs of cases in the resulting cluster. Both of these settings were found most effective in cluster computations in the oil correlation work by Whiticar and Snowdon (1999).

The values are then grouped into a hierarchical tree, termed a *dendrogram,* with the height of each branch representing the distance between the connected cases or clusters.

The dendrogram is a two dimensional diagram illustrating the similarities or differences of homogenous clusters made at each successive "stage" of analysis. Vertical lines join clusters that are similar, with the position of the line on the scale across the top of the dendrogram, labeled "Rescaled Distance Cluster Combined", indicating the distance at which clusters are joined (e.g., Figure 4.28). The distances are rescaled to fall into the range of 1 to 25; the ratio of the rescaled distances within the dendrogram is the same as the ratio of the original calculated distances. The greater the distances before two clusters are joined, the bigger the differences between the clusters.

The HCA software (SPSS; Statistical Package for the Social Sciences) requires a complete data set with no missing values for any variables within the cases being compared. Any missing values are interpreted as dissimilar variables (unrecognizable cases) by the HCA software, resulting in both the analyses and graphical output of entire time-series cases for all oils being disregarded.

A series of dendrograms have been constructed to illustrate the results similarities and differences between the 3 study oils using the HCA technique. Figure 4.28 presents the dendrogram output for the entire suite of weathering periods (cases) using all of the 19 individual compounds. Both the abundance and $\delta^{13}C$ data are considered as variables for each case. Figure 4.28 clearly shows the 3 oils are statistically distinct from each other, i.e., each oil occupies a separate branch of the cluster tree. This differentiation of the 3 oils is maintained even under moderate to extreme evaporation conditions. There are no linkages between oils for any of the cases until later in the clustering stages, i.e., at larger cluster distances. Figure 4.28 also illustrates that HCA is able to distinguish between earlier and later weathering period cases. The only exception of Lacula $T_2$ (Lac2 15 on the dendrogram).

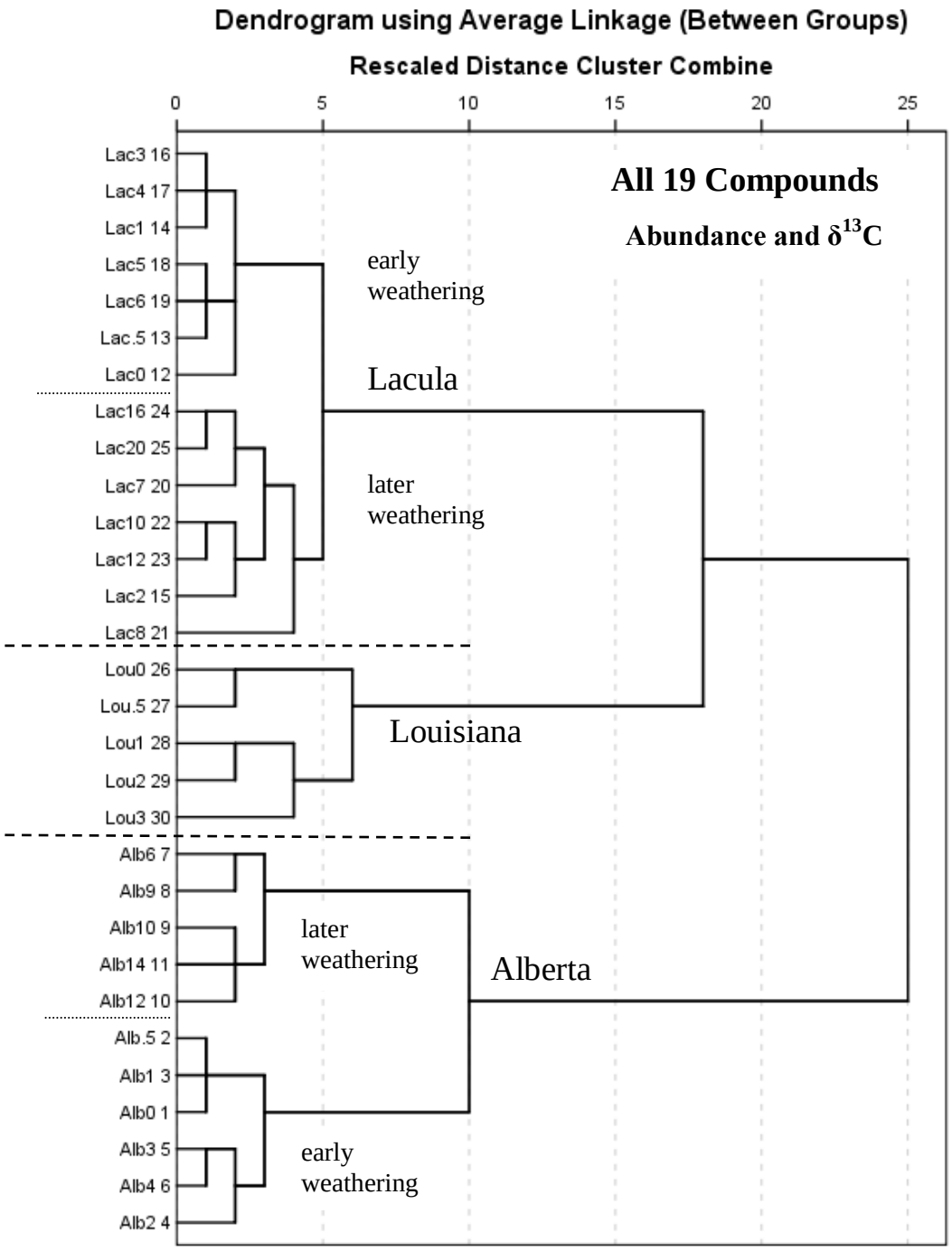



*Figure 4.28. Hierarchical cluster analysis dendrogram using statistical average linkages within the 3 study oils. All 19 compounds and their time series changes in abundances and $\delta^{13}C$ values are used in the analysis. Lac: Lacula; Lou: Louisiana; Alb: Alberta. Number suffixes after of oil abbreviations are the weathering times (hrs), case numbers are adjacent to the vertical axis.*

Figure 4.28 also shows that the differences between the earlier and later stage evaporation cases are greater in the Alberta oil compared to the other 2 oils. Furthermore, the dendrogram illustrates that the Lacula and Louisiana oils link at earlier cluster distances than to the Alberta oil, suggesting they are more similar to each than to Alberta. This illustrates the usefulness of the molecular and isotope composition in conjunction with HCA to distinguish oils despite varying degrees of weathering.

A dendrogram constructed of cases incorporating only the carbon isotope data (Figure 4.29) resulted in a very similar cluster diagram to Figure 4.28, With the 3 oils being discriminated and cases for earlier and later cases being closely clustered, the only exception again being Lacula $T_2$. This suggests that, under these study conditions, only the change in $\delta^{13}C$ values are required for oil-oil discrimination, as would be the case in a field collection scenario involving fugitive oils, where the degree of abundance losses would typically be unknown.

To further test the usefulness and sensitivity of the HCA technique, a series of dendrograms were constructed using a series of compounds from various chemical classes and carbon number. This will also potentially aid in identifying which compounds or groups of compounds are most effective in discriminating the oils.

Figure 4.30 presents the HCA outputs using abundance and isotope data for the n-alkane compounds common to all 3 oils for all stages of weathering. This figure shows that the n-alknes in the Louisiana oil clearly clusters separately from the other oils and remains different until linking with the Alberta data at maximum cluster distances. This may be due to the specific range in $\delta^{13}C$ values for n-alkanes shown in Louisiana compared to the other 2 oils (compare Figures 4.16a, 4.18a and 4.20a) and a

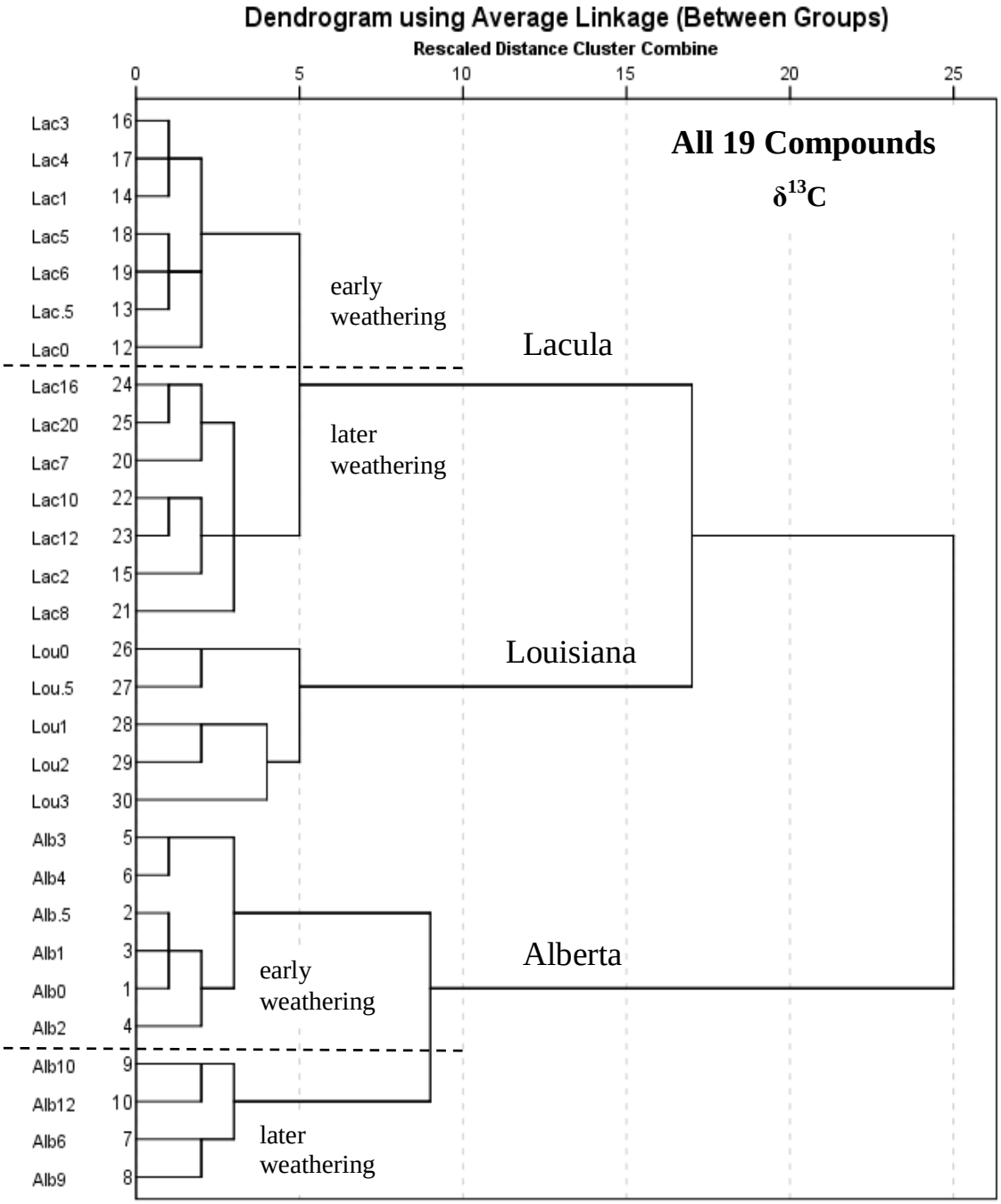



*Figure 4.29. Hierarchical cluster analysis dendrogram using statistical average linkages $\delta^{13}C$ values are used in the analysis. Lac: Lacula; Lou: Louisiana; Alb: Alberta.*

comparatively more rapid evaporation rate. The early weathering period cases in both the Lacula and Alberta oil also cluster at initial stage distances, however the oils begin to develop links after $T_6$ cases relatively early in the branching hierarchy.

Based on the HCA output for the n-alkanes using abundance and $\delta^{13}C$ data, the dendrogram illustrates that Alberta and Lacula oils can be discriminated during the beginning of the earlier stages of evaporation and that these early cases cluster with unweathered ($T_0$) cases. Plotting this same dendrogram using only the $\delta^{13}C$ data (Figure 4.31) reveals that the Louisiana oil is still clearly discriminated, however unlike Figure 4.30 later cases of the Alberta oil cluster with the Lacula oil at initial cluster stage. Earlier weathering cases of Alberta continue to cluster well. HCA results for n-alkanes using only isotope data is less discriminatory than results from the entire data suite.

The dendrogram for the branched alkanes also shows that the Louisiana oil clearly dissimilar to the other oils (Figure 4.32). As with the n-alkanes the Alberta and Lacula oils are distinct based on early weathering cases, but clustering becomes less distinct after $T_6$ cases. Figure 4.33 displaying $\delta^{13}\mathbf{C}$ data for the cyclic alkanes is very similar with only a few alternate linkages between the Alberta and Lacula oil cases compared to Figure 4.33.

HCA of the cyclic alkane compounds shows early stage clustering of the individual oil cases supporting the classification of 3 separate oils (Figure 4.34). The dendrogram using only the $\delta^{13}C$ data is almost identical (4.35), with the exception of a few alternate linkages based on comparison of the cyclic alkanes. The Lacula and Louisiana oils are more similar to each other and remain distinct for relatively fewer stages of cluster comparisons.

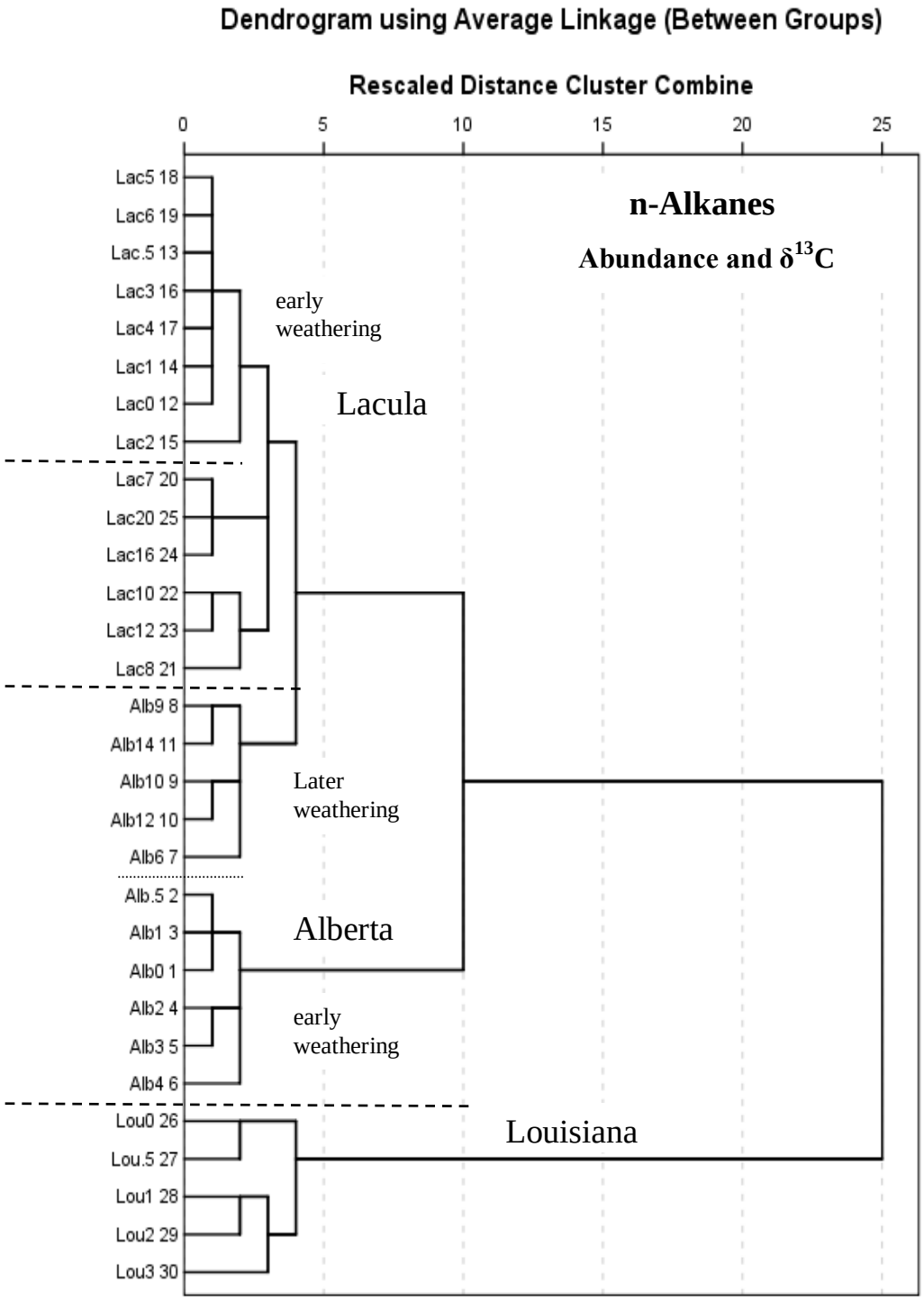



*Figure 4.30. Hierarchical cluster analysis dendrogram using statistical average linkages within the 3 study oils. Cases are for the n-alkane compounds, using both abundance and $\delta^{13}C$ as variables.*

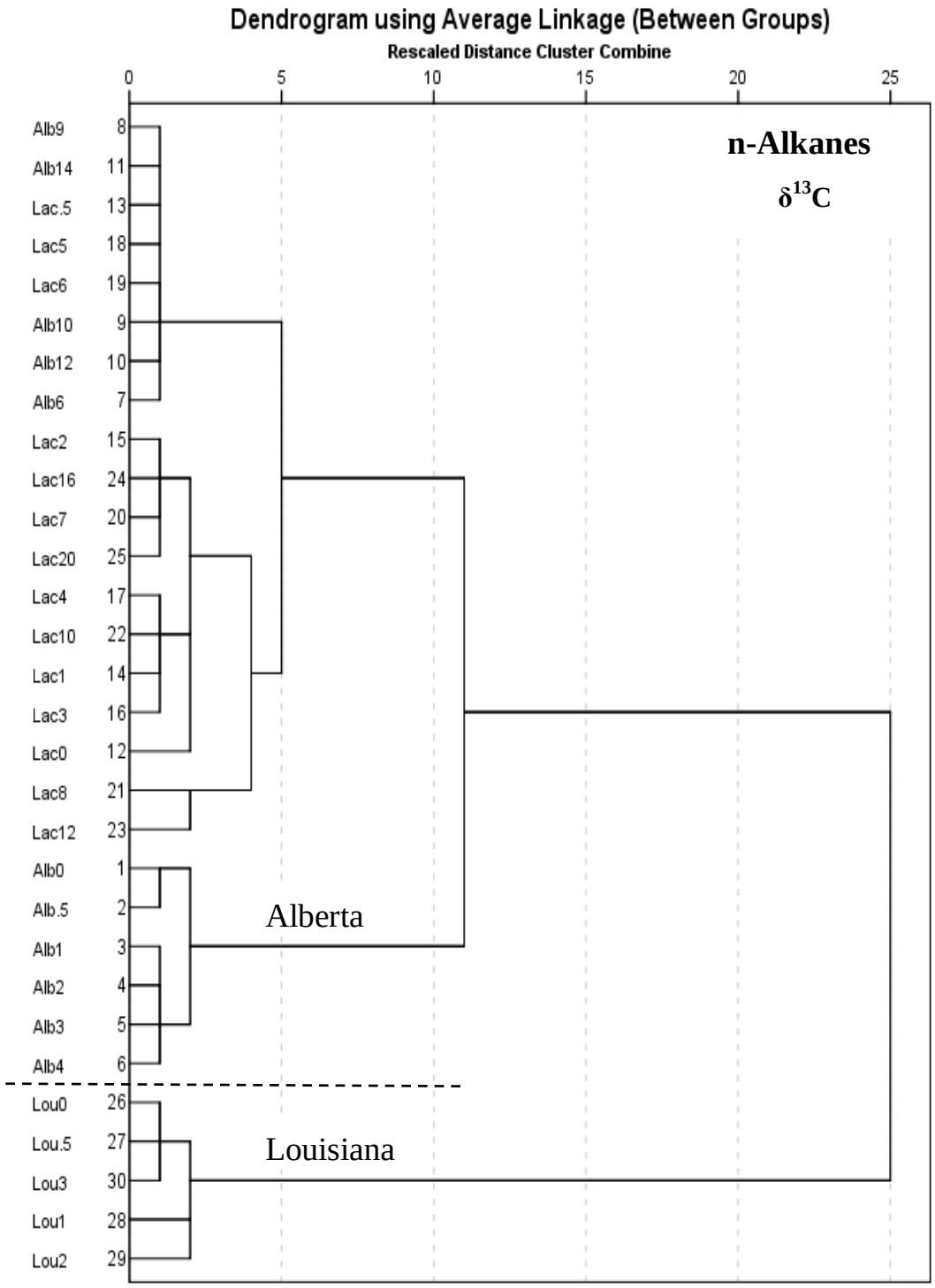



*Figure 4.31. Hierarchical cluster analysis dendrogram using statistical average linkage s within the 3 study oils. Cases are for the n-alkane compounds, using $\delta^{13}C$ as variables.*

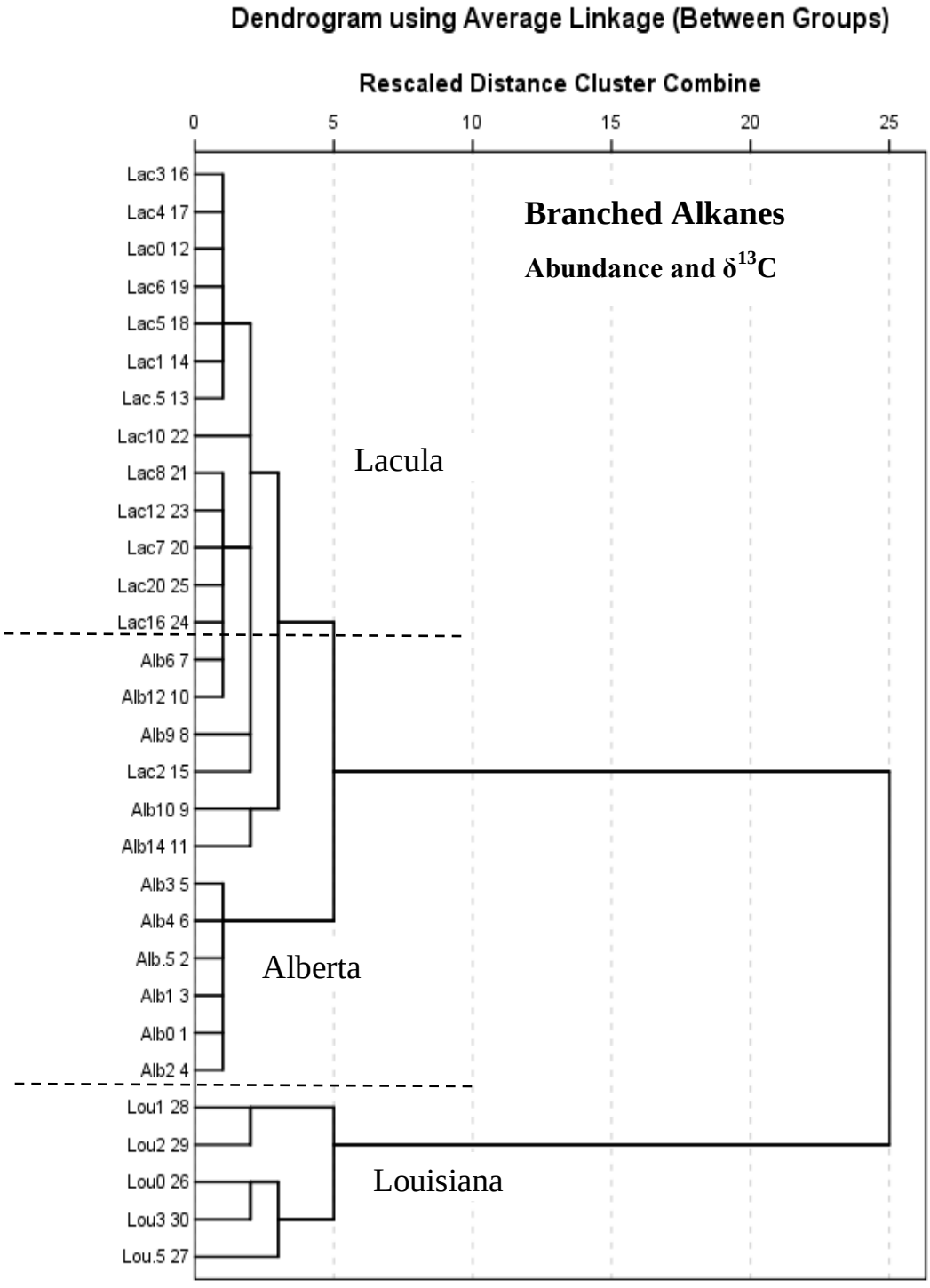



*Figure 4.32. Hierarchical cluster analysis dendrogram using statistical average linkages within the 3 study oils. Cases are for the branched alkane compounds, using both abundance and $\delta^{13}C$ as variables.*

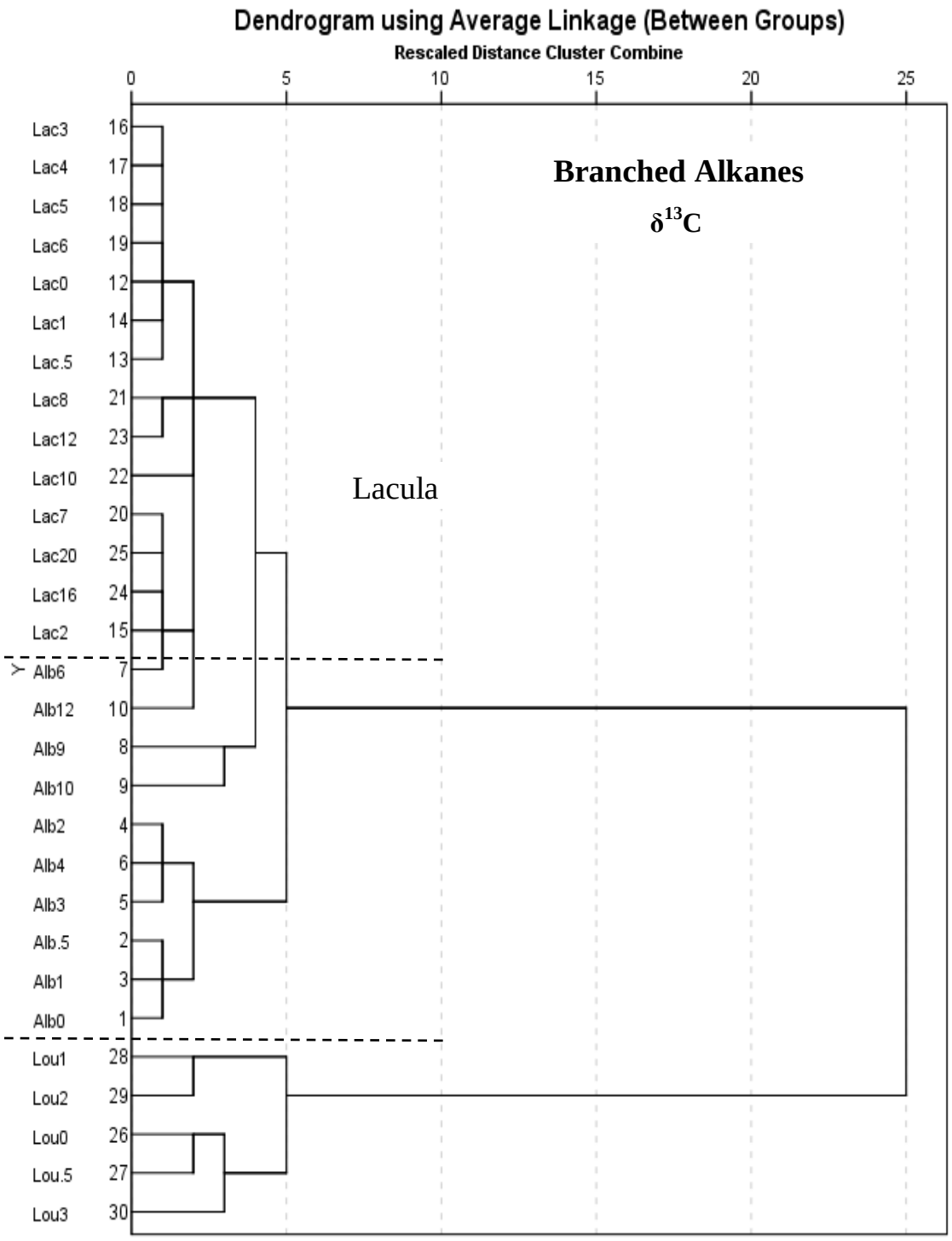



*Figure 4.33. Hierarchical cluster analysis dendrogram using statistical average linkages within the 3 study oils. Cases are for the branched alkane compounds, using abundance and $\delta^{13}C$ as variables.*

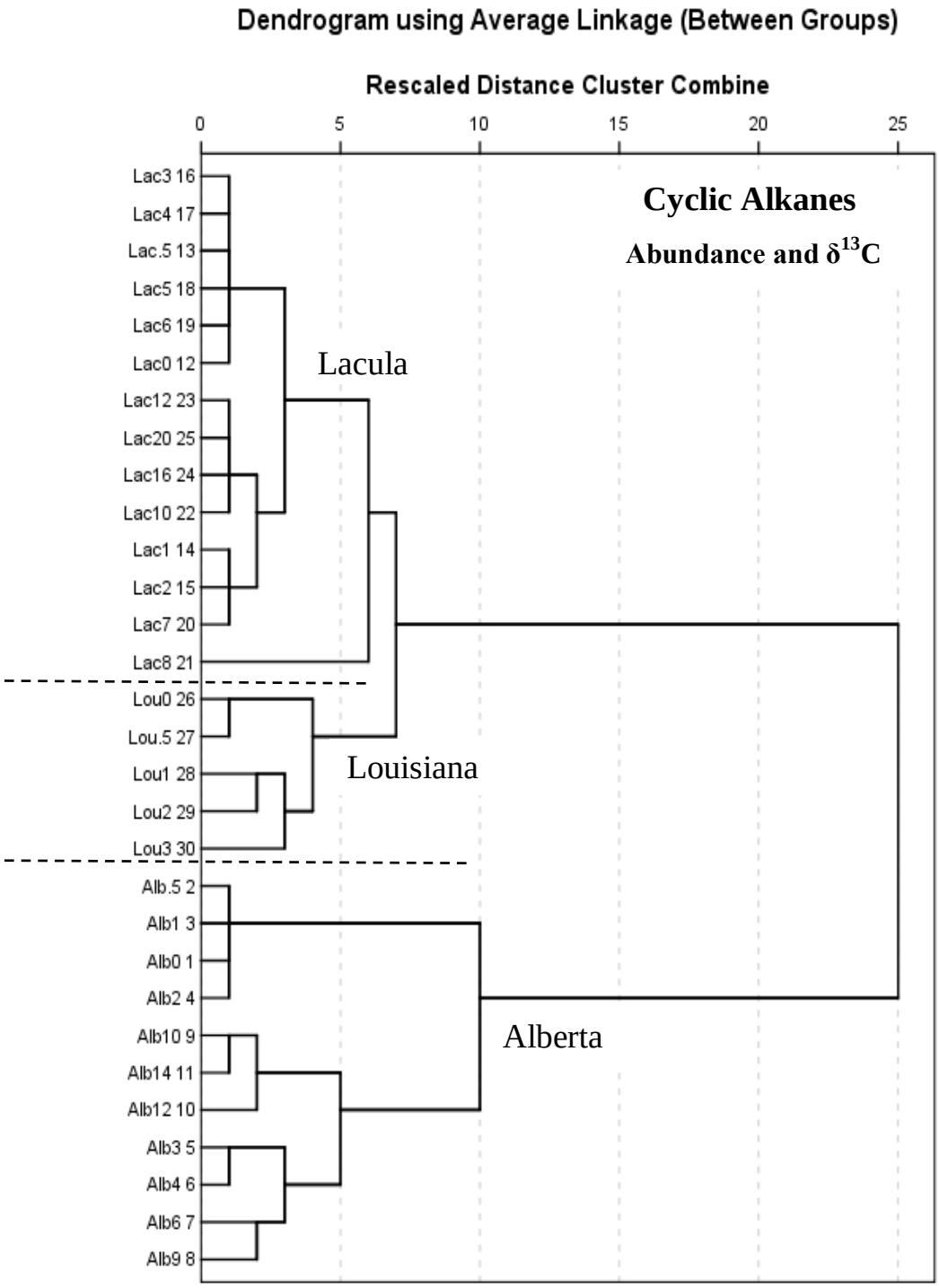



*Figure 4.34. Hierarchical cluster analysis dendrogram using statistical average linkages within the 3 study oils. Cases are for the cyclic alkane compounds, using both abundance and $\delta^{13}C$ as variables.*

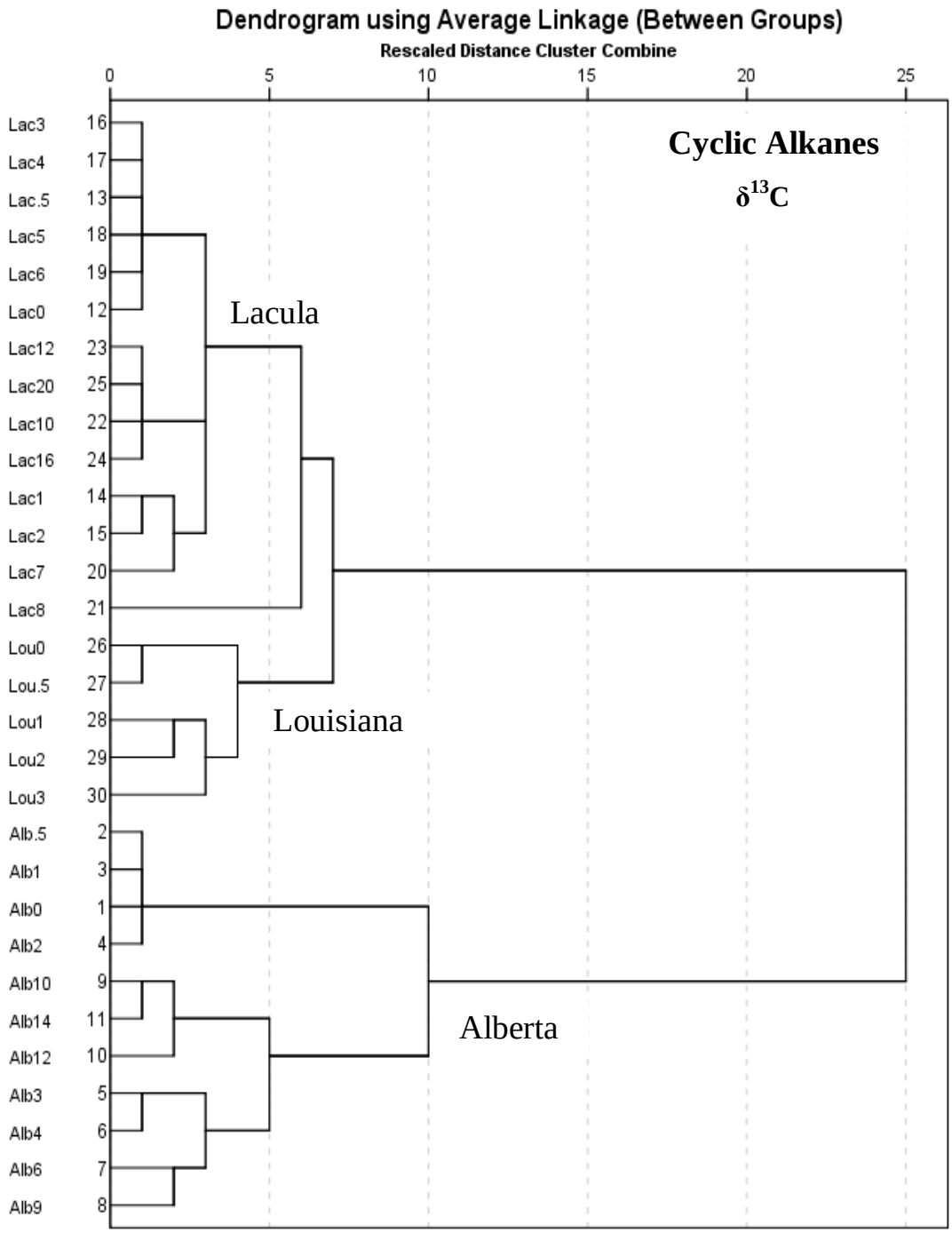



*Figure 4.35. Hierarchical cluster analysis dendrogram using statistical average linkages within the 3 study oils. Cases are for the cyclic alkane compounds, using $\delta^{13}C$ as variables.*

Despite having only a single compound for comparisons, the dendrogram for the only aromatic compound (toluene) shows initial clustering of the many early weathering cases of the Alberta, with only $T_{10}$ and $T_{14}$ cases linking with Lacula (Figure 4.36 and 4.37). Lacula and Louisiana cases however, cluster together in numerous cases at initial stages of comparison, providing poor discriminatory value. In the unweathered oils, toluene has a $\delta^{13}C$ approximately 3‰ lighter in the Alberta oil compared to Lacula and Louisiana, which would explain some of the clustering in most Alberta cases. The compound differed by only about 0.5‰ in the unweathered Lacula and Louisiana oils. The Louisiana final weathering case, $T_3$, is statistically distinct from all other cases, which may be attributed the magnitude of the fractionation observed between the $T_2$ and $T_3$ Louisiana analyses, displaying an approximate 2‰ $^{13}C$ enrichment in toluene (see Figure 4.19b).

Finally, dendrograms are constructed for comparing the clustering patterns of cases for compounds grouped into those comprised of 6,7 and 8 carbons (Figures 4.38 - 4.40). The Louisiana oil is clearly discriminated in all three dendrograms. Comparisons between the $\delta^{13}C$ values obtained for the 7 carbon compounds display the most distinct clustering of each individual oil. The 7 carbon HCA output is comparable in discriminatory value to the output for all 19 compounds displayed in Figure 4.28 and 4.29.

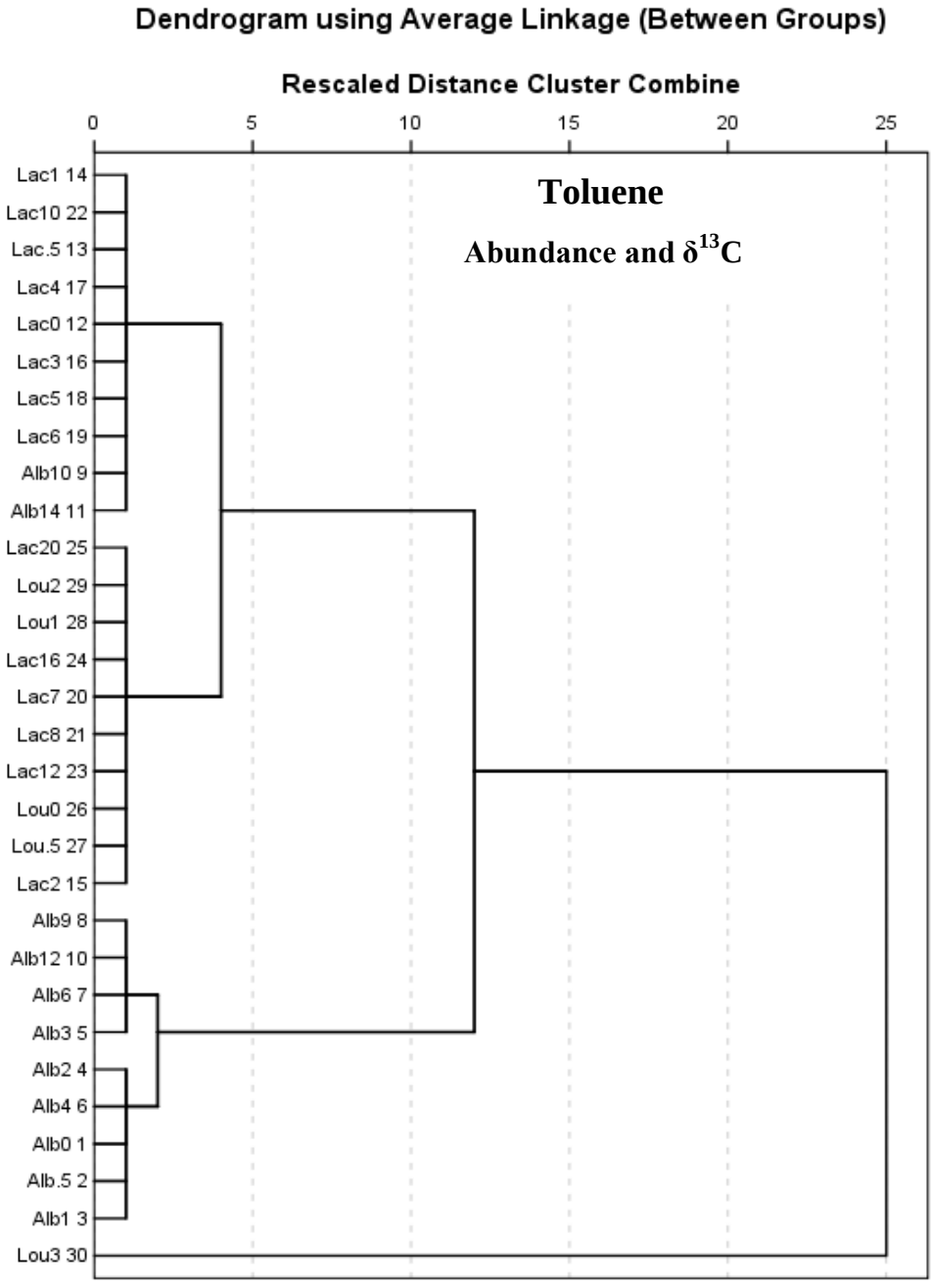



*Figure 4.36. Hierarchical cluster analysis dendrogram using statistical average linkages within the 3 study oils. Cases are for the aromatic compound toluene, using both abundance and $\delta^{13}C$ as variables.*

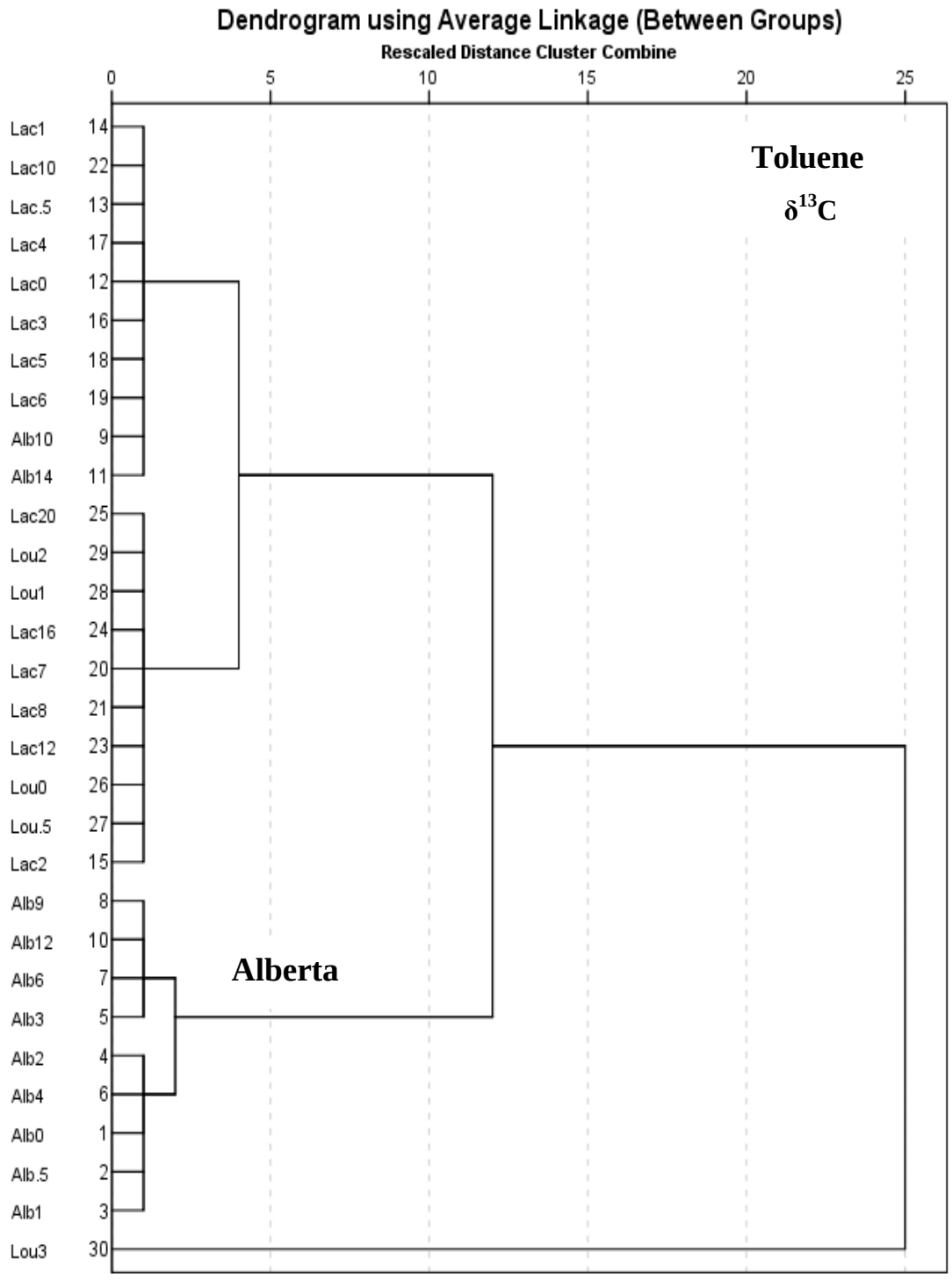



*Figure 4.37. Hierarchical cluster analysis dendrogram using statistical average linkages within the 3 study oils. Cases are for the aromatic compound toluene, using $\delta^{13}C$ as variables.*

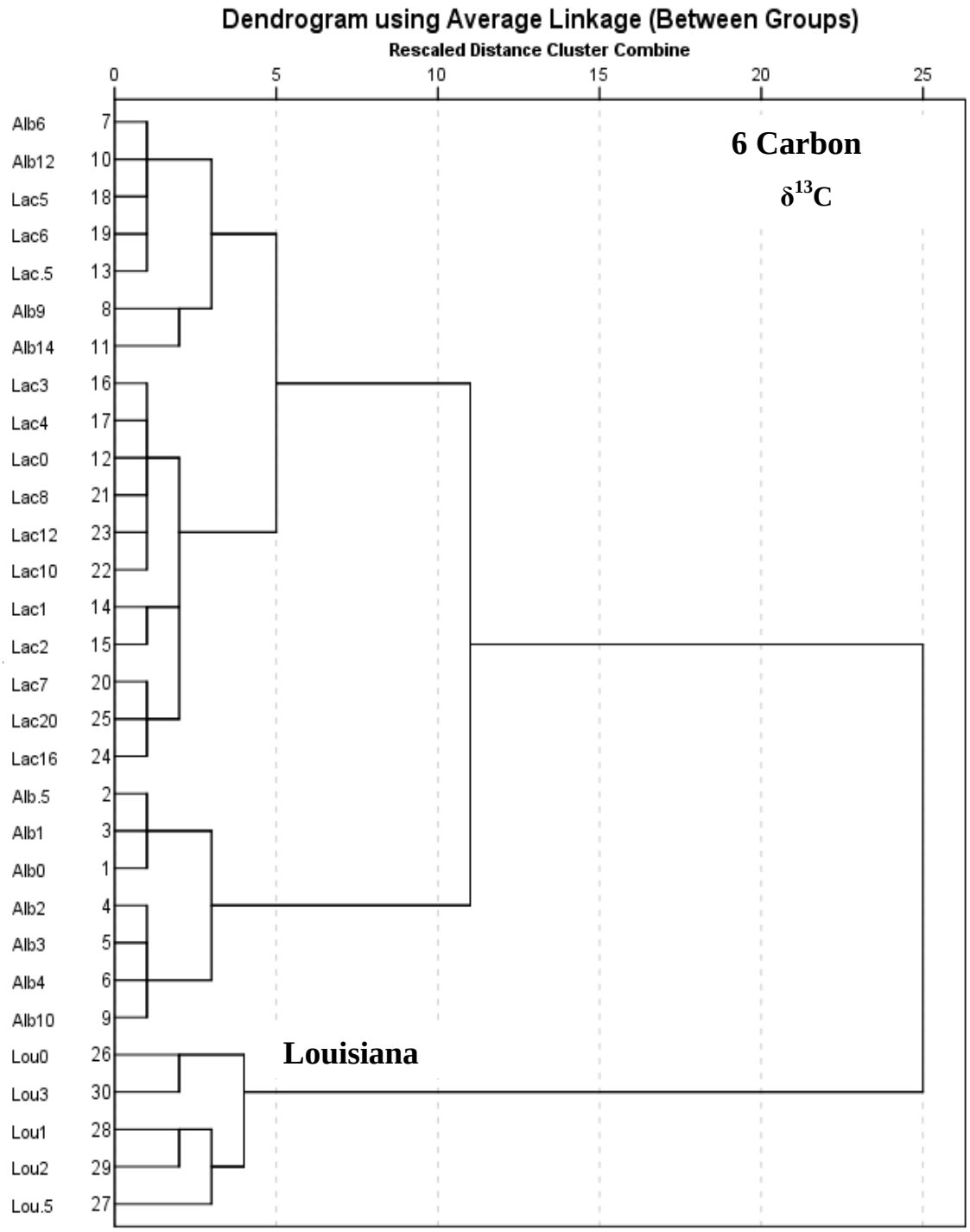



*Figure 4.38. Hierarchical cluster analysis dendrogram using statistical average linkages within the 3 study oils. Cases are for 6 carbon compounds using $\delta^{13}C$ as variables.*

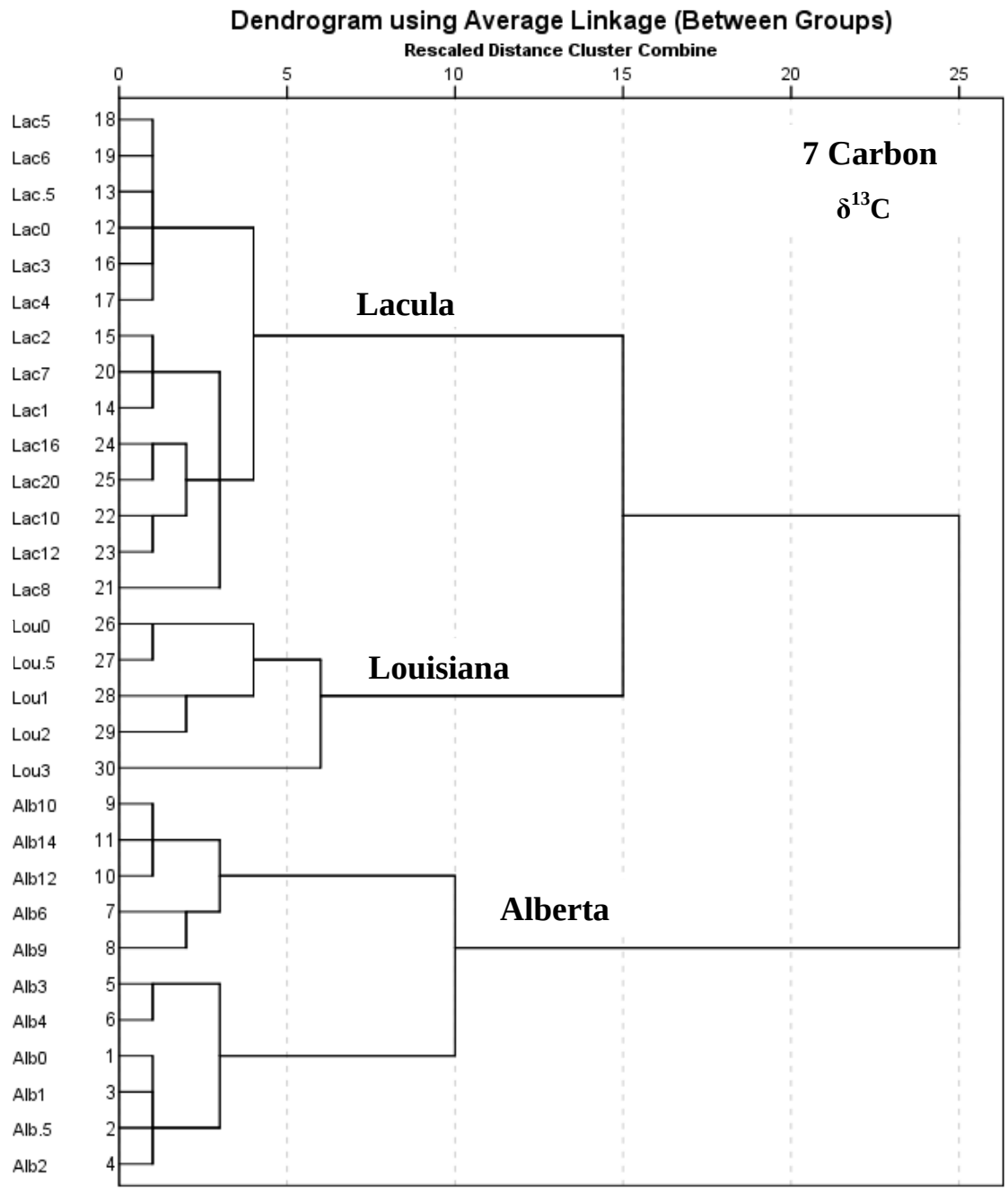



*Figure 4.39. Hierarchical cluster analysis dendrogram using statistical average linkages within the 3 study oils. Cases are for 7 carbon compounds using $\delta^{13}C$ as variables.*

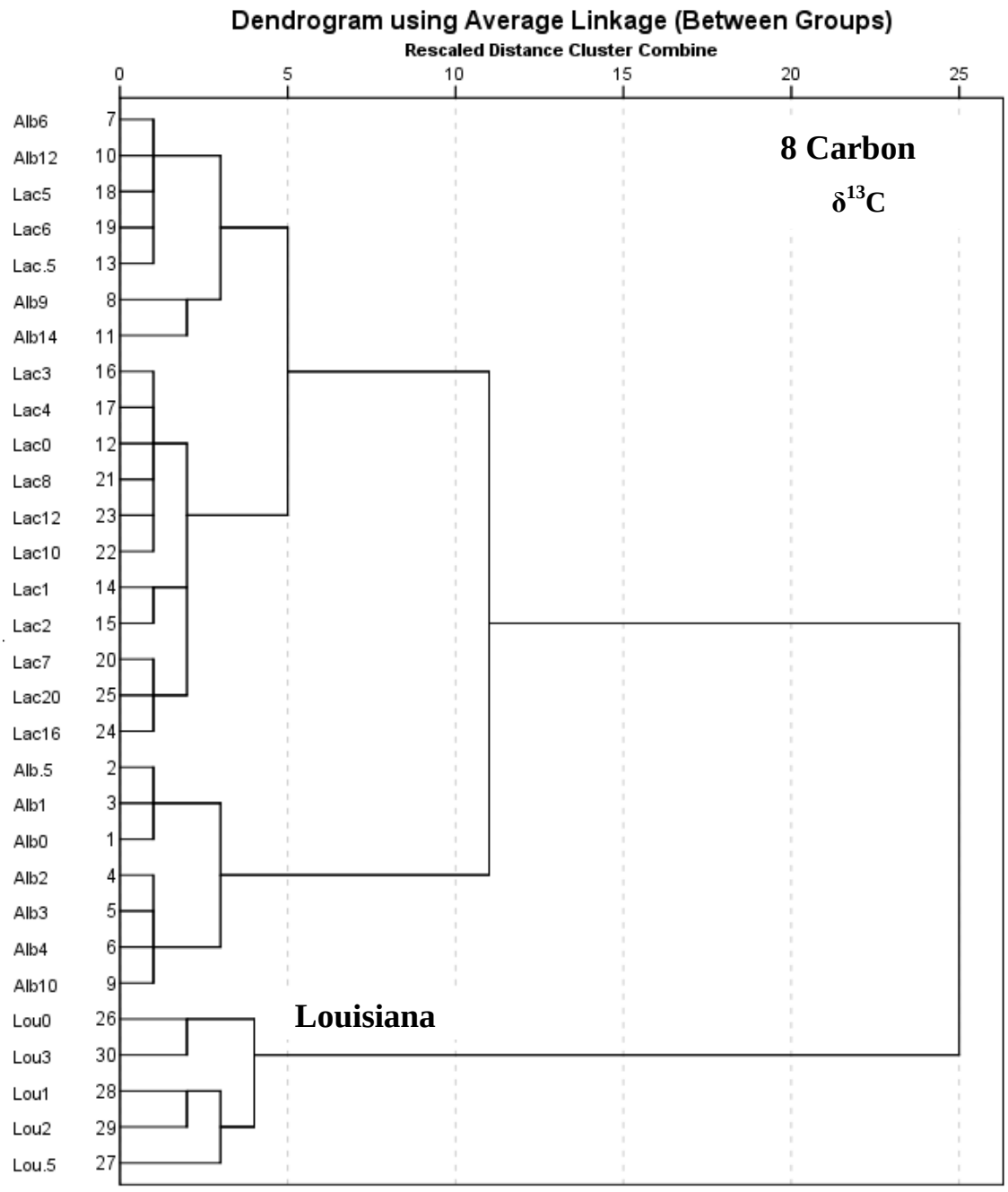



*Figure 4.40. Hierarchical cluster analysis dendrogram using statistical average linkages within the 3 study oils. Cases are for 8 carbon compounds using $\delta^{13}C$ as variables.*

# 5. CONCLUSIONS

This weathering experiment was performed to examine effects of short-term evaporation on the molecular abundance and carbon isotopic composition of gasoline-range hydrocarbon compounds in crude oil spilled on seawater. Gasoline-range fractions ($C_5$-$C_9$) were chosen due to their relatively high abundance in crude oils and low degree of isomerization associated with their smaller carbon number molecules.

The CSIC methodology, using a HSPME technique coupled with CF-IRMS analysis, was successful in measuring the carbon isotope ratios and the change in molecular abundance in as many as 27 gasoline-range hydrocarbon compounds in at least 1 of the 3 experimentally weathered oils. A total of 21 of these 27 compounds were common to all 3 oils. Due to rapid evaporative losses of fractions $\leq C_5$, 19 compounds are available for final comparisons and statistical treatment.

The evaporative rates and ultimate availability of the gasoline-range fractions varied significantly between the 3 oils, however measureable concentrations of $\geq C_6$ molecules were still present in the oils at the final time series analyses. The Lacula oil still had relatively high amounts of $C_5$ compounds in sufficient concentrations for CSIC analysis after 20 hours of weathering. Although results from numerous weathering studies suggest that these fractions are typically lost through evaporation from the bulk volume of the oil within 24-48 hours after a spill, evaporation trends observed in this study indicate that the physicochemical characteristics of an oil (e.g. wax formation) and specific weathering conditions may inhibit or slow evaporative losses.

The general trend in $^{13}C$ enrichment with progressive evaporation observed in 74% of the compounds is consistent with anticipated carbon isotope fractionation resulting from

kinetic isotope effects associated with unidirectional evaporation. 54% of all compounds showed an enrichment of the $^{13}$ C isotope of ≤ 5‰. Although various individual compounds show considerable variability in the rate and amount of $^{13}$C enrichment (0‰ to as high as 2.8‰), many follow a Rayleigh distillation process whereby the $^{13}$C isotopologues become progressively more concentrated in the liquid oil phase as evaporation progresses.

The weighted average amount of overall $\Delta\delta^{13}$C observed is 1.3‰ in the Alberta oil ($T_{f=14}$), 0.9‰ in Lacula ($T_{f=20}$) and 0.4‰ in the Louisiana oil ($T_{f=3}$); with an overall average $\Delta\delta^{13}$C for the 3 oils of about 1 ‰, not inconsistent with results from similar investigations using gasoline-range hydrocarbon fractions.

The amount of $^{13}$C enrichment observed for individual compounds in the study oils was variable, regardless of chemical structure or carbon number. Only 9 of the 19 target compounds were $^{13}$C-enriched in all three oils ($nC_6$, $nC_7$, $nC_9$, $3MC_6$, $CYC_6$, $MCYC_5$, $11DMCYC_5$, $1c3DMCYC_5$ and toluene); toluene being the only compound consistently exhibiting relatively high $^{13}$C enrichment in all 3 oils after weathering (1.8‰, Alberta; 1.6‰, Lacula; 2.8‰, Louisiana).

Isotopogram based comparisons increase in usefulness as the initial $\delta^{13}$C ranges of individual compound $\delta^{13}$C signatures in oils become wider and more distinct; outside the ranges of other oils being compared.

Hierarchical Cluster Analysis (HCA) it was possible to discriminate between the 3 study oils and to correlate weathered cases to their unweathered counterparts. Although various levels of success in oil-source correlation were observed using individual chemical classes of compounds, the most discriminating results were obtained from using the entire 19 compound $\delta^{13}$C data set and the 7 carbon species $\delta^{13}$C comparisons.

Typically, evaporative rates for the gasoline-range compounds are rapid, and therefore their availability in real ocean spill scenarios is potentially limited. Further investigations to determine the maximum temporal availability of all the resolvable gasoline-range fractions after evaporation, under various climactic conditions, would help establish the practical usefulness of the CSIC gasoline-range methodology. Future investigations involving hydrocarbon spills into sediments and groundwater, where evaporation can be inhibited, may provide additional insights into the potential uses of this CSIC technique.

Results from this CSIC study establishes this headspace isotope technique as an additional geochemical tool to aid in correlating fugitive oils, provided gasoline-range compounds are available in sufficient concentration for CF-IRMS analysis and unweathered samples of suspect oils are available for comparison. The technique, as with all strategies for successful oil fingerprinting, is not stand alone and should be used in conjunction with the other established methodologies, sampling, analytical approaches and data interpretations.

# REFERENCES

Abrajano, J. and Lollar, B.S., 1999. Compound-specific isotope analysis: tracing organic contaminant sources and processes in geochemical systems. Organic Geochemistry , vol.30, 8B, pp. 5-7.

Abrams, M.A and Logan, G., 2010 Geochemical Evaluation of Ocean Surface Slick Methods to Ground Truth Satellite Seepage Anomalies for Seepage Detection. Search and Discovery Article #40604. Adapted from oral presentation at AAPG Convention, New Orleans, Louisiana, April 11-14, 2010.

Alimi, H., Ertel, T. and Schug, B., 2003. Fingerprinting of hydrocarbon fuel contaminants: Literature Review. Environmental Forensics, vol. 4, pp.1-38

Anderson, T.F. and Arthur, M.A., 1983. Chapter 1: Stable isotopes of oxygen and carbon and their application to sedimentological and paleoenvironmental problems. Stable isotopes in sedimentary geology: SEPM Short Course No.10, Dallas.

Anderson, R.C., 1983. Economic perspectives on oil spill damage assessment. Oil Petrochemical Pollution, vol.1, no.2, pp.79-84.

Aranberri, I., Beverley K. J., Binks, B. P., Clint, J. H, and Fletcher, P.D., 2002 How Do Emulsions EVapourate? Surfactant & Colloid Group, Department of Chemistry, University of Hull. Langmuir vol. 18, pp. 3471-3475.

Auflem, I.H., 2002. Influence of asphaltene aggregation and pressure on crude oil emulsion stability. Ph.D. Thesis, Norwegian University of Science and Technology, Trondhein, Norway. 394pp.

Arthur, C.L., and Pawliszyn, J., 1990. Solid Phase MicroExtraction with thermal desorption using fused silica optical fibers. Analytical Chemistry, vol. 62, pp. 2145-2148.

Arthur, C.L., Killam, L., Buchholz, K.D., and Pawliszyn, J., 1992a. Automation and optimization of Solid-Phase MicroExtraction. Analytical Chemistry, vol.64, pp.1960-1966.

Arthur, C.L., Killam, L., Motlagh, S., Lim, M., Potter, D., and Pawliszyn, J., 1992b. Analysis of substituted benzene compounds in ground-water using SPME. Environmental Science and Technology, vol. 26, pp. 979-983.

Aske, N., Kallevik, H. and Sjöblom, J., 2002. Water-in-crude emulsion stability studied by critical field measurements. Correlation to physico-chemical parameters and near-infrared spectroscopy. Journal of Petroleum Science and Engineering, vol. 36, pp.1-17.

Atlas, R.M. and Bartha, R., 1972. Biodegradation of petroleum in seawater at low temperatures. Canadian Journal of Microbiology, vol.18, pp.1851-1855.

Baertschi , P., Kuhn, W. and Kuhn, H., 1953. Fractionation of isotopes by distillation of some organic substances. Nature, vol.171, pp.1018-1020.

Balabane, M. and Letolle, R., 1985. Inverse overall isotope fractionation effect through distillation of some aromatic molecules (anethole, benzene and toluene). Chemical Geology, vol. 52, pp. 391-396.

Bence, A. E., Kvenvolden, K. A. and Kennicutt, M.C., 1996. Organic geochemistry applied to environmental assessments of Prince William sound, Alaska, after the *Exxon Valdez* oil spill – a review. Organic Geochemistry, vol.24, pp.7-42.

Bigeleisen, J. and Mayer, M.G., 1947. Calculation of equilibrium constants for isotopic exchange reactions. Journal of Chemical Physics, vol.15, pp. 261-267.

Bigeleisen, J., 1952. The effects of isotopic substitutions on the rates of chemical reactions. Journal of Physical Chemistry, vol.56, pp. 823-824.

Bigeleisen, J., 1965. Chemistry of isotopes. Science, vol.147, pp. 463-471.

Bjorøy, M., Hall, P.B. and Moe, R.P., 1994. Variation in the isotopic composition of single components in the $C_4$-$C_{20}$ fraction of oils and condensates. Organic Geochemistry, vol.21, no. 6/7, pp. 761-776.

Bobra, M., 1991. Water-in-oil emulsions: A physicochemical study. Proceedings of the 1991 International Oil Spill Conference. American Petroleum Institute, Washington , D.C. pp. 483-488.

Bobra, M., 1992. A study of the evaporation of petroleum oils. Consultchem, Environmental Emergency Manuscript Report Number EE-135, Environment Canada, Ottawa, Ontario, Canada, May.

Bobra, M., 1992. A study of water-in-oil emulsification, Consultchem, Environmental Emergency Manuscript Report Number EE-132, Environment Canada, Ottawa, Ontario, Canada, May 1992.

Bobra, M., Fingas, M., Tennyson, E., 1992. When oil spills emulsify. Reprint from CHEMTECH, no. 22, pp. 236-241.

Boutton, T.W., 1991. Chapter 10: Stable carbon isotope ratios of natural materials: I. Sample preparation and mass spectrometric analysis. *In*: Carbon Isotope Techniques, D.C. Coleman and B. Fry (eds), Academic Press Limited, London, pp.155-171.

Boyd-Boland, A.A., Magdic S., and Pawliszyn, J., 1996. Simultaneous determination of 60 pesticides in water using Solid Phase MicroExtraction and Gas Chromatography-Mass Spectrometry, Analyst, vol.121, pp.929-937.

Bridie, A. L., T.H. Wander, W. Zegveld, and Van der Heijde, H.B., 1980. Formation, prevention and breaking of sea water in crude oil emulsions (chocolate mousses). Marine Pollution Bulletin, vol.11, pp.343-348.

Broeker, W.S. and Oversby, V.M., 1971. Chemical Equilibria in the Earth. McGraw-Hill, New York, 318pp.

Bruno, J.T., 1991. Ch.2: Gas chromatography. *In*: Chromatographic and Electrophoretic Methods, Prentice Hall Inc., New Jersey, pp. 17-73.

Carpentier, B., Ungerer, P., Kowalewski, I., Magnier, C., Courcy, J.P. and Huc, Y.A., 1996. Molecular and isotopic fractionation of light hydrocarbons between oil and gas phases. Organic Geochemistry, vol.24, no.12, pp. 1115-1139.

Canaveri, G. and Fiocco, R., 1997. Crude oil vanadium and nickel content can predict emulsification tendencies. International Oil Spill Conference.

Chapman, R.E., 1983. Petroleum Geology. Developments in Petroleum Science. Elsevier Science Publishers. New York. Vol.16, pp. 220.

Chung, H.M., Brand, S.H. and Grizzle, P.L. 1981. Carbon isotope chemistry of Paleozoic oils from Big Horn basin. Geochemica Cosmochemica Acta, vol.45, pp.1803-1815.

Coplen, T.G., 1994. Reporting of stable hydrogen, carbon and oxygen isotopic abundances. Pure and Applied Chemistry. Vol. 66, pp. 273-276.

Craig, H., 1953. The geochemistry of stable carbon isotopes. Geochemica et Cosmochimica Acta, vol.3, pp. 53-92.

Dias, R.F., and Freeman, K.H. 1997. Carbon isotope analyses of semi-volatile organic compounds in aqueous media using Solid-Phase Microextraction and isotope ratio monitoring GC/MS. Analytical Chemistry, vol.69, pp. 944-950.

Dickens, D., Buist, I., Krajczar, K., Rueggeburg, H., Booth, J., Fink, R. Solsberg, L. and Griffin, B. 1990. Marine Oil Transportation Systems: Evaluation of Environmental Risk & Alternative for Risk Reduction. Final report for States/British Columbia Oil Task Force. vol.1, 152pp.

Dodd, E.N., 1975. The effects of natural factors on the movement, dispersal and destruction of oil at sea. *In* Petroleum in the Marine Environment. National Academy of Science. Wash., D.C. 47pp.

Doerffer, J.W., 1992. Oil Spill Response in the Marine Environment. Ship Research Institute, Technical University of Gdansk, Poland. Pergamon Press, New York, 391p.

Epstein, P.R. and Selber, J., 2002. A life Cycle Analysis of Its Health and Environmental Impacts. The Center for Health and the Global Environmental, Harvard Medical School. 73p.

El-Nemr, A., 2006. Petroleum Contamination in Warm and Cold Environments. Nova Science Publishers Inc. New York. 141p.

Fallah, M.H., and Stark, R.M., 1976. Random model of evaporation of oil at sea. The Science of the Total Environment. Elevier Scientific Publishing Company, Amsterdam, vol. 5, pp 95-109.

Farran, A., Grimalt, J., Albaiges, J., Botello, A.V. and Macko, S.,1987. Assessment of petroleum pollution in a Mexican river by molecular markers and carbon isotope ratios. Pollution Bulletin, vol.18, pp.284-289.

Faure, G., 1986. Principals of Isotope Geology. Second edition. John Wiley and Sons, New York, 580 pp.

Fingas, M.F., Duval, W.S. and Stevenson, G.B., 1979. The basics of oil spill cleanup. Environmental Protection Service, Environment Canada.

Fingas, M.F., Fieldhouse, B., Gamble, L. and Mullin, J. A., 1995a. Studies of water-in-oil emulsions: Stability classes and measurement. Proceedings of the 18th Arctic and Marine Oil Spill Program Technical Seminar, Environment Canada, Ottawa, Ontario, pp. 21-42.

Fingas, M.F., 1995. A literature review of the physics and predictive modeling of oil spill evaporation. Journal of Hazardous Materials, vol. 42, pp.157-175.

Fingas, M.F., 1997. Studies on the evaporation of crude oil and petroleum products; I. the relationship between evaporative rate and time. Journal of Hazardous Materials, vol. 56, pp. 227-236.

Fingas, M., 1998. The Evaporation of Oil Spills: Development and Implementation of New Prediction Methodology. Pre-issued Proceedings, 2nd International Marine Environmental Modeling Seminar, Lillehammer Norway.

Fingas, M.F., Fieldhouse, B., Lane, J., Mullin, J.V., 2000. Studies of water-in-oil emulsions: long-term stability, oil properties, and emulsions formed at sea. In: Proceedings of the Twenty-Third Arctic and Marine Oil Spill Program Technical Seminar, Environment Canada, Ottawa, Ontario.

Fingas, M. F., Fieldhouse, B. and Wang, Z., 2003. The long term weathering of water-in-oil emulsions. Spill Science and Technology Bulletin, vol. 8, Issue 2, pp.137-143.

Fingas, M., 2004. Modeling evaporation using models that are not boundary-layer regulated. Journal of Hazardous Materials, vol. 107 (1-2), pp. 27-36.

Freeman, K.H., Hayes, J.H., Trendel, J.M., and Albrecht, P., 1990. Evidence from carbon isotope measurements for diverse origins of sedimentary hydrocarbons. Nature, vol.343, pp. 254-356.

Galt, J.A., Lehr, W.J. and Payton, D.L., 1991. Fate and transport of the *Exxon Valdez* oil spill. National Oceanic and Atmospheric Administration. Environmental Science and Technology, vol.25, no.2, pp. 202-209.

Goodwin, S.R., Mackay, D., and Shiu,W.Y., 1976. Characterization of the evaporation rates of complex hydrocarbon mixtures under Environmental conditions. Canadian Journal of Chemical Engineering, vol.54, pp.290-294.

Goodwin, N.S., Park, J.D. and Rawlinson, A. P., 1983. Crude oil biodegradation under simulated and natural conditions. Advances in Organic Geochemistry, New York, J Wiley and Sons, pp. 650-658.

Habfast, K., 1991. The methodology and instrumentation of GC-IRMS. Manuscript of a talk presented at the seminar on "Authentication and quality assessment of food products-Recent advances in isotope analysis", Finnigan Mat Publication.

Hampton, S., Kelly, P.R. and Carter, H.R ,. 2003. Tank vessel operations, seabirds and chronic oil pollution in California. *Marine Ornithology* 31: 29-34.

Harper, J.R. and Kory, M.,1995. Stranded oil in coarse sediment experiments (SOCSEX II). Manuscript Report EE-155, Emergencies Science Division, Environment Canada, Ottawa, ON, Canada, 60pp.

Harrington, R.R., Poulson, S.R., Drever, J.I., Colberg, P.J.S. and Kelly, E.F., 1997. Stable carbon isotope systematics of aromatic hydrocarbons. Geologica; Society of America Abstracts with Programs, vol,29, no.6, pp. A184.

Harrington, R.R., Poulson, S.R., Drever, J.I., Colberg,P.J.S. and Kelly, E.F., 1999. Carbon isotope systematics of monoaromatic hydrocarbons: Vapourization and adsorption experiments. Organic Geochemistry, vol.30 (8A), pp.765-775.

Harris, S.A., 1999. Compound specific isotope correlation (CSIC). Using gasoline range hydrocarbons: a novel approach for petroleum exploration. M.Sc. thesis, University of Victoria, 151 pp.

Harris, S.A., Whiticar, M.J. and Eek, M.K., 1999. Molecular isotopic analysis of oils by solid phase micro extraction of gasoline range hydrocarbons. Organic Geochemistry, vol.30, pp.1-17.

Hayes, J.M., 1982. Fractionation et al.: An introduction to isotopic measurements and terminology. Spectra, vol.8, pp. 3-8.

Hayes, J.M., Freeman, K.H., Popp, B.N. and Hoham, C.H., 1990. Compound specific isotope analysis; a novel tool for reconstruction of ancient biogeochemical processes. Organic Geochemistry, vol.16, pp.1115-1128.

Head, I.M., Jones, M. and Roling, F. M., 2009. Marine microorganisms make a meal of oil. Nature Reviews Microbiology, vol. 4, pp.173-182.

Hocking, M.B., 1985. Modern Chemical Technology and Emission Control. Springer -Verlag, Berlin, 460 pp.

Hostettler, F.D. and Kvenvolden, K. A., 1994. Geochemical changes in crude oil spilled from the Exxon Valdez supertanker into Prince William Sound, Alaska. Organic Geochemistry, vol.21, no.8/9, pp. 927-936.

Huang, C.P. and. Elliot, H.A., 1977. The stability of emulsified crude oils as affected by suspended particles. *In* Fates and Effects of Petroleum Hydrocarbons in the Marine Organisms and Ecosystems. D.A. Wolfe Ed. Permagon Press. 473 pp.

Huang, L., Sturchio, N.C., Abrajano, T., Heraty, L.J. and Holt, B.D., 1999. Carbon and chlorine isotope fractionation of chlorinated aliphatic hydrocarbons by evaporation. Organic Geochemistry, vol.30, pp.777-785.

Hunkeler D. and Aravena, R., 2000. Determination of compound-specific carbon isotope ratios of chlorinated methanes, ethanes, and ethenes in aqueous samples. Environmental Science and Technology. Vol 34, no.13, pp. 2839-2844.

ITOPF, 2002. Fate of Marine Oil Spills. Technical Information Paper. The International Tanker Owners Pollution Federation Limited (ITOPF), United Kingdom. 8 pp.

Jokuty, P., Whiticar, S., Wang, Z., Fieldhouse, B., and Fingas, M., 1999. A catalogue of crude oil and oil properties for the Pacific region. Environment Canada, Ottawa, Ontario.

Kaplan, I.R, Galperin, Y., Lu, S.T. and Lee R.P., 1997. Forensic Environmental Geochemistry: differentiation of fuel types, their sources and release time. Organic Geochemistry, vol.27, no.5/6, pp. 289-317.

Kvenvolden, K.A.,Hostettler, F.D., Carlson, P.R., Bapp, J.B., Threelkeld, C.N., Warden, A., 1995. Ubiquitous tar balls with California-source signature on shorelines of Prince William Sound Alaska. Environmental Science and Technology, vol. 29(10): pp. 2684-2694.

Lafargue, E. and Thiez, P.LE., 1996. Effects of water washing on light ends compositional heterogeneity. Organic Geochemistry, vol.24, no.12, pp.1141-1150.

Langevin, D., Poteau, I. H. and Argillier, J.F., 2004. Crude oil emulsion properties and their application to heavy oil transportation. Oil Gas Science and Technology Review, IFF, vol. 59, pp. 511-521.

Leckrone, K.J. and. Hayes, J.M., 1998. Water-induced errors in continuous-flow carbon isotope ratio mass spectrometry. Analytical Chemistry, vol.70, pp. 2737-2744.

Li, Y., Xiong, Y., Yang, W., Xie, Y., Li, S., Sun, Y., 2009. Compound-specific stable carbon isotopic composition of petroleum hydrocarbons as a toll for tracing the source of oils spills. Marine Pollution Bulletin, vol. 58, pp. 114-117.

Louch, D., Motlagh, S., and Pawliszyn, J., 1992. Dynmics of organic compound extraction from water using liquid-coated fused silica fibers. Analytical Chemistry, vol.64, pp.187-1199.

Ludzack, F.L and Kinkead, D., 1956. Persistence of oil wastes in polluted water under aerobic conditions. Industrial Engineering Chemistry. Vol.48, pp. 263-367.

MacGillivray, B., Pawliszyn, J., Fowlei, P., and Sagara, C., 1994. Headspace Solid-Phase Micro Extraction versus purge and trap for the determination of substituted benzene compounds in water. Journal of Chromatographic Science, vol.32, pp. 317-322.

Mackay, D. and Matsugu, R.S., 1973. Evaporation rates of liquid hydrocarbon spills on land and water. Canadian Journal of Chemical Engineering, vol. 51, pp. 434-439.

Macko, S.A., Parker, P.L. and Botello, A.V., 1981. Environmental Pollution Bulletin, vol.2, pp.119-128.

Mango, F.D., 1997. The light hydrocarbons in petroleum: a critical review. Organic Geochemistry, vol. 26, no. 7/8, pp. 417-440.

Mansuy, l., Philip, P. and Allen, J., 1997. Source identification of oil spills based on the isotopic composition of individual components in weathered oil samples. Environmental Science and Technology, vol.31, pp. 3417-3425.

Margesin, R., and Schinner, F., 2001. Biodegradation and bioremediation of hydrocarbons in extreme marine environments. Microbiology and Biotechnology, vol.56, pp. 650-663.

Masterson, W.D., Dzou, I.P., Holba, A.J., Fincannon, A.L. and Ellis, L., 2001. Evidence for biodegradation and evaporative fractionation in West Sak, Kuparuk and Prudhoe Bay field areas, North Slope, Alaska. Organic Geochemistry. Vol. 32, no.11, pp. 411-441.

Matthews, D.E. and Hayes, J.M., 1978. Isotope-ratio-monitoring gas chromatography-mass spectrometry. Analytical Chemistry, vol.50, no.11, p.1465-1473.

Mazeas, L and Budzinski, H., 2002. Stable carbon isotopic study ($^{12}C/^{13}C$) of the fate of petrogenic PAHs (methyphenanthrenes) during an in situ oil spill simulation experiment, Organic Geochemistry, vol.33, pp. 1253–1258.

McAuliffe, C.D., 1977. Dispersal and alteration of oil discharged on a water surface. In: Petroleum Hydrocarbons in Marine Ecosystems and Organisms. Permagon Press, Oxford. pp. 19-35.

McAuliffe, C.D., 1989. Dispersion and weathering of chemically treated crude oils on the ocean. Environmental Science and Technology, vol.14, no.12, pp. 1509-1518.

McDonald, T. J., Brooks, J.M. and Kenicutt, M.C., 1984. Release of volatile liquid hydrocarbons from spilled petroleum. Bulletin of Environmental Contamination and Toxicology, vol. 32, pp. 621-638.

Merritt, D.A., Freeman, K.H.; Ricci, M.P.; Studley, S.A. and Hayes, J.M., 1995. Performance and optimization of a combustion interface for isotope ratio monitoring chromatography/mass spectrometry. Analytical Chemistry, vol. 67, pp. 2461-73.

Merritt, D.A., Brand, W.A., and Hayes, J.M., 1994. Isotope-ratio-monitoring gas chromatography-mass spectrometry: methods for isotopic calibration. Organic Geochemistry, vol.21, no.6/7, pp. 573-583.

Merritt, D.A. and Hayes, J.M., 1994. Factors controlling precision and accuracy in isotope-ratio-mass spectrometry. Analytical Chemistry, vol.66, pp. 2336-47.

Mook, W.B., 2000. Isotopes in the hyrdological cycle. Principals and applications. International Hydrological Program. Technical Documents in Hydrology, Vol. 1, no. 39, pp. 179-184.

Mouawad, J. and Schwartz, J., 2010. Cleanup Costs and Lawsuits Rattle BP's Investors. New York Times, June, 2010.

Murphy, D. E., 1995. GC-C-IRMS: A new technique to characterize and correlate oils and source rocks. M.Sc. thesis, SEOS, University of Victoria, 368 pp.

National Research Council. 1989. Using Oil Dispersants on the Sea. Marine Board Commission on Engineering and Technical Systems, National Research Council. National Academy Press Washington, D.C. 335pp.

National Research Council. 2003. Oil in the Sea III; Inputs, Fates, and Effects. Committee on Oil in the Sea: Inputs, Fates, and Effects, National Research Council. The National Academies Press Washington, D.C. 280pp.

Okamoto, K., Watanabe, N., Hagimoto, Y., Miwa, K., and & Ohtani, H., 2009. Changes in evaporation rate and vapour pressure of gasoline with progress of evaporation. Fire Safety Journal, vol. 44, pp. 756-763.

Okamoto, K., Watanabe, N., Hagimoto, Y., Miwa, K., and & Ohtani, H., 2010. Evaporation characteristics of multi-component liquid. Journal of Loss Prevention in the Process Industries, vol. 23, pp.89-97.

O'Malley, V.P., Abrajano, T.A. and Hellou, J., 1994. Determination of the 13C/12C ratios of individual PAH from environmental samples: can PAH be apportioned? Organic Geochemistry, vol.21, no.6/7, pp.809-822.

O'Neil, J.R., 1986. Theoretical and experimental aspects of isotopic fractionation. Reviews in Mineralogy, vol.16, pp.1-40.

O'Sullivan, G and Kalin, R M., 2008. Investigation of the range of carbon and hydrogen isotopes within a global set of gasolines. Environmental Forensics, vol.9: 2, pp.166-176.

Owens, E.H., 1985. Factors affecting the persistence of stranded oil on low-energy coasts. In: Proceedings of the Oil Spill Conference, American Petroleum Institute, Washington, D.C. Publication no. 4385, pp59-365.

Owens, E.H., Taylor, E., and Humphrey, B., 2008. The persistence and character of stranded oil on coarse-sediment beaches. Marine Pollution Bulletin, vol. 56, pp14-26.

Owens, E.H. and Lee, k., 2003. Interaction of oil and mineral fines on shorelines; review and assessment. Marine Pollution Bulletin, vol. 47 (9-12), pp 397-405.

Payne, J.R. and McNabb, G,D. Jr., 1984. Weathering of petroleum in the marine environment. Marine Technology Society Journal, vol. 18, pp. 24-42.

Payne, J.R., and Phillips, C.R., 1985. Petroleum spills in the marine environment. *In* The Chemistry and Formation of Water-in-Oil Emulsions and Tar Balls. Chelsea Mich.: Lewis Publishers. 148 pp.

Potter, D. and Pawliszyn, J., 1994. Rapid determination of polyaromatic hydrocarbons and polychlorinated biphenyls in water using Solid Phase Micro Extraction and GC/MS. Environmental Science and Technology, vol.28, pp.298-305.

Preston, T., Hough, R.L., Fallick, A.E., Pollard, Simon, J.T., Whittaker, M., Farmer, J.G., 2005. Identifying source correlation parameters for hydrocarbon wastes using compound-specific isotope analysis. Environmental Pollution, vol. 143(3), pp. 489-498.

Ramseur, J.L, 2008. Environmental Activities of the U.S Coast. Congressional Research Service Report to Congress. 6pp.

Reijnhart, R. and Rose, R., 1982. Evaporation of crude oil at sea. Water Research, vol. 16, no. 8, pp.1319-1325.

Riazi, M. and Edalat, M., 1996. Prediction of the rate of oil removal from seawater by evaporation and dissolution. Journal of Petroleum Science and Engineering, vol. 16, pp. 291-300.

Ricci, M.P., Merritt, D.A., Freeman, K.H., and Hayes, J.M., 1994. Acquisition and processing of data for isotope-ratio-monitoring mass spectrometry. Organic Geochemistry, vol.21, no.6/7, pp.561-571.

Rooney, M. A., Vuletich, A. K. and Griffith, C. E., 1998. Compound-specific isotope Analysis for characterizing mixed oils: an example from the west of Shetlands area. Organic Geochemistry, vol. 29, issues1-3, pp.241-254.

Ross, S.L. and Mackay, D., 1988. Laboratory studies of the behavior and fate of waxy crude oil spills. S.L. Ross Environmental Research Ltd. And D. Mackay Environmental Research Ltd. Environmental Studies Research Fund Report, no.084, 247pp.

Santrock, J., Studley, S.A., and Hayes, J.M., 1995. Isotopoic analyses base on the mass spectrum of carbon dioxide. Analytical Chemistry, vol.57, pp.1444-1448.

Serra-Sogas, N., 2010. Modeling risk of chronic oil pollution from vessel operations in Canada's West Coast. M.Sc. Thesis. Department of Geography. University of Victoria. 133pp.

Sherwood Lollar, B., Slater, G.F., Ahad, J., Sleep, B., Spivack, J., Brennan,M., and MacKenzie, P., 1999. Contrasting carbon isotope fractionation during biodegradation of trichloroethylene and toluene: Implications for intrinsic bioremediation. Organic Geochemistry, vol. 30, issue 8, part 1, pp.813-820.

Shin,Woo-Jin, and Lee, Kwang, 2010. Carbon isotope fractionation of benzene and toluene by progressive evaporation. Rapid Communications in Mass Spectrometry, vol. 24, no.11, pp. 1636-1640.

Short,J.W., Lindeberg, M., Harris, P.M., Maselko, J.M., Pella, J.J. and Rice, S.D., 2004. Estimate of oil persisting on the beaches of Prince William Sound 12 years after the Exxon Valdez oil spill. Environmental Science Technology, vol. 38, pp19-25.

Silverman, S.R., 1964. Investigation of petroleum origin and evolution mechanisms by carbon isotope studies. *In*: Isotope and Cosmic Chemistry, H. Craig, S.L. Miller, and C.J. Wasserburg (eds), N. Holland Publishing Company, Amsterdam, pp.92-102.

Slater, G.F., Dempster, H.S., Lollar, B.S. and Ahad, J., 1999. Headspace analysis; A new application for isotopic characterization of dissolved organic contaminants. Environmental Science and Technology, vol.33, pp.190-194.

Smallwood, B.J., Philip, R.P., and Allen, J.D., 2002. Stable carbon isotopic composition of gasolines determined by isotope ratio monitoring gas chromatography mass spectrometry. Organic Geochemistry, vol.33, pp.149-159.

Smith, C.L. and MacIntyre, W.G., 1971. Initial aging of fuel oils films of seawater. In: Proceedings of 1971 Joint Conference on Prevention and Control of Oil Spills. American Petroleum Institute, Washington, D.C. pp. 457-61.

Sofer, Z., 1984. Stable carbon isotope composition of crude oils: Application to source depositional environments and petroleum alteration. AAPG Bulletin, vol.68, pp. 321-49.

Stahl, W.J., 1977. Carbon and nitrogen isotopes in hydrocarbon research and exploration. Chemical Geology, vol.20, pp.121-149.

Stahl, W.J., 1979. Carbon isotopes in petroleum geochemistry. In E. Jager and J.C. Hunzicker, eds., Lectures in Isotope Geology, pp. 274-282. Springer-Verlag, Berlin, 329pp.

Stahl, W.J., 1980. Compositional changes and $^{13}C/^{12}C$ fractionations during the degradation of hydrocarbons by bacteria. Geochemica Cosmochemica Acta, vol.44, pp.1903-1907.

Steffen, A. and Pawliszyn, J., 1996. The analysis of flavour volatiles using Headspace Solid Phase Micro Extraction. Journal of Agricultural Food Chemistry, vol.44, pp. 2187-2193.

Stiver, W., Shiu, W. and Mackay, D., 1989. Evaporation times and rates of specific hydrocarbons in oil spills. Journal of Environmental Science and Technology, vol. 23, no. 23, pp.101-105.

Stout, S. A., Uhler, A. D., and McCarthy, K. J., 2001. A strategy and methodology for defensibly correlating spilled oil to source candidates. Environmental Forensics, vol. 2, pp. 87-98.

Stout, S. A. , Douglas, G. S., Uhler, A. D., McCarthy, K .J. and Emsbo-Mattingly, S. D., 2005. Identifying the source of mystery waterborne oil Spills: A case for quantitative chemical fingerprinting. Environmental Claims Journal, vol. 17: 1, pp.71-88.

Tasaki, R. and Ogawa, A., 1995. Weathering of crude oil spilled on water. Evaporation, emulsification and oil properties. Ship and Ocean Foundation, 131pp.

Thomson, R.E., 1981. Oceanography of the British Columbia Coast. Canadian Special Publication. Fisheries Aquatic Science, vol.56, p.29.

Thompson, D., Davis, R.A. and Hillis, T., 1991. Effects of operational discharges from ships on marine life. Report by LGL Research Ltd. for Government Consulting Group and Canadian Coast Guard, Ottawa, Canada. 30pp.

Tkalin, A.V., 1986. Evaporation of petroleum hydrocarbons from films on a smooth sea surface. Oceanology of the Academy of Sciences of the U.S.S.R, vol. 26, American Geophisical Union, Washington, D.C., pp. 473-474.

Urey, H.C., Brickwedde, F.G. and Murphy, G.M., 1932. An isotope of Hydrogen of mass 2 and its concentration. Abstract Physical Review, vol.39, p.864.

Urey, H.C., 1947. The thermodynamic properties of isotopic substances. Journal of the Chemical Society, vol.1947, pp. 562-581.

Walker, J. D.; Petrakis, L.; Colwell, R. R., (1978).Degradation of petroleum by pure culture of bacteria, algae, yeast and filamentous fungi. Archives of Microbiology, vol.30, pp.79-81.

Wang, Z., Fingas, M. and Sergy G., 1994. Study of 22-year old Arrow samples using biomarker compounds by GC/MS. Emergency Sciences Division, ETC, Environment Canada. Environmental Science and Technology, vol.28, pp.1733-1746.

Wang, Z ., Fingas, M. and Li, K., 1994. Fractionation of ASMB oil, identification and quantitation of aliphatic aromatic and biomarker compounds by GC/FID and GC/MSD. Journal of Chromatographic Science, vol.18, pp.361-382.

Wang, Z .and Fingas, M., 1999. Identification of the source(s) of unknown spilled oils. Proceedings from the 1999 International Oil Spill Conference, no.162, 9 pp.

Wang, Z., Fingas, M., and Page, D. S. 1999. Oil spill identification. Journal of Chromatographic Analysis, vol. 842, pp. 369-411.

Wang, Z. and Fingas, M.F., 2003. Development of oil hydrocarbon fingerprinting and identification techniques. Marine Pollution Bulletin, vol. 47, pp. 423-452.

Wang, Z. and Stout, S., 2007. Oil Spill Environmental Forenzics. Fingerprinting and source identification. Elsevier Press, 565 pp.

Wen, J., 1991. Kinetic study of non-mass-dependant oxygen isotope effects in gas phase reactions and applications for nature. Ph. D. dissertation, University of California, San Diego.

Werner, R.A. and Brand, W.A., 2001. Referencing strategies and techniques in stable isotope ratio analysis, Rapid Communications in Mass Spectrometry, vol. 15, pp. 501-519.

White, W. M., 1997. Geochemistry. John-Hopkins University Press, 698pp.

Whiticar, M.J. and Snowdon, L.R., 1999. Geochemical characterization of selected western Canada oils by $C_5$-$C_8$ Compound Specific Isotope Correlation (CSIC). Organic Geochemistry, vol.30, pp.1127-1161.

Woulé Ebongué, V., Geypens B., Berglund M., Taylor P., (2009a) Headspace Solid Phase Micro Extraction .GC/C-IRMS for d13CVPDB measurements of mono-aromatic hydrocarbons using EA-IRMS calibration, Isotopes in Environmental and Health Studies. Vol 45 (1), pp 53-58.

Zhang, Z. and Pawliszyn, J., 1993a. Headspace Solid Phase MicroExtraction. Analytical Chemistry, vol.65, pp. 1843-1852.

Zhang, Z. and Pawliszyn, J., 1993b. Analysis of organic compounds in environmental samples using headspace Solid Phase Micro Extraction. Journal of High Resolution Chromatography, vol.16, pp. 689-692.

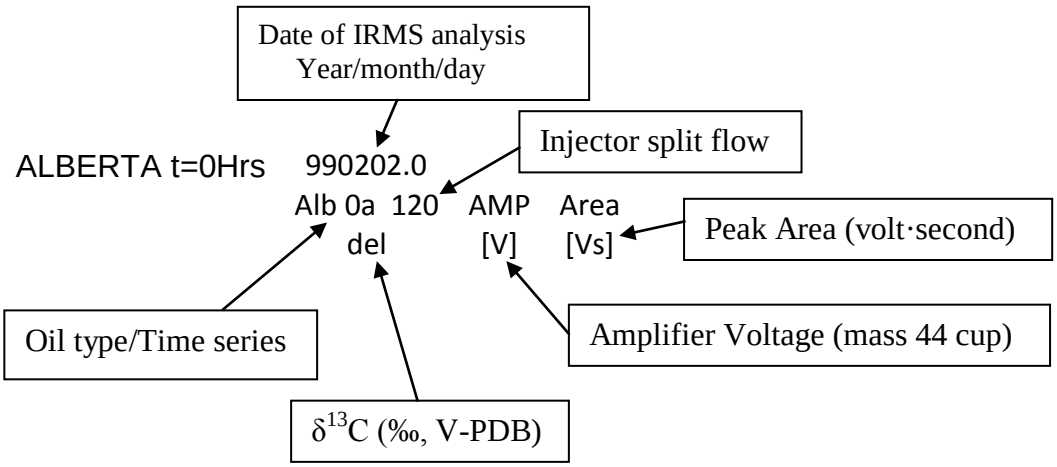
Zhang, Z., Yang, M. and Pawliszyn, J., 1994. Solid Phase Micro Extraction: A new solvent-free alternative for sample preparation. Analytical Chemistry, vol.66, pp. 844A-853A.

Zang, G., Liu, G., Chen, F. and Peng, X., 2004. Stable carbon and hydrogen isotopic fractionations of alkane compounds and crude oil during aerobically microbial degradation. Chinese Science Bulletin, vol. 49, issue 24, pp. 2620-2626.

# APPENDIX A

Appendix A contains the raw IRMS output data for all time series periods for all three study oils.

Each time period consisted of typically 3 IRMS runs. The labels for the data columns used in this study are explained as follows:



| ALBERTA t=0Hrs | | 990202.0 | | | 990202.0 | | | 990202.0 | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Alb 0a 120 del | AMP [V] | Area [Vs] | Alb 0b 120 del | AMP [V] | Area [Vs] | Alb 0c 120 del | AMP [V] | Area [Vs] |
| number | Compound | | | | | | | | | |
| 1 | iC5 | -28.7 | 6.2 | 20.5 | -28.5 | 6.2 | 20.4 | -28.4 | 6.3 | 20.5 |
| 2 | nC5 | -29.1 | 7.8 | 24.9 | -29.0 | 7.8 | 24.6 | -29.4 | 7.8 | 24.5 |
| 3 | 22DMC4 | -30.6 | 0.1 | 0.4 | | | | | | |
| 4 | CYC5 | -27.9 | 0.9 | 4.6 | | | | | | |
| 5 | 23DMC4 | | | | -27.7 | 0.9 | 4.6 | -28.1 | 0.7 | 3.4 |
| 6 | 2MC5 | -28.6 | 4.0 | 14.1 | -28.5 | 3.9 | 14.0 | -28.4 | 3.9 | 13.4 |
| 7 | 3MC5 | -27.5 | 2.5 | 8.9 | -27.5 | 2.4 | 8.8 | -27.4 | 2.1 | 8.6 |
| 8 | nC6 | -29.9 | 6.6 | 22.6 | -29.7 | 6.4 | 22.2 | -30.1 | 6.6 | 22.4 |
| 9 | 22DMC5 | -26.2 | 0.1 | 0.4 | | | | | | |
| 10 | MCYC5 | -26.3 | 4.0 | 14.1 | -26.3 | 3.9 | 13.9 | -26.4 | 3.7 | 13.2 |
| 11 | 24DMc5 | -31.8 | 0.3 | 1.2 | | | | | | |
| 12 | 223TMC4 | | | | | | | | | |
| 13 | Benzene | -29.8 | 1.4 | 5.1 | -29.9 | 1.3 | 5.0 | -29.7 | 1.2 | 4.9 |
| 14 | 33DMC5 | | | | | | | | | |
| 15 | CYC6 | -29.8 | 2.8 | 10.7 | -29.9 | 2.7 | 10.6 | -29.6 | 2.8 | 10.6 |
| 16 | 2MC6 | -28.2 | 1.7 | 6.3 | -28.1 | 1.6 | 6.2 | -27.6 | 1.7 | 6.2 |
| 17 | 23DMC5 | -30.8 | 0.7 | 2.7 | -30.7 | 0.7 | 2.7 | -30.4 | 0.7 | 3.0 |
| 18 | 11DMCYC5 | -27.6 | 0.5 | 2.2 | -27.0 | 0.5 | 2.1 | -27.3 | 0.5 | 2.1 |
| 19 | 3McC6 | -28.2 | 2.1 | 8.2 | -28.0 | 2.1 | 8.0 | -27.8 | 2.1 | 8.0 |
| 20 | 1c3DMCYC5 | -25.5 | 1.4 | 5.4 | -25.7 | 1.4 | 5.3 | -25.2 | 1.3 | 5.4 |
| 21 | 1t3DMCYC5 | -25.0 | 1.3 | 5.7 | -25.2 | 1.3 | 5.6 | -25.4 | 1.3 | 5.6 |
| 22 | 1t2DMCYC5 | -25.9 | 2.4 | 9.8 | -25.9 | 2.3 | 9.7 | -25.8 | 3.7 | 9.7 |
| 23 | nC7 | -29.8 | 5.4 | 20.3 | -30.0 | 5.2 | 19.8 | -30.4 | 5.2 | 19.9 |
| 24 | 22DMC6 | | | | | | | | | |
| 25 | MCYC6 | -28.1 | 5.1 | 22.0 | -27.8 | 5.0 | 21.6 | -27.7 | 5.0 | 21.4 |
| 26 | 1c2DMCYC5 | -30.7 | 0.7 | 3.4 | -30.5 | 0.7 | 3.3 | -30.4 | 0.6 | 3.3 |
| 27 | EtCYC5 | -27.5 | 0.7 | 3.0 | -27.3 | 0.7 | 3.0 | -27.6 | 0.8 | 2.7 |
| 28 | 25DMC6 | -32.2 | 0.3 | 1.2 | -31.5 | 0.3 | 1.2 | -30.7 | 0.2 | 1.2 |
| 29 | 24DMC6 | -26.9 | 0.8 | 3.7 | -26.7 | 0.8 | 3.6 | -27.0 | 8.0 | 3.7 |
| 30 | 1t2c4TMCYC5 | -26.1 | 1.0 | 4.1 | -26.4 | 1.0 | 4.0 | -26.5 | 1.0 | 4.3 |
| 31 | 33DMC6 | | | | | | | | | |
| 32 | 1t2c3TMCYC5 | | | | | | | | | |
| 33 | 223TMCYC6 | | | | | | | | | |
| 34 | Toluene | -29.6 | 3.2 | 13.5 | -29.7 | 3.1 | 13.3 | -29.6 | 3.2 | 13.3 |
| 35 | 2MC7 | -28.1 | 2.2 | 9.1 | -27.9 | 2.2 | 8.9 | -28.0 | 2.3 | 9.0 |
| 36 | 3MC7 | -26.4 | 1.3 | 6.9 | -26.3 | 1.3 | 6.7 | -26.8 | 1.3 | 6.8 |
| 37 | 1c4DMCYC6 | -28.4 | 0.7 | 3.1 | -28.3 | 0.7 | 3.0 | -28.3 | 0.8 | 3.0 |
| 38 | nC8 | -29.8 | 3.9 | 16.4 | -29.5 | 3.1 | 15.5 | -29.2 | 3.4 | 16.0 |
| 39 | nC9 | -30.2 | 3.2 | 15.1 | -30.1 | 3.0 | 14.2 | -29.8 | 3.0 | 14.8 |

| ALBERTA 0.5 Hrs | | 990202.0 | | | 990202.0 | | | 990205.0 | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Alb 0.5a 80 del | AMP [V] | Area [Vs] | Alb 0.5b 80 del | AMP [V] | Area [Vs] | Alb 0.5c 80 del | AMP [V] | Area [Vs] |
| number | Compound | | | | | | | | | |
| 1 | iC5 | -28.4 | 2.1 | 6.7 | -28.2 | 3.0 | 9.8 | -28.4 | 3.5 | 11.2 |
| 2 | nC5 | -28.8 | 2.7 | 8.3 | -28.8 | 3.9 | 12.3 | -29.2 | 4.5 | 14.0 |
| 3 | 22DMC4 | | | | | | | | | |
| 4 | CYC5 | | | | | | | | | |
| 5 | 23DMC4 | -27.5 | 0.4 | 2.1 | -27.5 | 0.6 | 3.2 | -28.1 | 0.7 | 3.5 |
| 6 | 2MC5 | -28.5 | 1.9 | 6.9 | -28.4 | 2.9 | 10.2 | -28.4 | 3.2 | 11.4 |
| 7 | 3MC5 | -27.5 | 1.3 | 4.6 | -27.5 | 1.9 | 6.7 | -27.4 | 2.1 | 7.4 |
| 8 | nC6 | -29.8 | 3.4 | 11.8 | -29.6 | 5.1 | 17.4 | -30.1 | 5.6 | 19.4 |
| 9 | 22DMC5 | | | | | | | | | |
| 10 | MCYC5 | -26.8 | 2.3 | 8.2 | -26.3 | 3.4 | 12.0 | -26.4 | 3.7 | 13.2 |
| 11 | 24DMc5 | | | | | | | | | |
| 12 | 223TMC4 | | | | | | | | | |
| 13 | Benzene | -29.5 | 0.8 | 2.9 | -29.4 | 1.1 | 4.3 | -29.7 | 1.2 | 4.6 |
| 14 | 33DMC5 | | | | | | | | | |
| 15 | CYC6 | -30.0 | 1.7 | 7.0 | -29.7 | 2.6 | 10.1 | -29.6 | 2.8 | 11.1 |
| 16 | 2MC6 | -27.9 | 1.1 | 4.3 | -27.8 | 1.7 | 6.3 | -27.6 | 1.8 | 6.8 |
| 17 | 23DMC5 | -30.9 | 0.5 | 1.9 | -30.6 | 0.7 | 2.8 | -30.4 | 0.7 | 3.0 |
| 18 | 11DMCYC5 | -27.5 | 0.4 | 1.5 | -27.1 | 0.6 | 2.2 | -27.3 | 0.6 | 2.4 |
| 19 | 3McC6 | -28.0 | 1.5 | 5.6 | -27.5 | 2.2 | 8.3 | -27.8 | 2.3 | 9.0 |
| 20 | 1c3DMCYC5 | -25.7 | 1.0 | 3.7 | -25.5 | 1.4 | 5.5 | -25.2 | 1.5 | 5.9 |
| 21 | 1t3DMCYC5 | -25.3 | 0.9 | 4.0 | -25.0 | 1.3 | 5.9 | -25.4 | 1.4 | 6.4 |
| 22 | 1t2DMCYC5 | -25.8 | 1.7 | 7.1 | -25.6 | 2.5 | 10.2 | -25.8 | 2.7 | 11.1 |
| 23 | nC7 | -29.8 | 3.8 | 14.6 | -29.5 | 5.6 | 21.4 | -30.4 | 6.1 | 23.9 |
| 24 | 22DMC6 | | | | | | | | | |
| 25 | MCYC6 | -28.0 | 3.8 | 16.8 | -27.3 | 5.7 | 24.3 | -27.7 | 6.0 | 26.2 |
| 26 | 1c2DMCYC5 | -29.9 | 0.5 | 2.6 | -29.9 | 0.8 | 3.8 | -30.4 | 0.8 | 4.2 |
| 27 | EtCYC5 | -27.7 | 0.6 | 2.3 | -27.5 | 0.8 | 3.4 | -27.6 | 0.9 | 3.7 |
| 28 | 25DMC6 | -31.6 | 0.2 | 1.0 | -32.1 | 0.3 | 1.4 | -30.7 | 0.3 | 1.5 |
| 29 | 24DMC6 | -27.4 | 0.6 | 3.0 | -27.0 | 0.9 | 4.3 | -27.0 | 1.0 | 4.7 |
| 30 | 1t2c4TMCYC5 | -27.6 | 0.8 | 3.3 | -25.9 | 1.2 | 4.8 | -26.5 | 1.2 | 5.3 |
| 31 | 33DMC6 | | | | | | | | | |
| 32 | 1t2c3TMCYC5 | | | | | | | | | |
| 33 | 223TMCYC6 | | | | | | | | | |
| 34 | Toluene | -29.8 | 2.5 | 10.5 | -29.1 | 3.6 | 15.1 | -29.6 | 3.9 | 16.3 |
| 35 | 2MC7 | -27.9 | 1.9 | 7.7 | -27.4 | 2.7 | 10.9 | -28.0 | 3.0 | 12.2 |
| 36 | 3MC7 | -26.6 | 1.1 | 5.8 | -25.9 | 1.6 | 8.4 | -26.8 | 1.8 | 9.2 |
| 37 | 1c4DMCYC6 | -29.4 | 0.6 | 2.8 | -27.8 | 0.9 | 3.9 | -28.3 | 1.0 | 4.2 |
| 38 | nC8 | -29.8 | 3.5 | 14.2 | -29.1 | 5.0 | 20.5 | -29.2 | 5.4 | 23.0 |
| 39 | nC9 | -30.5 | 3.1 | 14.6 | -29.7 | 4.5 | 21.2 | -29.8 | 5.0 | 24.0 |

| ALBERTA 1 Hrs | | 990205.0 | | | 990205.0 | | | 990205.0 | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Alb 1.0a 40 del | AMP [V] | Area [Vs] | Alb 1.0b 50 del | AMP [V] | Area [Vs] | Alb 1.0c 50 del | AMP [V] | Area [Vs] |
| number | Compound | | | | | | | | | |
| 1 | iC5 | -28.5 | 4.2 | 13.6 | -28.5 | 3.3 | 10.4 | -28.0 | 2.6 | 8.3 |
| 2 | nC5 | -29.0 | 5.4 | 16.8 | -28.8 | 4.2 | 13.0 | -28.7 | 3.4 | 10.6 |
| 3 | 22DMC4 | | | | | | | | | |
| 4 | CYC5 | | | | | | | | | |
| 5 | 23DMC4 | -27.8 | 0.9 | 4.7 | -27.7 | 0.7 | 3.8 | -27.6 | 0.6 | 3.4 |
| 6 | 2MC5 | -28.4 | 4.3 | 15.2 | -28.5 | 3.5 | 12.4 | -28.1 | 3.2 | 11.2 |
| 7 | 3MC5 | -27.3 | 2.8 | 10.2 | -27.5 | 2.3 | 8.3 | -27.1 | 2.1 | 7.6 |
| 8 | nC6 | -29.5 | 7.5 | 25.9 | -29.9 | 6.3 | 21.4 | -29.3 | 5.8 | 20.0 |
| 9 | 22DMC5 | | | | | | | | | |
| 10 | MCYC5 | -26.2 | 5.2 | 18.6 | -26.6 | 4.3 | 15.3 | -26.1 | 4.1 | 14.5 |
| 11 | 24DMc5 | | | | | | | | | |
| 12 | 223TMC4 | | | | | | | | | |
| 13 | Benzene | -29.7 | 1.6 | 6.2 | -29.9 | 1.4 | 5.2 | -29.5 | 1.3 | 4.9 |
| 14 | 33DMC5 | | | | | | | | | |
| 15 | CYC6 | -29.7 | 4.1 | 16.2 | -29.9 | 3.4 | 13.5 | -29.6 | 3.3 | 13.0 |
| 16 | 2MC6 | -27.8 | 2.6 | 9.9 | -27.9 | 2.2 | 8.4 | -28.0 | 2.1 | 8.2 |
| 17 | 23DMC5 | -30.7 | 1.1 | 4.4 | -30.6 | 0.9 | 3.7 | -30.7 | 0.9 | 3.7 |
| 18 | 11DMCYC5 | -27.1 | 0.9 | 3.6 | -27.1 | 0.7 | 3.0 | -27.4 | 0.7 | 3.0 |
| 19 | 3MC6 | -27.9 | 3.4 | 13.2 | -27.7 | 2.9 | 11.1 | -27.7 | 2.8 | 10.9 |
| 20 | 1c3DMCYC5 | -25.2 | 2.2 | 8.7 | -25.6 | 1.9 | 7.3 | -25.4 | 1.8 | 7.2 |
| 21 | 1t3DMCYC5 | -25.1 | 2.1 | 9.4 | -25.5 | 1.8 | 7.9 | -25.0 | 1.7 | 7.8 |
| 22 | 1t2DMCYC5 | -25.7 | 4.1 | 16.5 | -26.2 | 3.4 | 13.9 | -25.8 | 3.3 | 13.7 |
| 23 | nC7 | -28.7 | 8.6 | 34.8 | -30.3 | 7.5 | 29.9 | -29.9 | 7.4 | 29.7 |
| 24 | 22DMC6 | | | | | | | | | |
| 25 | MCYC6 | -26.1 | 8.9 | 39.5 | -27.7 | 7.7 | 33.5 | -27.3 | 7.6 | 33.3 |
| 26 | 1c2DMCYC5 | -30.2 | 1.3 | 6.5 | -30.5 | 1.1 | 5.4 | -30.2 | 1.1 | 5.5 |
| 27 | EtCYC5 | -27.1 | 1.3 | 5.6 | -27.3 | 1.1 | 4.8 | -27.1 | 1.1 | 4.8 |
| 28 | 25DMC6 | -31.6 | 0.5 | 2.3 | -32.0 | 0.5 | 2.0 | -31.2 | 0.4 | 2.0 |
| 29 | 24DMC6 | -27.1 | 1.6 | 7.3 | -27.2 | 1.3 | 6.1 | -26.8 | 1.3 | 6.1 |
| 30 | 1t2c4TMCYC5 | -26.8 | 1.9 | 8.1 | -27.1 | 1.6 | 6.8 | -26.9 | 1.6 | 6.8 |
| 31 | 33DMC6 | | | | | | | | | |
| 32 | 1t2c3TMCYC5 | | | | | | | | | |
| 33 | 223TMCYC6 | | | | | | | | | |
| 34 | Toluene | -30.3 | 5.8 | 23.9 | -29.7 | 5.0 | 21.0 | -29.4 | 5.0 | 21.1 |
| 35 | 2MC7 | -27.9 | 4.5 | 18.7 | -28.0 | 3.9 | 16.3 | -27.4 | 3.9 | 16.1 |
| 36 | 3MC7 | -26.4 | 2.7 | 14.4 | -26.6 | 2.4 | 12.5 | -26.5 | 2.4 | 12.3 |
| 37 | 1c4DMCYC6 | -27.9 | 1.6 | 6.8 | -28.1 | 1.3 | 5.7 | -28.2 | 1.3 | 5.8 |
| 38 | nC8 | -28.2 | 8.1 | 35.7 | -29.2 | 7.1 | 30.3 | -29.1 | 7.2 | 31.1 |
| 39 | nC9 | | | | -29.9 | 6.7 | 33.5 | -29.6 | 6.7 | 33.9 |

| ALBERTA 2 Hrs | | 990205.0 Alb 2a(2).30 | AMP | Area | 990205.0 Alb 2b 40 | AMP | Area | 990206.0 Alb 2c 40 | AMP | Area |
|---|---|---|---|---|---|---|---|---|---|---|
| | | del | [V] | [Vs] | del | [V] | [Vs] | del | [V] | [Vs] |
| number | Compound | | | | | | | | | |
| 1 | iC5 | -28.2 | 4.0 | 12.5 | -28.0 | 2.2 | 6.9 | -28.2 | 2.0 | 6.5 |
| 2 | nC5 | -28.7 | 4.3 | 13.2 | -28.5 | 2.5 | 7.6 | -28.6 | 2.0 | 6.4 |
| 3 | 22DMC4 | | | | | | | | | |
| 4 | CYC5 | | | | | | | | | |
| 5 | 23DMC4 | -27.5 | 0.7 | 3.9 | -27.6 | 0.5 | 2.5 | -27.6 | 0.3 | 2.0 |
| 6 | 2MC5 | -28.1 | 3.5 | 12.5 | -28.1 | 2.3 | 8.2 | -28.4 | 1.7 | 6.3 |
| 7 | 3MC5 | -27.1 | 2.3 | 8.3 | -26.9 | 1.6 | 5.6 | -26.9 | 1.2 | 4.2 |
| 8 | nC6 | -29.5 | 5.9 | 20.2 | -29.3 | 4.0 | 13.9 | -29.6 | 2.8 | 9.9 |
| 9 | 22DMC5 | | | | | | | | | |
| 10 | MCYC5 | -26.1 | 4.4 | 15.7 | -25.9 | 3.1 | 11.0 | -26.4 | 2.2 | 8.0 |
| 11 | 24DMc5 | | | | | | | | | |
| 12 | 223TMC4 | | | | | | | | | |
| 13 | Benzene | -29.4 | 1.4 | 5.2 | -29.5 | 1.0 | 3.6 | -29.5 | 0.6 | 2.5 |
| 14 | 33DMC5 | | | | | | | | | |
| 15 | CYC6 | -29.5 | 3.7 | 14.6 | -29.5 | 2.7 | 10.7 | -29.6 | 1.9 | 7.7 |
| 16 | 2MC6 | -27.4 | 2.3 | 9.0 | -27.3 | 1.8 | 6.7 | -27.5 | 1.2 | 4.7 |
| 17 | 23DMC5 | -30.7 | 1.0 | 4.1 | -30.5 | 0.8 | 3.1 | -30.7 | 0.5 | 2.2 |
| 18 | 11DMCYC5 | -27.2 | 0.8 | 3.4 | -26.7 | 0.6 | 2.6 | -27.4 | 0.5 | 1.9 |
| 19 | 3McC6 | -27.6 | 3.1 | 12.2 | -27.4 | 2.3 | 9.2 | -27.7 | 1.6 | 6.4 |
| 20 | 1c3DMCYC5 | -25.0 | 2.0 | 8.0 | -25.1 | 1.5 | 6.0 | -25.4 | 1.1 | 4.2 |
| 21 | 1t3DMCYC5 | -24.9 | 2.0 | 8.7 | -24.6 | 1.5 | 6.6 | -24.9 | 1.0 | 4.7 |
| 22 | 1t2DMCYC5 | -25.7 | 3.8 | 15.7 | -25.3 | 2.9 | 11.8 | -25.7 | 2.0 | 8.5 |
| 23 | nC7 | -29.2 | 8.2 | 33.2 | -29.8 | 6.5 | 25.8 | -30.2 | 4.4 | 17.8 |
| 24 | 22DMC6 | | | | | | | | | |
| 25 | MCYC6 | -25.7 | 8.9 | 39.2 | -27.4 | 6.9 | 30.4 | -27.4 | 5.0 | 22.0 |
| 26 | 1c2DMCYC5 | -29.8 | 1.3 | 6.6 | -30.2 | 1.0 | 5.2 | -30.3 | 0.7 | 3.8 |
| 27 | EtCYC5 | -26.7 | 1.4 | 5.7 | -27.2 | 1.1 | 4.4 | -27.5 | 0.7 | 3.2 |
| 28 | 25DMC6 | -30.9 | 0.5 | 2.5 | -31.3 | 0.4 | 1.9 | -31.9 | 0.3 | 1.4 |
| 29 | 24DMC6 | -26.4 | 1.6 | 7.6 | -26.6 | 1.3 | 5.9 | -27.0 | 0.9 | 4.3 |
| 30 | 1t2c4TMCYC5 | -26.4 | 2.0 | 8.5 | -26.5 | 1.6 | 6.7 | -26.3 | 1.2 | 5.0 |
| 31 | 33DMC6 | | | | | | | | | |
| 32 | 1t2c3TMCYC5 | | | | | | | | | |
| 33 | 223TMCYC6 | | | | | | | | | |
| 34 | Toluene | -28.9 | 5.9 | 25.3 | -29.1 | 4.7 | 19.9 | -29.4 | 3.3 | 14.1 |
| 35 | 2MC7 | -27.4 | 4.9 | 21.0 | -27.1 | 4.0 | 16.4 | -27.6 | 3.0 | 12.2 |
| 36 | 3MC7 | -26.3 | 3.0 | 16.0 | -26.0 | 2.4 | 12.8 | -26.4 | 1.8 | 9.7 |
| 37 | 1c4DMCYC6 | -27.4 | 1.8 | 7.7 | -27.5 | 1.4 | 6.2 | -27.7 | 1.1 | 4.8 |
| 38 | nC8 | -26.6 | 9.0 | 40.9 | -28.5 | 7.6 | 33.4 | -28.7 | 6.1 | 26.3 |
| 39 | nC9 | -26.6 | 9.3 | 50.1 | -28.5 | 8.0 | 41.5 | -29.3 | 7.1 | 36.3 |

| ALBERTA 3 Hrs | | 990226.0 | | | 990226.0 | | | 990226.0 | | |
|---|---|---|---|---|---|---|---|---|---|---|
| number | Compound | Alb 3a 15 del | AMP [V] | Area [Vs] | Alb 3b 30 del | AMP [V] | Area [Vs] | Alb 3c 30 del | AMP [V] | Area [Vs] |
| 1 | iC5 | -28.0 | 3.4 | 11.1 | -27.6 | 0.9 | 2.7 | -27.7 | 1.1 | 3.2 |
| 2 | nC5 | -28.5 | 3.8 | 11.6 | -27.7 | 1.0 | 2.8 | -28.0 | 1.2 | 3.3 |
| 3 | 22DMC4 | | | | | | | | | |
| 4 | CYC5 | | | | | | | | | |
| 5 | 23DMC4 | -27.6 | 0.8 | 4.0 | -26.7 | 0.3 | 1.3 | -27.2 | 0.3 | 1.4 |
| 6 | 2MC5 | -27.9 | 3.6 | 12.3 | -27.7 | 1.2 | 4.1 | -27.8 | 1.3 | 4.5 |
| 7 | 3MC5 | -27.2 | 2.4 | 8.6 | -26.6 | 0.9 | 3.0 | -26.8 | 0.9 | 3.2 |
| 8 | nC6 | -29.5 | 5.6 | 19.9 | -28.9 | 2.0 | 7.0 | -28.9 | 2.1 | 7.5 |
| 9 | 22DMC5 | | | | | | | | | |
| 10 | MCYC5 | -26.1 | 4.7 | 16.4 | -26.1 | 1.8 | 6.5 | -25.9 | 1.9 | 6.8 |
| 11 | 24DMc5 | | | | | | | | | |
| 12 | 223TMC4 | | | | | | | | | |
| 13 | Benzene | -29.1 | 1.3 | 4.9 | -29.0 | 0.5 | 2.0 | -28.9 | 0.5 | 2.0 |
| 14 | 33DMC5 | | | | | | | | | |
| 15 | CYC6 | -29.7 | 4.1 | 15.7 | -29.8 | 1.7 | 6.7 | -30.1 | 1.8 | 7.1 |
| 16 | 2MC6 | -28.5 | 2.4 | 9.3 | -27.3 | 1.1 | 4.3 | -27.1 | 1.1 | 4.3 |
| 17 | 23DMC5 | -28.5 | 1.1 | 4.7 | -30.9 | 0.5 | 2.1 | -31.0 | 0.5 | 2.2 |
| 18 | 11DMCYC5 | -27.0 | 0.9 | 3.9 | -27.6 | 0.5 | 1.8 | -27.7 | 0.5 | 1.8 |
| 19 | 3McC6 | -27.6 | 3.3 | 12.9 | -27.3 | 1.5 | 6.0 | -27.5 | 1.5 | 6.1 |
| 20 | 1c3DMCYC5 | -24.8 | 2.2 | 8.5 | -25.0 | 1.0 | 3.9 | -25.0 | 1.0 | 4.0 |
| 21 | 1t3DMCYC5 | -25.7 | 2.1 | 9.2 | -24.9 | 1.0 | 4.4 | -24.5 | 1.0 | 4.5 |
| 22 | 1t2DMCYC5 | -25.1 | 4.3 | 17.2 | -25.4 | 1.9 | 8.1 | -25.5 | 2.0 | 8.3 |
| 23 | nC7 | -29.5 | 8.4 | 33.4 | -30.1 | 4.2 | 17.0 | -30.1 | 4.1 | 16.9 |
| 24 | 22DMC6 | | | | | | | | | |
| 25 | MCYC6 | -26.5 | 9.6 | 43.0 | -27.9 | 5.1 | 22.5 | -27.9 | 5.1 | 22.1 |
| 26 | 1c2DMCYC5 | -26.3 | 1.5 | 7.4 | -29.3 | 0.8 | 3.7 | -28.7 | 0.7 | 3.8 |
| 27 | EtCYC5 | -26.9 | 1.5 | 6.2 | -26.8 | 0.8 | 3.3 | -26.9 | 0.7 | 3.2 |
| 28 | 25DMC6 | -31.1 | 0.6 | 2.8 | -31.3 | 0.3 | 1.5 | -31.8 | 0.3 | 1.5 |
| 29 | 24DMC6 | -26.5 | 1.8 | 8.6 | -26.3 | 1.0 | 4.6 | -26.5 | 0.9 | 4.5 |
| 30 | 1t2c4TMCYC5 | -27.0 | 2.4 | 9.9 | -26.0 | 1.3 | 5.4 | -26.0 | 1.2 | 5.2 |
| 31 | 33DMC6 | | | | | | | | | |
| 32 | 1t2c3TMCYC5 | | | | | | | | | |
| 33 | 223TMCYC6 | | | | | | | | | |
| 34 | Toluene | -29.2 | 6.0 | 25.6 | -29.1 | 3.3 | 14.3 | -29.1 | 3.1 | 13.7 |
| 35 | 2MC7 | -28.4 | 5.4 | 23.7 | -27.7 | 3.1 | 13.1 | -27.8 | 3.0 | 12.4 |
| 36 | 3MC7 | -26.5 | 3.5 | 19.2 | -26.7 | 2.0 | 10.6 | -26.9 | 1.9 | 10.1 |
| 37 | 1c4DMCYC6 | -27.4 | 2.2 | 9.9 | -27.4 | 1.2 | 5.3 | -27.8 | 1.1 | 5.1 |
| 38 | nC8 | -34.0 | 10.2 | 48.2 | -29.3 | 6.5 | 28.5 | -29.5 | 6.2 | 26.6 |
| 39 | nC9 | -61.9 | 10.7 | 69.5 | -29.3 | 8.0 | 42.0 | -29.3 | 7.7 | 40.2 |

| ALBERTA 4 Hrs | | 990227.0 | | | 990227.0 | | | 990227.0 | | | 990523.0 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| number | Compound | Alb 4a 15 del | AMP [V] | Area [Vs] | Alb 4b 20 del | AMP [V] | Area [Vs] | Alb 4c del | AMP [V] | Area [Vs] | Alb 4d del | AMP [V] | Area [Vs] |
| 1 | iC5 | -27.8 | 1.5 | 5.0 | -27.6 | 0.9 | 2.7 | -27.6 | 0.9 | 2.6 | -29.1 | 0.2 | 0.5 |
| 2 | nC5 | -28.0 | 1.7 | 5.6 | -27.9 | 1.0 | 3.2 | -27.8 | 1.0 | 3.1 | -27.8 | 0.2 | 0.6 |
| 3 | 22DMC4 | | | | | | | | | | | | |
| 4 | CYC5 | | | | | | | | | | | | |
| 5 | 23DMC4 | -27.3 | 0.5 | 2.6 | -27.3 | 0.3 | 1.7 | -27.3 | 0.3 | 1.7 | | | |
| 6 | 2MC5 | -27.8 | 2.2 | 8.40.14 | -27.9 | 1.5 | 5.8 | -27.8 | 1.5 | 5.6 | -27.7 | 0.4 | 1.5 |
| 7 | 3MC5 | -27.0 | 1.5 | 6.0 | -27.0 | 1.1 | 4.3 | -27.0 | 1.1 | 4.1 | -28.0 | 0.3 | 1.1 |
| 8 | nC6 | -29.2 | 3.8 | 14.4 | -29.3 | 2.9 | 10.9 | -29.2 | 2.8 | 10.3 | -28.8 | 0.7 | 2.9 |
| 9 | 22DMC5 | | | | | | | | | | | | |
| 10 | MCYC5 | -26.3 | 3.3 | 12.8 | -26.0 | 2.6 | 9.8 | -25.7 | 2.6 | 9.4 | -26.5 | 0.7 | 2.8 |
| 11 | 24DMc5 | | | | | | | | | | | | |
| 12 | 223TMC4 | | | | | | | | | | | | |
| 13 | Benzene | -29.2 | 0.9 | 3.7 | -29.0 | 0.7 | 3.0 | -29.0 | 0.7 | 2.8 | -28.8 | 0.2 | 0.9 |
| 14 | 33DMC5 | | | | | | | | | | | | |
| 15 | CYC6 | -29.6 | 3.2 | 13.2 | -29.8 | 2.6 | 10.5 | -29.5 | 2.5 | 10.0 | -29.4 | 0.8 | 3.4 |
| 16 | 2MC6 | -28.4 | 1.9 | 7.4 | -28.0 | 1.6 | 6.4 | -27.8 | 1.5 | 6.0 | -27.4 | 0.5 | 2.1 |
| 17 | 23DMC5 | -27.4 | 0.9 | 4.2 | -29.2 | 0.8 | 3.4 | -29.2 | 0.7 | 3.2 | -31.3 | 0.3 | 1.1 |
| 18 | 11DMCYC5 | -27.3 | 0.8 | 3.4 | -27.3 | 0.7 | 2.8 | -27.6 | 0.6 | 2.7 | -27.8 | 0.2 | 1.0 |
| 19 | 3McC6 | -27.5 | 2.6 | 10.8 | -27.6 | 2.2 | 9.3 | -27.5 | 2.1 | 8.7 | -27.6 | 0.7 | 3.1 |
| 20 | 1c3DMCYC5 | -24.3 | 1.7 | 7.1 | -25.1 | 1.5 | 6.0 | -24.7 | 1.4 | 5.6 | -25.1 | 0.5 | 2.1 |
| 21 | 1t3DMCYC5 | -25.6 | 1.6 | 7.8 | -25.1 | 1.4 | 6.7 | -24.9 | 1.4 | 6.3 | -25.2 | 0.5 | 2.3 |
| 22 | 1t2DMCYC5 | -25.3 | 3.5 | 14.9 | -25.8 | 3.0 | 12.7 | -25.8 | 2.8 | 11.8 | -25.9 | 1.0 | 4.5 |
| 23 | nC7 | -30.3 | 6.7 | 28.0 | -30.4 | 6.2 | 25.7 | -29.9 | 5.7 | 23.5 | -30.2 | 2.0 | 9.1 |
| 24 | 22DMC6 | | | | | | | | | | | | |
| 25 | MCYC6 | -27.1 | 8.4 | 37.4 | -28.1 | 7.6 | 33.5 | -28.1 | 7.1 | 31.2 | -27.8 | 2.7 | 12.9 |
| 26 | 1c2DMCYC5 | -27.7 | 1.3 | 6.7 | -28.3 | 1.1 | 6.0 | -28.5 | 1.1 | 5.5 | -30.7 | 0.4 | 2.6 |
| 27 | EtCYC5 | -26.7 | 1.2 | 5.2 | -26.5 | 1.1 | 4.7 | -26.5 | 1.0 | 4.4 | -27.6 | 0.4 | 1.9 |
| 28 | 25DMC6 | -32.4 | 0.5 | 2.5 | -31.5 | 0.5 | 2.3 | -32.1 | 0.4 | 2.1 | -33.4 | 0.2 | 0.9 |
| 29 | 24DMC6 | -26.2 | 1.5 | 7.4 | -26.6 | 1.4 | 6.7 | -26.4 | 1.3 | 6.2 | -26.4 | 0.6 | 2.8 |
| 30 | 1t2c4TMCYC5 | -26.3 | 1.9 | 8.5 | -26.3 | 1.8 | 7.7 | -26.3 | 1.6 | 7.1 | -27.6 | 0.7 | 3.2 |
| 31 | 33DMC6 | | | | | | | | | | | | |
| 32 | 1t2c3TMCYC5 | | | | | | | | | | | | |
| 33 | 223TMCYC6 | | | | | | | | | | | | |
| 34 | Toluene | -28.9 | 4.7 | 21.4 | -30.0 | 4.6 | 19.9 | -29.9 | 4.1 | 18.1 | -29.2 | 1.8 | 8.0 |
| 35 | 2MC7 | -28.6 | 4.5 | 19.6 | -28.7 | 4.3 | 18.1 | -28.7 | 4.0 | 16.4 | -28.2 | 1.9 | 8.4 |
| 36 | 3MC7 | -26.2 | 2.9 | 16.3 | -26.7 | 2.8 | 15.1 | -26.1 | 2.5 | 13.8 | -29.9 | 1.3 | 10.1 |
| 37 | 1c4DMCYC6 | -27.6 | 1.7 | 4.6 | -27.2 | 1.6 | 7.4 | -27.6 | 1.5 | 6.8 | -30.7 | 0.8 | 3.7 |
| 38 | nC8 | -27.3 | 8.4 | 38.5 | -27.7 | 8.5 | 38.5 | -28.7 | 7.8 | 34.5 | -29.3 | 4.3 | 19.3 |
| 39 | nC9 | -29.4 | 9.9 | 55.4 | -33.7 | 10.1 | 56.9 | -29.9 | 9.3 | 50.8 | -30.1 | 7.0 | 36.5 |

| ALBERTA 6 Hrs | | 990301.0 | | | 990301.0 | | | 990301.0 | | |
|---|---|---|---|---|---|---|---|---|---|---|
| number | Compound | 1028.0 Alb 6a 10 del | AMP [V] | Area [Vs] | 1153.0 Alb 6b 10 del | AMP [V] | Area [Vs] | 1334.0 Alb 6c 8 del | AMP [V] | Area [Vs] |
| 1 | iC5 | -27.7 | 0.7 | 2.1 | -27.5 | 1.4 | 4.6 | -26.9 | 0.6 | 1.8 |
| 2 | nC5 | -27.9 | 0.7 | 2.4 | -27.6 | 1.4 | 4.6 | -27.2 | 0.6 | 2.0 |
| 3 | 22DMC4 | | | | | | | | | |
| 4 | CYC5 | | | | | | | | | |
| 5 | 23DMC4 | -26.9 | 0.3 | 1.6 | -26.9 | 0.4 | 2.6 | -26.5 | 0.3 | 1.6 |
| 6 | 2MC5 | -27.8 | 1.4 | 5.4 | -27.6 | 2.1 | 8.3 | -27.2 | 1.4 | 5.5 |
| 7 | 3MC5 | -26.9 | 1.0 | 4.2 | -26.7 | 1.6 | 6.1 | -26.6 | 1.1 | 4.3 |
| 8 | nC6 | -29.0 | 2.6 | 10.1 | -28.9 | 3.7 | 14.1 | -28.5 | 2.7 | 10.4 |
| 9 | 22DMC5 | | | | | | | | | |
| 10 | MCYC5 | -26.0 | 2.7 | 10.4 | -25.5 | 3.7 | 13.9 | -25.1 | 2.9 | 11.0 |
| 11 | 24DMc5 | | | | | | | | | |
| 12 | 223TMC4 | | | | | | | | | |
| 13 | Benzene | -29.0 | 0.7 | 3.0 | -28.6 | 0.9 | 3.8 | -28.6 | 0.8 | 3.1 |
| 14 | 33DMC5 | | | | | | | | | |
| 15 | CYC6 | -29.5 | 2.9 | 12.2 | -29.3 | 3.7 | 15.5 | -29.2 | 3.2 | 13.4 |
| 16 | 2MC6 | -28.4 | 1.8 | 7.2 | -27.6 | 2.2 | 8.8 | -27.1 | 2.0 | 7.9 |
| 17 | 23DMC5 | -27.7 | 0.9 | 4.1 | -28.4 | 1.1 | 4.9 | -29.5 | 1.0 | 4.3 |
| 18 | 11DMCYC5 | -27.0 | 0.8 | 3.5 | -27.1 | 1.0 | 4.2 | -26.7 | 0.9 | 3.8 |
| 19 | 3McC6 | -27.5 | 2.6 | 10.9 | -27.3 | 3.1 | 13.0 | -27.0 | 2.9 | 11.7 |
| 20 | 1c3DMCYC5 | -24.6 | 1.7 | 7.1 | -24.4 | 2.1 | 8.4 | -24.2 | 1.9 | 7.7 |
| 21 | 1t3DMCYC5 | -25.1 | 1.7 | 8.1 | -25.3 | 2.0 | 9.6 | -24.4 | 1.8 | 8.8 |
| 22 | 1t2DMCYC5 | -25.3 | 3.6 | 15.8 | -25.1 | 4.3 | 18.8 | -25.2 | 4.0 | 17.1 |
| 23 | nC7 | -30.2 | 7.0 | 30.0 | -29.5 | 8.0 | 33.9 | -29.9 | 7.5 | 31.8 |
| 24 | 22DMC6 | | | | | | | | | |
| 25 | MCYC6 | -26.1 | 9.3 | 42.3 | -45.8 | 10.6 | 48.6 | -32.4 | 10.1 | 45.8 |
| 26 | 1c2DMCYC5 | -27.4 | 1.5 | 7.8 | -29.0 | 1.7 | 9.0 | -29.7 | 1.7 | 8.5 |
| 27 | EtCYC5 | -26.6 | 1.3 | 5.9 | -26.1 | 1.5 | 6.7 | -26.1 | 1.4 | 6.4 |
| 28 | 25DMC6 | -30.8 | 0.6 | 2.9 | -30.8 | 0.7 | 3.3 | -31.4 | 0.7 | 3.2 |
| 29 | 24DMC6 | -26.5 | 1.7 | 8.6 | -26.1 | 2.0 | 9.9 | -26.3 | 1.9 | 9.4 |
| 30 | 1t2c4TMCYC5 | -25.7 | 2.3 | 10.1 | -25.1 | 2.7 | 11.7 | -24.9 | 2.6 | 11.2 |
| 31 | 33DMC6 | | | | | | | | | |
| 32 | 1t2c3TMCYC5 | | | | | | | | | |
| 33 | 223TMCYC6 | | | | | | | | | |
| 34 | Toluene | -29.4 | 5.4 | 23.5 | -28.7 | 5.9 | 26.4 | -28.7 | 5.7 | 25.2 |
| 35 | 2MC7 | -28.4 | 5.5 | 23.7 | -28.2 | 5.9 | 26.7 | -27.7 | 5.9 | 25.9 |
| 36 | 3MC7 | -26.1 | 3.6 | 20.2 | -26.2 | 4.0 | 22.5 | -26.5 | 4.0 | 22.3 |
| 37 | 1c4DMCYC6 | -27.6 | 2.3 | 10.1 | -28.0 | 2.5 | 11.2 | -27.3 | 2.5 | 10.9 |
| 38 | nC8 | -41.2 | 10.5 | 49.5 | -51.1 | 10.6 | 52.6 | -49.3 | 10.6 | 51.7 |
| 39 | nC9 | -71.8 | 10.7 | 76.3 | -73.6 | 10.7 | 78.0 | -74.8 | 10.7 | 79.4 |
| ALBERTA 8 Hrs | | 990313.0 | | | 990307.0 | | | 990307.0 | | |

| number | Compound | Alb 8a 13 del | AMP [V] | Area [Vs] | Alb 8b 0 del | AMP [V] | Area [Vs] | Alb 8c 0 del | AMP [V] | Area [Vs] | Alb 8d 10 del | AMP [V] | Area [Vs] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | iC5 | -26.9 | 0.6 | 2.3 | -27.2 | 0.4 | 1.6 | -26.4 | *.138 | 0.5 | -27.2 | 0.1 | 0.2 |
| 2 | nC5 | -27.5 | 0.6 | 2.2 | -27.3 | 0.4 | 1.6 | -26.8 | *.137 | 0.5 | -28.2 | 0.1 | 0.2 |
| 3 | 22DMC4 | | | | | | | | | | | | |
| 4 | CYC5 | | | | | | | | | | | | |
| 5 | 23DMC4 | -26.2 | 0.3 | 1.9 | -26.6 | 0.2 | 1.4 | | | | | | **0.2** |
| 6 | 2MC5 | -27.3 | 1.4 | 6.1 | -27.4 | 1.1 | 4.6 | -27.4 | 0.4 | 1.9 | -27.6 | 0.2 | 0.6 |
| 7 | 3MC5 | -26.4 | 1.1 | 4.9 | -26.4 | 0.9 | 3.8 | -26.5 | *.379 | 1.5 | -27.7 | 0.2 | 0.5 |
| 8 | nC6 | -28.1 | 2.7 | 11.1 | -28.1 | 2.0 | 8.6 | -28.0 | 0.9 | 3.8 | -28.5 | 0.4 | 1.3 |
| 9 | 22DMC5 | | | | | | | | | | | | |
| 10 | MCYC5 | -24.6 | 3.1 | 13.1 | -24.8 | 2.4 | 10.5 | -25.5 | 1.2 | 5.1 | -26.1 | 0.5 | 1.7 |
| 11 | 24DMc5 | | | | | | | | | | | | |
| 12 | 223TMC4 | | | | | | | | | | | | |
| 13 | Benzene | -28.2 | 0.8 | 3.8 | -28.2 | 0.7 | 3.0 | -28.0 | *.407 | 1.9 | -28.8 | 0.1 | 0.5 |
| 14 | 33DMC5 | | | | | | | | | | | | |
| 15 | CYC6 | -28.6 | 3.7 | 17.2 | -28.6 | 3.0 | 14.4 | -28.6 | 1.7 | 8.2 | -29.4 | 0.6 | 2.5 |
| 16 | 2MC6 | -24.6 | 2.3 | 10.6 | -26.3 | 1.9 | 8.6 | -25.2 | 1.2 | 5.1 | -26.5 | 0.4 | 1.6 |
| 17 | 23DMC5 | -32.1 | 1.2 | 6.1 | -28.6 | 1.0 | 5.4 | -31.1 | 0.6 | 3.1 | -30.8 | 0.2 | 0.9 |
| 18 | 11DMCYC5 | -26.7 | 1.1 | 5.3 | -26.7 | 0.9 | 4.8 | -26.5 | 0.6 | 2.8 | -27.0 | 0.2 | 0.8 |
| 19 | 3McC6 | -26.4 | 3.5 | 16.1 | -26.6 | 2.9 | 13.7 | -26.6 | 1.8 | 8.4 | -27.3 | 0.6 | 2.4 |
| 20 | 1c3DMCYC5 | -23.4 | 2.2 | 10.4 | -23.8 | 1.9 | 9.1 | -23.5 | 1.2 | 5.4 | -24.8 | 0.4 | 1.6 |
| 21 | 1t3DMCYC5 | -23.4 | 2.3 | 12.2 | -24.2 | 1.9 | 10.5 | -23.4 | 1.2 | 6.6 | -24.6 | 0.4 | 1.9 |
| 22 | 1t2DMCYC5 | -25.2 | 5.0 | 24.2 | -24.7 | 4.3 | 21.4 | -25.1 | 2.7 | 14.0 | -25.6 | 0.9 | 3.8 |
| 23 | nC7 | -28.9 | 9.6 | 43.7 | -28.3 | 8.0 | 37.5 | -28.9 | 5.7 | 26.8 | -29.8 | 1.8 | 7.4 |
| 24 | 22DMC6 | | | | | | | | | | | | |
| 25 | MCYC6 | -72.4 | 10.7 | 66.0 | -62.1 | 10.7 | 59.4 | -24.4 | 9.0 | 45.1 | -27.3 | 2.8 | 12.4 |
| 26 | 1c2DMCYC5 | -30.7 | 2.4 | 13.0 | -28.6 | 2.3 | 13.7 | -31.3 | 1.7 | 10.8 | -30.8 | 0.5 | 2.5 |
| 27 | EtCYC5 | -25.0 | 2.1 | 10.4 | -25.3 | 1.9 | 9.1 | -25.1 | 1.5 | 7.0 | -26.3 | 0.4 | 1.8 |
| 28 | 25DMC6 | -32.5 | 1.0 | 5.3 | -30.8 | 0.9 | 5.5 | -30.6 | 0.7 | 4.6 | -31.7 | 0.2 | 1.0 |
| 29 | 24DMC6 | -25.7 | 2.9 | 16.4 | -26.1 | 2.6 | 14.6 | -25.8 | 2.1 | 11.8 | -26.2 | 0.6 | 3.0 |
| 30 | 1t2c4TMCYC5 | -24.5 | 4.0 | 19.9 | -24.3 | 3.6 | 17.7 | -24.4 | 2.9 | 14.5 | -26.7 | 0.8 | 3.6 |
| 31 | 33DMC6 | | | | | | | | | | | | |
| 32 | 1t2c3TMCYC5 | | | | | | | | | | | | |
| 33 | 223TMCYC6 | | | | | | | | | | | | |
| 34 | Toluene | -27.3 | 8.0 | 38.8 | -28.0 | 7.3 | 35.3 | -27.9 | 6.0 | 30.2 | -28.4 | 1.7 | 7.6 |
| 35 | 2MC7 | -23.9 | 9.5 | 49.2 | -25.3 | 8.6 | 42.9 | -25.4 | 7.7 | 38.5 | -26.8 | 2.3 | 9.5 |
| 36 | 3MC7 | -25.1 | 6.7 | 43.7 | -24.7 | 6.2 | 39.8 | -25.1 | 5.6 | 36.1 | -26.1 | 1.6 | 8.7 |
| 37 | 1c4DMCYC6 | -26.6 | 4.7 | 24.7 | -26.9 | 4.4 | 22.7 | -26.8 | 4.0 | 21.5 | -27.6 | 1.1 | 4.7 |
| 38 | nC8 | -87.6 | 10.7 | 90.7 | -83.2 | 10.7 | 83.6 | | | | -28.0 | 5.7 | 23.7 |
| 39 | nC9 | | | | | | | | | | | | |

| ALBERTA 9 Hrs | | 990808.0 1704.0 | | | 990808.0 1513.0 | | |
|---|---|---|---|---|---|---|---|
| number | Compound | Alb 9a 0 del | AMP [V] | Area [Vs] | Alb 9a 0 del | AMP [V] | Area [Vs] |
| 1.0 | iC5 | -26.1 | 0.3 | 0.9 | -26.7 | 0.4 | 1.4 |
| 2.0 | nC5 | -27.9 | 0.3 | 0.9 | -26.5 | 0.4 | 1.5 |
| 3.0 | 22DMC4 | | | | | | |
| 4.0 | CYC5 | | | | | | |
| 5.0 | 23DMC4 | -27.8 | 0.7 | 2.8 | | | |
| 6.0 | 2MC5 | -26.6 | 0.5 | 2.2 | -27.9 | 1.0 | 4.5 |
| 7.0 | 3MC5 | -28.4 | 1.1 | 4.7 | -26.8 | 0.9 | 3.5 |
| 8.0 | nC6 | | | | -28.8 | 1.9 | 7.7 |
| 9.0 | 22DMC5 | | | | | | |
| 10.0 | MCYC5 | -25.7 | 1.3 | 5.7 | -25.4 | 2.2 | 9.1 |
| 11.0 | 24DMc5 | | | | | | |
| 12.0 | 223TMC4 | | | | | | |
| 13.0 | Benzene | -27.2 | 0.3 | 1.4 | -28.5 | 0.5 | 2.3 |
| 14.0 | 33DMC5 | | | | | | |
| 15.0 | CYC6 | -29.1 | 1.6 | 7.6 | -29.3 | 2.5 | 11.7 |
| 16.0 | 2MC6 | -25.4 | 1.0 | 4.4 | -25.8 | 1.5 | 7.0 |
| 17.0 | 23DMC5 | -31.5 | 0.5 | 2.6 | -30.9 | 0.8 | 4.0 |
| 18.0 | 11DMCYC5 | -27.2 | 0.5 | 2.3 | -27.4 | 0.7 | 3.7 |
| 19.0 | 3McC6 | -26.8 | 1.4 | 6.7 | -27.4 | 2.3 | 10.7 |
| 20.0 | 1c3DMCYC5 | -24.1 | 0.9 | 4.3 | -24.2 | 1.5 | 7.0 |
| 21.0 | 1t3DMCYC5 | -24.1 | 0.9 | 5.0 | -24.0 | 1.5 | 8.1 |
| 22.0 | 1t2DMCYC5 | -26.0 | 2.1 | 10.3 | -25.9 | 3.3 | 16.3 |
| 23.0 | nC7 | -29.6 | 3.7 | 17.4 | -29.8 | 5.6 | 27.2 |
| 24.0 | 22DMC6 | | | | | | |
| 25.0 | MCYC6 | -27.0 | 5.7 | 29.1 | -27.1 | 7.7 | 42.6 |
| 26.0 | 1c2DMCYC5 | -30.9 | 1.0 | 6.5 | -30.0 | 1.5 | 9.5 |
| 27.0 | EtCYC5 | -26.0 | 0.8 | 4.1 | -26.0 | 1.2 | 6.3 |
| 28.0 | 25DMC6 | -34.7 | 0.4 | 2.1 | -31.5 | 0.6 | 3.8 |
| 29.0 | 24DMC6 | -26.2 | 1.1 | 6.5 | -26.7 | 1.6 | 9.3 |
| 30.0 | 1t2c4TMCYC5 | -25.0 | 1.5 | 7.9 | -25.5 | 2.2 | 11.1 |
| 31.0 | 33DMC6 | | | | | | |
| 32.0 | 1t2c3TMCYC5 | | | | | | |
| 33.0 | 223TMCYC6 | | | | | | |
| 34.0 | Toluene | -28.4 | 2.7 | 14.3 | -29.1 | 4.1 | 21.3 |
| 35.0 | 2MC7 | -26.8 | 3.6 | 19.1 | -28.0 | 4.8 | 26.2 |
| 36.0 | 3MC7 | -28.6 | 2.6 | 26.6 | -28.5 | 3.4 | 35.8 |
| 37.0 | 1c4DMCYC6 | -27.4 | 1.8 | 9.7 | -28.2 | 2.3 | 12.6 |
| 38.0 | nC8 | -27.9 | 7.0 | 45.8 | -27.5 | 8.4 | 58.1 |
| 39.0 | nC9 | -33.4 | 10.5 | 107.5 | | | |

| ALBERTA 10 Hrs | | 990524.0 | | | 990524.0 | | | 990808.0 | | | 990813.0 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1830.0 | | | 2003.0 | | | 1843.0 | | | 955.0 | | |
| number | Compound | Alb 10a 0 | AMP | Area | Alb 10b 7 | AMP | Area | Alb 10c 0 | AMP | Area | Alb 10c 0 | AMP | Area |
| | | del | [V] | [Vs] | del | [V] | [Vs] | del | [V] | [Vs] | del | [V] | [Vs] |
| 1.0 | iC5 | -27.4 | 1.2 | 4.6 | -27.2 | 0.4 | 1.3 | -27.0 | 0.5 | 1.7 | -26.9 | 0.3 | 1.1 |
| 2.0 | nC5 | -27.4 | 1.1 | 4.4 | -27.3 | 0.4 | 1.3 | -27.4 | 0.5 | 1.6 | -28.1 | 0.2 | 0.9 |
| 3.0 | 22DMC4 | | | | | | | | | | | | |
| 4.0 | CYC5 | | | | | | | | | | | | |
| 5.0 | 23DMC4 | | | | | | | | | | | | |
| 6.0 | 2MC5 | -27.5 | 2.2 | 11.1 | -27.4 | 0.8 | 3.2 | -27.6 | 0.9 | 3.9 | -27.5 | 0.6 | 2.8 |
| 7.0 | 3MC5 | -26.3 | 1.7 | 9.1 | -26.8 | 0.6 | 2.5 | -26.6 | 0.7 | 3.0 | -27.2 | 0.5 | 2.2 |
| 8.0 | nC6 | -28.6 | 4.2 | 18.9 | -28.5 | 1.3 | 5.6 | -28.4 | 1.5 | 6.2 | -28.5 | 1.0 | 4.5 |
| 9.0 | 22DMC5 | | | | | | | | | | | | |
| 10.0 | MCYC5 | -25.4 | 4.7 | 22.1 | -25.4 | 1.5 | 6.3 | -25.0 | 1.7 | 7.2 | -26.6 | 1.3 | 5.8 |
| 11.0 | 24DMc5 | | | | | | | | | | | | |
| 12.0 | 223TMC4 | | | | | | | | | | | | |
| 13.0 | Benzene | -28.2 | 1.2 | 6.0 | -27.9 | 0.4 | 1.7 | -28.1 | 0.4 | 1.8 | -28.4 | 0.2 | 1.2 |
| 14.0 | 33DMC5 | | | | | | | | | | | | |
| 15.0 | CYC6 | -28.9 | 5.3 | 26.7 | -28.9 | 1.6 | 7.7 | -29.0 | 1.9 | 9.0 | -29.3 | 1.6 | 7.9 |
| 16.0 | 2MC6 | -28.3 | 2.8 | 14.2 | -26.3 | 1.0 | 4.5 | -25.2 | 1.1 | 5.2 | -25.1 | 0.9 | 4.3 |
| 17.0 | 23DMC5 | -30.2 | 1.7 | 9.6 | -30.0 | 0.5 | 2.5 | -31.5 | 0.6 | 3.1 | -32.0 | 0.6 | 2.7 |
| 18.0 | 11DMCYC5 | -29.8 | 1.3 | 8.3 | -26.9 | 0.5 | 2.3 | -27.0 | 0.6 | 2.8 | -27.2 | 0.5 | 2.4 |
| 19.0 | 3McC6 | -28.1 | 4.5 | 22.9 | -27.0 | 1.4 | 6.6 | -26.8 | 1.6 | 7.9 | -27.4 | 1.3 | 6.7 |
| 20.0 | 1c3DMCYC5 | -25.4 | 2.9 | 15.1 | -24.5 | 1.0 | 4.3 | -23.7 | 1.1 | 5.0 | -23.8 | 0.9 | 4.3 |
| 21.0 | 1t3DMCYC5 | -24.9 | 2.6 | 13.9 | -24.4 | 0.9 | 4.9 | -23.7 | 1.1 | 5.8 | -24.3 | 0.9 | 5.1 |
| 22.0 | 1t2DMCYC5 | -26.8 | 6.5 | 38.5 | -25.6 | 2.0 | 9.8 | -25.6 | 2.4 | 11.7 | -26.2 | 2.1 | 10.7 |
| 23.0 | nC7 | | 10.6 | | -29.5 | 3.8 | 16.6 | -29.5 | 4.1 | 19.7 | -29.9 | 3.5 | 16.6 |
| 24.0 | 22DMC6 | | | | | | | | | | | | |
| 25.0 | MCYC6 | | 10.7 | | -27.2 | 5.7 | 26.6 | -26.8 | 6.1 | 31.8 | -27.4 | 5.8 | 29.5 |
| 26.0 | 1c2DMCYC5 | -28.2 | 3.2 | 20.3 | -29.4 | 1.0 | 5.6 | -31.2 | 1.1 | 7.1 | -31.6 | 1.0 | 6.9 |
| 27.0 | EtCYC5 | -20.9 | 1.7 | 8.3 | -26.8 | 0.7 | 3.7 | -25.2 | 0.9 | 4.4 | -25.7 | 0.8 | 4.2 |
| 28.0 | 25DMC6 | -31.0 | 0.9 | 4.9 | -32.7 | 0.4 | 1.8 | -32.8 | 0.4 | 2.3 | -32.6 | 0.4 | 2.7 |
| 29.0 | 24DMC6 | -30.7 | 1.1 | 6.0 | -26.2 | 1.1 | 5.7 | -25.8 | 1.2 | 7.0 | -26.7 | 1.1 | 6.5 |
| 30.0 | 1t2c4TMCYC5 | -22.9 | 3.4 | 17.2 | -25.1 | 1.5 | 6.7 | -24.7 | 1.7 | 8.5 | -25.2 | 1.5 | 7.9 |
| 31.0 | 33DMC6 | | | | | | | | | | | | |
| 32.0 | 1t2c3TMCYC5 | | | | | | | | | | | | |
| 33.0 | 223TMCYC6 | | | | | | | | | | | | |
| 34.0 | Toluene | -24.1 | 4.5 | 25.0 | -28.2 | 3.0 | 12.7 | -28.1 | 3.0 | 15.4 | -28.7 | 2.3 | 12.1 |
| 35.0 | 2MC7 | | | | -27.9 | 3.5 | 15.5 | -26.3 | 3.8 | 20.3 | -26.4 | 3.6 | 18.0 |
| 36.0 | 3MC7 | | | | -28.0 | 2.4 | 19.5 | -28.5 | 2.7 | 27.7 | -23.5 | 1.8 | 10.2 |
| 37.0 | 1c4DMCYC6 | | | | -28.8 | 1.6 | 7.2 | -27.3 | 1.8 | 10.1 | -28.6 | 1.7 | 9.0 |
| 38.0 | nC8 | | | | -28.0 | 7.0 | 31.2 | -27.3 | 7.3 | 47.1 | -27.9 | 6.8 | 41.0 |
| 39.0 | nC9 | | | | | 10.7 | | | 10.6 | | -33.8 | 10.4 | 98.3 |

ALBERTA

| 12 Hrs | | 1345.0 | | | 15062.0 | | |
|---|---|---|---|---|---|---|---|
| number | Compound | Alb 12a 0 del | AMP [V] | Area [Vs] | Alb 12b 0 del | AMP [V] | Area [Vs] |
| 1.0 | iC5 | -27.0 | 0.3 | 1.1 | -27.5 | 0.4 | 1.4 |
| 2.0 | nC5 | -26.9 | 0.3 | 1.0 | -27.4 | 0.4 | 1.4 |
| 3.0 | 22DMC4 | | | | | | |
| 4.0 | CYC5 | | | | | | |
| 5.0 | 23DMC4 | | | | | | |
| 6.0 | 2MC5 | -28.0 | 0.7 | 3.1 | -27.9 | 0.8 | 3.5 |
| 7.0 | 3MC5 | -26.4 | 0.6 | 2.5 | -27.4 | 0.6 | 2.7 |
| 8.0 | nC6 | -28.5 | 1.1 | 5.0 | -28.8 | 1.3 | 5.5 |
| 9.0 | 22DMC5 | | | | | | |
| 10.0 | MCYC5 | -25.9 | 1.4 | 6.2 | -25.8 | 1.5 | 6.5 |
| 11.0 | 24DMc5 | | | | | | |
| 12.0 | 223TMC4 | | | | | | |
| 13.0 | Benzene | -28.1 | 0.3 | 1.4 | -28.8 | 0.3 | 1.5 |
| 14.0 | 33DMC5 | | | | | | |
| 15.0 | CYC6 | -28.9 | 1.7 | 8.3 | -29.1 | 1.7 | 8.4 |
| 16.0 | 2MC6 | -25.1 | 1.0 | 4.6 | -25.4 | 1.0 | 4.6 |
| 17.0 | 23DMC5 | -31.5 | 0.6 | 2.8 | -31.7 | 0.6 | 2.8 |
| 18.0 | 11DMCYC5 | -27.0 | 0.5 | 2.6 | -27.0 | 0.5 | 2.5 |
| 19.0 | 3McC6 | -27.1 | 1.5 | 7.1 | -27.2 | 1.4 | 7.0 |
| 20.0 | 1c3DMCYC5 | -24.0 | 1.0 | 4.6 | -24.4 | 0.9 | 4.5 |
| 21.0 | 1t3DMCYC5 | -24.3 | 1.0 | 5.4 | -24.3 | 0.9 | 5.2 |
| 22.0 | 1t2DMCYC5 | -26.1 | 2.3 | 11.2 | -26.3 | 2.2 | 10.8 |
| 23.0 | nC7 | -29.8 | 3.8 | 17.6 | -29.9 | 3.5 | 16.9 |
| 24.0 | 22DMC6 | | | | | | |
| 25.0 | MCYC6 | -27.2 | 5.9 | 30.5 | -27.1 | 5.5 | 28.1 |
| 26.0 | 1c2DMCYC5 | -31.1 | 1.1 | 7.0 | -31.5 | 1.0 | 6.5 |
| 27.0 | EtCYC5 | -25.5 | 0.8 | 4.3 | -26.2 | 0.7 | 3.9 |
| 28.0 | 25DMC6 | -31.9 | 0.5 | 2.8 | -34.1 | 0.4 | 2.1 |
| 29.0 | 24DMC6 | -26.3 | 1.2 | 6.8 | -27.0 | 1.1 | 6.3 |
| 30.0 | 1t2c4TMCYC5 | -25.4 | 1.6 | 8.2 | -25.5 | 1.5 | 7.5 |
| 31.0 | 33DMC6 | | | | | | |
| 32.0 | 1t2c3TMCYC5 | | | | | | |
| 33.0 | 223TMCYC6 | | | | | | |
| 34.0 | Toluene | -28.8 | 2.6 | 13.6 | -28.7 | 2.4 | 12.6 |
| 35.0 | 2MC7 | -27.1 | 3.7 | 18.8 | -26.7 | 3.3 | 17.1 |
| 36.0 | 3MC7 | -28.9 | 2.6 | 26.8 | -29.2 | 2.4 | 22.4 |
| 37.0 | 1c4DMCYC6 | -27.9 | 1.8 | 9.7 | -28.6 | 1.6 | 8.3 |
| 38.0 | nC8 | -28.0 | 6.6 | 42.4 | -27.6 | 6.1 | 37.6 |
| 39.0 | nC9 | -27.6 | 9.8 | 94.3 | -27.9 | 9.5 | 87.2 |

| ALBERTA 14 Hrs | | 990812.0 1259.0 | | | 990813.0 829.0 | | |
|---|---|---|---|---|---|---|---|
| | | Alb 14a 0 | AMP | Area | Alb 14b 0 | AMP | Area |
| number | Compound | del | [V] | [Vs] | del | [V] | [Vs] |
| 1.0 | iC5 | -27.1 | 0.2 | 0.9 | -27.6 | 0.3 | 1.3 |
| 2.0 | nC5 | -26.9 | 0.2 | 0.8 | -27.3 | 0.3 | 1.2 |
| 3.0 | 22DMC4 | | | | | | |
| 4.0 | CYC5 | | | | | | |
| 5.0 | 23DMC4 | | | | | | |
| 6.0 | 2MC5 | -27.5 | 0.6 | 2.4 | -28.0 | 0.8 | 3.3 |
| 7.0 | 3MC5 | -25.6 | 0.5 | 3.2 | -26.0 | 0.7 | 3.6 |
| 8.0 | nC6 | -28.6 | 0.9 | 4.1 | -28.8 | 1.2 | 5.6 |
| 9.0 | 22DMC5 | | | | | | |
| 10.0 | MCYC5 | -26.2 | 1.1 | 5.3 | -25.5 | 1.6 | 7.2 |
| 11.0 | 24DMc5 | | | | | | |
| 12.0 | 223TMC4 | | | | | | |
| 13.0 | Benzene | -27.9 | 0.2 | 1.1 | -28.0 | 0.3 | 1.5 |
| 14.0 | 33DMC5 | | | | | | |
| 15.0 | CYC6 | -28.9 | 1.5 | 7.4 | -30.2 | 2.0 | 9.4 |
| 16.0 | 2MC6 | -24.7 | 0.9 | 4.1 | -25.0 | 1.2 | 5.5 |
| 17.0 | 23DMC5 | -31.9 | 0.5 | 2.6 | -32.0 | 0.7 | 3.4 |
| 18.0 | 11DMCYC5 | -27.1 | 0.5 | 2.3 | -27.4 | 0.6 | 3.1 |
| 19.0 | 3McC6 | -27.0 | 1.3 | 6.6 | -27.1 | 1.8 | 8.6 |
| 20.0 | 1c3DMCYC5 | -24.0 | 0.9 | 4.2 | -24.3 | 1.1 | 5.6 |
| 21.0 | 1t3DMCYC5 | -24.2 | 0.9 | 4.9 | -24.3 | 1.2 | 6.5 |
| 22.0 | 1t2DMCYC5 | -26.3 | 2.1 | 10.4 | -26.4 | 2.8 | 13.5 |
| 23.0 | nC7 | -30.0 | 3.5 | 16.4 | -29.6 | 4.5 | 21.3 |
| 24.0 | 22DMC6 | | | | | | |
| 25.0 | MCYC6 | -27.2 | 5.8 | 29.4 | -26.9 | 7.1 | 37.2 |
| 26.0 | 1c2DMCYC5 | -30.8 | 1.0 | 6.7 | -32.3 | 1.3 | 8.6 |
| 27.0 | EtCYC5 | -25.4 | 0.8 | 4.0 | -25.8 | 1.0 | 5.3 |
| 28.0 | 25DMC6 | -31.9 | 0.4 | 2.7 | -33.1 | 0.5 | 3.4 |
| 29.0 | 24DMC6 | -26.4 | 1.1 | 6.4 | -26.3 | 1.4 | 8.3 |
| 30.0 | 1t2c4TMCYC5 | -25.3 | 1.5 | 7.9 | -25.0 | 2.0 | 9.9 |
| 31.0 | 33DMC6 | | | | | | |
| 32.0 | 1t2c3TMCYC5 | | | | | | |
| 33.0 | 223TMCYC6 | | | | | | |
| 34.0 | Toluene | -28.7 | 2.3 | 12.3 | -28.6 | 3.1 | 15.6 |
| 35.0 | 2MC7 | -26.5 | 3.5 | 17.7 | -26.3 | 4.3 | 22.2 |
| 36.0 | 3MC7 | -26.3 | 2.5 | 16.2 | -26.2 | 3.0 | 20.2 |
| 37.0 | 1c4DMCYC6 | -28.1 | 1.6 | 8.5 | -27.9 | 2.1 | 10.7 |
| 38.0 | nC8 | -27.3 | 6.5 | 35.7 | -26.5 | 7.4 | 43.7 |
| 39.0 | nC9 | -27.6 | 9.4 | 84.1 | -27.8 | 9.9 | 92.0 |

| LACULA 0 Hrs | | 990226.0 | | | 990226.0 | | | 990226.0 | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 1600.0 | | | 1756.0 | | | 1915.0 | | |
| | | Lacula 0a 90 | AMP | Area | Lacula 0b 87 | AMP | Area | Lacula 0c 87 | AMP | Area |
| | | del | [V] | [Vs] | del | [V] | [Vs] | del | [V] | [Vs] |
| number | Compound | | | | | | | | | |
| 1 | iC5 | -28.0 | 5.6 | 17.3 | -28.3 | 5.5 | 17.5 | -28.1 | 5.2 | 16.7 |
| 2 | nC5 | -28.0 | 7.8 | 24.0 | -28.4 | 7.6 | 24.3 | -28.4 | 7.3 | 23.4 |
| 3 | 22DMC4 | | | | | | | | | |
| 4 | CYC5 | | | | | | | | | |
| 5 | 23DMC4 | -25.6 | 1.0 | 4.2 | -25.9 | 1.0 | 4.2 | -25.6 | 0.9 | 4.0 |
| 6 | 2MC5 | -28.1 | 3.8 | 13.6 | -28.6 | 3.8 | 13.9 | -28.3 | 3.5 | 13.2 |
| 7 | 3MC5 | -27.3 | 1.6 | 6.0 | -27.5 | 1.6 | 6.1 | -27.4 | 1.5 | 5.8 |
| 8 | nC6 | -28.4 | 6.4 | 22.9 | -28.9 | 6.5 | 23.4 | -28.7 | 6.1 | 22.2 |
| 9 | 22DMC5 | | | | | | | | | |
| 10 | MCYC5 | -24.1 | 2.9 | 10.7 | -24.6 | 3.0 | 10.9 | -24.7 | 2.8 | 10.4 |
| 11 | 24DMc5 | | | | | | | | | |
| 12 | 223TMC4 | | | | | | | | | |
| 13 | Benzene | -24.9 | 0.4 | 1.7 | -25.2 | 0.4 | 1.6 | -25.3 | 0.4 | 1.6 |
| 14 | 33DMC5 | | | | | | | | | |
| 15 | CYC6 | -26.3 | 2.4 | 9.6 | -26.7 | 2.4 | 9.9 | -26.4 | 2.3 | 9.4 |
| 16 | 2MC6 | -26.1 | 1.3 | 5.1 | -26.9 | 1.3 | 5.2 | -27.0 | 1.2 | 4.9 |
| 17 | 23DMC5 | -29.5 | 0.5 | 2.2 | -29.1 | 0.5 | 2.3 | -28.5 | 0.5 | 2.3 |
| 18 | 11DMCYC5 | -26.9 | 0.4 | 1.4 | -27.2 | 0.4 | 1.4 | -27.1 | 0.3 | 1.4 |
| 19 | 3MC6 | -27.1 | 1.5 | 6.3 | -27.5 | 1.5 | 6.5 | -27.4 | 1.4 | 6.2 |
| 20 | 1c3DMCYC5 | -23.0 | 0.9 | 3.4 | -23.1 | 0.9 | 3.4 | -22.8 | 0.8 | 3.3 |
| 21 | 1t3DMCYC5 | -23011.0 | 0.8 | 3.6 | -23.2 | 0.8 | 3.7 | -23.3 | 0.8 | 3.6 |
| 22 | 1t2DMCYC5 | -23.9 | 1.6 | 6.9 | -24.4 | 1.7 | 7.1 | -24.1 | 1.6 | 6.8 |
| 23 | nC7 | -28.6 | 5.7 | 23.3 | -28.6 | 5.9 | 24.1 | -28.6 | 5.5 | 22.9 |
| 24 | 22DMC6 | | | | | | | | | |
| 25 | MCYC6 | -25.3 | 4.3 | 18.7 | -25.6 | 4.4 | 19.3 | -25.7 | 4.2 | 18.4 |
| 26 | 1c2DMCYC5 | -27.1 | 0.4 | 2.2 | -26.5 | 0.4 | 2.4 | -25.8 | 0.4 | 2.3 |
| 27 | EtCYC5 | -24.6 | 0.5 | 2.0 | -24.8 | 0.5 | 2.1 | -24.7 | 0.5 | 2.0 |
| 28 | 25DMC6 | -29.3 | 0.2 | 1.0 | -30.0 | 0.2 | 1.0 | -30.5 | 0.2 | 1.0 |
| 29 | 24DMC6 | -25.0 | 0.5 | 2.2 | -25.5 | 0.5 | 2.2 | -25.6 | 0.4 | 2.1 |
| 30 | 1t2c4TMCYC5 | -22.9 | 0.8 | 3.4 | -23.0 | 0.8 | 3.3 | -23.3 | 0.7 | 3.2 |
| 31 | 33DMC6 | | | | | | | | | |
| 32 | 1t2c3TMCYC5 | | | | | | | | | |
| 33 | 223TMCYC6 | | | | | | | | | |
| 34 | Toluene | -27.1 | 0.9 | 4.4 | -27.3 | 0.9 | 4.3 | -27.6 | 0.9 | 4.3 |
| 35 | 2MC7 | -27.2 | 2.0 | 8.7 | -27.5 | 2.1 | 8.8 | -27.5 | 1.9 | 8.5 |
| 36 | 3MC7 | -24.0 | 1.3 | 7.1 | -24.6 | 1.4 | 7.3 | -24.3 | 1.3 | 6.9 |
| 37 | 1c4DMCYC6 | -26.3 | 0.8 | 3.6 | -26.6 | 0.8 | 3.8 | -26.3 | 0.8 | 3.6 |
| 38 | nC8 | -27.0 | 4.4 | 19.4 | -27.3 | 4.5 | 20.0 | -27.3 | 4.2 | 19.0 |
| 39 | nC9 | -27.1 | 3.8 | 18.5 | -27.1 | 3.9 | 19.2 | -26.9 | 3.7 | 18.2 |

| LACULA 1.0 Hrs | | 990306.0 1223.0 | | | 990306.0 1406.0 | | | 990306.0 1543.0 | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Lacula 1.0 55 del | AMP [V] | Area [Vs] | Lacula 1.0 55 del | AMP [V] | Area [Vs] | Lacula1. 0 54 del | AMP [V] | Area [Vs] |
| number | Compound | | | | | | | | | |
| 1 | iC5 | -28.0 | 4.8 | 15.6 | -27.8 | 4.8 | 15.9 | -26.9 | 3.0 | 9.9 |
| 2 | nC5 | -28.1 | 6.4 | 20.7 | -27.8 | 6.4 | 21.7 | -27.3 | 4.4 | 15.3 |
| 3 | 22DMC4 | | | | | | | | | |
| 4 | CYC5 | | | | | | | | | |
| 5 | 23DMC4 | -25.2 | 0.9 | 3.9 | -25.0 | 0.9 | 3.9 | -24.6 | 0.7 | 3.3 |
| 6 | 2MC5 | -28.2 | 3.3 | 12.8 | -27.9 | 3.4 | 12.9 | -27.8 | 2.9 | 11.3 |
| 7 | 3MC5 | -26.9 | 1.5 | 6.1 | -29.9 | 1.5 | 6.3 | -27.2 | 1.3 | 5.0 |
| 8 | nC6 | -28.3 | 5.4 | 20.8 | -28.2 | 5.5 | 21.3 | -28.0 | 5.0 | 19.6 |
| 9 | 22DMC5 | | | | | | | | | |
| 10 | MCYC5 | -24.5 | 2.7 | 10.1 | -24.1 | 2.8 | 10.2 | -23.9 | 2.6 | 9.5 |
| 11 | 24DMc5 | | | | | | | | | |
| 12 | 223TMC4 | | | | | | | | | |
| 13 | Benzene | -25.2 | 0.3 | 1.4 | -25.2 | 0.4 | 1.4 | -24.9 | 0.3 | 1.3 |
| 14 | 33DMC5 | | | | | | | | | |
| 15 | CYC6 | -26.1 | 2.3 | 9.6 | -26.0 | 2.3 | 9.6 | -26.0 | 2.2 | 9.2 |
| 16 | 2MC6 | -26.5 | 1.2 | 4.8 | -26.5 | 1.2 | 4.8 | -26.4 | 1.2 | 4.7 |
| 17 | 23DMC5 | -29.2 | 0.5 | 2.2 | -29.3 | 0.5 | 2.2 | -29.3 | 0.5 | 2.2 |
| 18 | 11DMCYC5 | -26.9 | 0.4 | 1.4 | -26.6 | 0.4 | 1.4 | -26.5 | 0.3 | 1.4 |
| 19 | 3MC6 | -27.5 | 1.4 | 6.1 | -27.0 | 1.4 | 6.1 | -27.1 | 1.4 | 6.0 |
| 20 | 1c3DMCYC5 | -22.8 | 0.8 | 3.2 | -22.8 | 0.8 | 3.2 | -22.7 | 0.8 | 3.1 |
| 21 | 1t3DMCYC5 | -23.1 | 0.8 | 3.5 | -22.8 | 0.8 | 3.6 | -22.9 | 0.8 | 3.5 |
| 22 | 1t2DMCYC5 | -24.5 | 1.6 | 6.9 | -24.0 | 1.6 | 7.1 | -23.6 | 1.6 | 7.0 |
| 23 | nC7 | -28.2 | 5.3 | 22.5 | -28.2 | 5.3 | 22.6 | -28.1 | 5.2 | 22.4 |
| 24 | 22DMC6 | | | | | | | | | |
| 25 | MCYC6 | -25.4 | 4.3 | 18.7 | -25.1 | 4.3 | 18.7 | -24.9 | 4.2 | 18.5 |
| 26 | 1c2DMCYC5 | -27.0 | 0.4 | 2.7 | -28.3 | 0.4 | 2.6 | -28.7 | 0.4 | 2.6 |
| 27 | EtCYC5 | -24.5 | 0.5 | 2.0 | -23.9 | 0.5 | 1.9 | -23.9 | 0.5 | 1.9 |
| 28 | 25DMC6 | -30.3 | 0.2 | 1.0 | -30.8 | 0.2 | 1.0 | -30.4 | 0.2 | 0.9 |
| 29 | 24DMC6 | -25.8 | 0.5 | 2.2 | -25.7 | 0.5 | 2.2 | -25.2 | 0.5 | 2.1 |
| 30 | 1t2c4TMCYC5 | -23.1 | 0.8 | 3.3 | -22.9 | 0.8 | 3.3 | -23.1 | 0.8 | 3.2 |
| 31 | 33DMC6 | | | | | | | | | |
| 32 | 1t2c3TMCYC5 | | | | | | | | | |
| 33 | 223TMCYC6 | | | | | | | | | |
| 34 | Toluene | -27.1 | 0.8 | 4.0 | -27.2 | 0.8 | 4.0 | -26.8 | 0.8 | 3.9 |
| 35 | 2MC7 | -27.8 | 2.0 | 8.5 | -27.3 | 2.0 | 8.5 | -27.3 | 2.0 | 8.5 |
| 36 | 3MC7 | -24.1 | 1.4 | 7.2 | -24.1 | 1.4 | 7.1 | -23.8 | 1.4 | 7.2 |
| 37 | 1c4DMCYC6 | -26.4 | 0.8 | 3.7 | -26.6 | 0.8 | 3.7 | -26.7 | 0.8 | 3.7 |
| 38 | nC8 | -27.2 | 4.4 | 18.9 | -27.0 | 4.4 | 18.7 | -26.8 | 4.4 | 18.7 |
| 39 | nC9 | -26.9 | 4.2 | 20.0 | -26.9 | 4.0 | 19.6 | -27.0 | 4.0 | 19.3 |

| LACULA 2. Hrs | | 990306.0 | | | 990306.0 | | | 990306.0 | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Lacula 2.0 35 del | AMP [V] | Area [Vs] | Lacula 2.0 46 del | AMP [V] | Area [Vs] | Lacula 2.0 43 del | AMP [V] | Area [Vs] |
| number | Compound | | | | | | | | | |
| 1 | iC5 | -27.7 | 7.3 | 22.9 | -27.6 | 5.3 | 17.4 | -27.6 | 5.6 | 18.8 |
| 2 | nC5 | -27.5 | 9.5 | 31.4 | -27.5 | 7.0 | 24.0 | -27.6 | 7.5 | 25.3 |
| 3 | 22DMC4 | | | | | | | | | |
| 4 | CYC5 | | | | | | | | | |
| 5 | 23DMC4 | -24.9 | 1.2 | 5.8 | -25.0 | 1.0 | 4.4 | -24.8 | 1.0 | 4.4 |
| 6 | 2MC5 | -27.8 | 5.1 | 18.9 | -27.9 | 3.8 | 14.3 | -27.8 | 4.1 | 15.6 |
| 7 | 3MC5 | -26.8 | 2.3 | 9.2 | -26.8 | 1.7 | 7.0 | -26.6 | 1.8 | 7.6 |
| 8 | nC6 | -27.5 | 8.3 | 30.6 | -27.8 | 6.1 | 23.2 | -27.8 | 6.7 | 25.4 |
| 9 | 22DMC5 | | | | | | | | | |
| 10 | MCYC5 | -23.8 | 4.2 | 15.1 | -23.7 | 3.1 | 11.4 | -23.8 | 3.4 | 12.4 |
| 11 | 24DMc5 | | | | | | | | | |
| 12 | 223TMC4 | | | | | | | | | |
| 13 | Benzene | -24.7 | 0.5 | 2.1 | -24.9 | 0.4 | 1.5 | -24.6 | 0.4 | 1.7 |
| 14 | 33DMC5 | | | | | | | | | |
| 15 | CYC6 | -25.5 | 3.6 | 14.4 | -25.7 | 2.6 | 10.8 | -25.4 | 2.9 | 11.8 |
| 16 | 2MC6 | -26.7 | 1.9 | 7.1 | -26.0 | 1.4 | 5.4 | -26.2 | 1.5 | 5.9 |
| 17 | 23DMC5 | -27.7 | 0.8 | 3.4 | -28.9 | 0.6 | 2.5 | -27.9 | 0.6 | 2.7 |
| 18 | 11DMCYC5 | -26.6 | 0.5 | 2.3 | -26.1 | 0.4 | 1.6 | -26.3 | 0.4 | 1.8 |
| 19 | 3MC6 | -27.0 | 2.2 | 9.5 | -26.6 | 1.6 | 6.9 | -26.9 | 1.8 | 7.5 |
| 20 | 1c3DMCYC5 | -22.6 | 1.2 | 4.9 | -22.3 | 0.9 | 3.6 | -22.7 | 1.0 | 3.9 |
| 21 | 1t3DMCYC5 | -22.7 | 1.2 | 5.5 | -22.4 | 0.9 | 4.1 | -22.6 | 0.9 | 4.4 |
| 22 | 1t2DMCYC5 | -23.8 | 2.5 | 11.1 | -23.5 | 1.8 | 8.0 | -23.4 | 2.0 | 8.7 |
| 23 | nC7 | -27.8 | 7.9 | 33.4 | -27.7 | 5.9 | 24.9 | -27.8 | 6.4 | 27.3 |
| 24 | 22DMC6 | | | | | | | | | |
| 25 | MCYC6 | -24.9 | 6.5 | 28.2 | -24.5 | 4.9 | 21.2 | -24.6 | 5.3 | 23.1 |
| 26 | 1c2DMCYC5 | -28.0 | 0.7 | 3.9 | -29.1 | 0.5 | 2.9 | -27.7 | 0.5 | 3.2 |
| 27 | EtCYC5 | -24.3 | 0.7 | 3.0 | -24.2 | 0.5 | 2.2 | -24.4 | 0.6 | 2.4 |
| 28 | 25DMC6 | -30.4 | 0.3 | 1.4 | -30.7 | 0.2 | 1.1 | -30.8 | 0.3 | 1.2 |
| 29 | 24DMC6 | -25.1 | 0.7 | 3.3 | -25.4 | 0.5 | 2.4 | -25.2 | 0.6 | 2.7 |
| 30 | 1t2c4TMCYC5 | -22.5 | 1.2 | 5.0 | -22.7 | 0.9 | 3.7 | -22.6 | 0.9 | 4.0 |
| 31 | 33DMC6 | | | | | | | | | |
| 32 | 1t2c3TMCYC5 | | | | | | | | | |
| 33 | 223TMCYC6 | | | | | | | | | |
| 34 | Toluene | -26.4 | 1.3 | 6.0 | -26.4 | 0.9 | 4.3 | -26.1 | 1.0 | 4.8 |
| 35 | 2MC7 | -27.4 | 3.1 | 13.1 | -26.8 | 2.3 | 9.6 | -27.0 | 2.5 | 10.5 |
| 36 | 3MC7 | -24.2 | 2.2 | 10.9 | -23.9 | 1.6 | 8.1 | -24.2 | 1.8 | 8.8 |
| 37 | 1c4DMCYC6 | -25.8 | 1.3 | 5.7 | -26.3 | 0.9 | 4.2 | -25.9 | 1.0 | 4.6 |
| 38 | nC8 | -26.6 | 6.5 | 28.3 | -26.4 | 4.9 | 21.1 | -26.7 | 5.4 | 22.9 |
| 39 | nC9 | -26.3 | 6.0 | 29.7 | -26.6 | 4.5 | 22.0 | -26.5 | 4.9 | 23.9 |

| LACULA 3 Hrs | | 990308.0 | | | 990308.0 | | | 990308.0 | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Lacula 3.0 35 | AMP | Area | Lacula 3.0 47 | AMP | Area | Lacula 3.0c | AMP | Area |
| | | del | [V] | [Vs] | del | [V] | [Vs] | del | [V] | [Vs] |
| number | Compound | | | | | | | | | |
| 1 | iC5 | -26.9 | 8.4 | 27.2 | -27.6 | 6.4 | 21.1 | -27.7 | 3.2 | 10.5 |
| 2 | nC5 | | . | . | -26.6 | 8.6 | 28.0 | -27.7 | 4.2 | 17.1 |
| 3 | 22DMC4 | | | | | | | | | |
| 4 | CYC5 | | | | | | | | | |
| 5 | 23DMC4 | -25.0 | 1.5 | 6.9 | -25.1 | 1.1 | 5.3 | -25.1 | 0.7 | 2.9 |
| 6 | 2MC5 | -27.9 | 6.1 | 22.4 | -27.9 | 4.6 | 17.2 | -27.9 | 2.7 | 10.4 |
| 7 | 3MC5 | -26.7 | 2.8 | 10.8 | -27.0 | 2.0 | 8.2 | -27.3 | 1.2 | 5.4 |
| 8 | nC6 | -36.6 | 10.0 | 35.9 | -27.8 | 7.5 | 27.6 | -28.3 | 4.4 | 17.5 |
| 9 | 22DMC5 | | | | | | | | | |
| 10 | MCYC5 | -23.9 | 5.1 | 18.2 | -24.0 | 3.8 | 17.8 | -23.4 | 2.4 | 8.6 |
| 11 | 24DMc5 | | | | | | | | | |
| 12 | 223TMC4 | | | | | | | | | |
| 13 | Benzene | -25.1 | 0.6 | 2.4 | -25.2 | 0.4 | 1.8 | -25.5 | 0.3 | 1.2 |
| 14 | 33DMC5 | | | | | | | | | |
| 15 | CYC6 | -25.9 | 4.4 | 17.1 | -25.9 | 3.3 | 13.0 | -25.6 | 2.1 | 8.7 |
| 16 | 2MC6 | -26.8 | 2.3 | 8.8 | -26.4 | 1.7 | 6.6 | -25.9 | 1.1 | 4.3 |
| 17 | 23DMC5 | -27.4 | 0.9 | 3.9 | -28.7 | 0.7 | 3.0 | -29.6 | 0.5 | 2.1 |
| 18 | 11DMCYC5 | -26.1 | 0.6 | 2.6 | -26.4 | 0.5 | 2.0 | -26.8 | 0.3 | 1.5 |
| 19 | 3McC6 | -26.8 | 2.7 | 11.1 | -27.0 | 2.0 | 8.3 | -27.1 | 1.3 | 5.9 |
| 20 | 1c3DMCYC5 | -22.6 | 1.5 | 5.8 | -22.9 | 1.1 | 4.4 | -23.2 | 0.8 | 3.0 |
| 21 | 1t3DMCYC5 | -22.7 | 1.4 | 6.6 | -22.6 | 1.0 | 4.9 | -22.7 | 0.7 | 3.4 |
| 22 | 1t2DMCYC5 | -23.6 | 3.1 | 12.8 | -23.9 | 2.3 | 9.6 | -24.0 | 1.5 | 7.1 |
| 23 | nC7 | -25.8 | 9.4 | 39.5 | -27.9 | 7.3 | 29.8 | -28.1 | 4.8 | 20.6 |
| 24 | 22DMC6 | | | | | | | | | |
| 25 | MCYC6 | -24.4 | 8.0 | 34.1 | -24.8 | 6.0 | 25.6 | -24.7 | 4.1 | 17.7 |
| 26 | 1c2DMCYC5 | -28.0 | 0.8 | 4.2 | -27.6 | 0.6 | 3.2 | -29.7 | 0.4 | 2.7 |
| 27 | EtCYC5 | -24.1 | 0.9 | 3.6 | -24.7 | 0.6 | 2.7 | -24.0 | 0.4 | 1.8 |
| 28 | 25DMC6 | -28.5 | 0.4 | 1.8 | -29.4 | 0.3 | 1.3 | -31.7 | 0.2 | 0.9 |
| 29 | 24DMC6 | -25.1 | 0.9 | 4.0 | -24.9 | 0.6 | 3.0 | -25.2 | 0.4 | 2.1 |
| 30 | 1t2c4TMCYC5 | -22.9 | 1.4 | 6.1 | -22.9 | 1.1 | 4.5 | -23.1 | 0.7 | 3.2 |
| 31 | 33DMC6 | | | | | | | | | |
| 32 | 1t2c3TMCYC5 | | | | | | | | | |
| 33 | 223TMCYC6 | | | | | | | | | |
| 34 | Toluene | -26.8 | 1.5 | 7.0 | -26.7 | 1.1 | 5.2 | -26.9 | 0.7 | 3.6 |
| 35 | 2MC7 | -27.6 | 3.9 | 16.1 | -27.3 | 2.8 | 11.9 | -26.5 | 1.9 | 8.2 |
| 36 | 3MC7 | -24.5 | 2.7 | 13.4 | -24.2 | 2.0 | 9.9 | -24.2 | 1.4 | 7.0 |
| 37 | 1c4DMCYC6 | -26.1 | 1.6 | 6.9 | -26.2 | 1.1 | 5.1 | -26.7 | 0.8 | 3.6 |
| 38 | nC8 | -26.2 | 7.9 | 35.4 | -26.5 | 6.0 | 26.0 | -26.4 | 4.2 | 18.1 |
| 39 | nC9 | -26.5 | 7.4 | 37.9 | -26.7 | 5.6 | 27.5 | -27.1 | 4.1 | 19.6 |

| LACULA 4 Hrs | | 990308.0 | | | 990308.0 | | | 990308.0 | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Lacula 4.0 40 del | AMP [V] | Area [Vs] | Lacula 4.0 54 del | AMP [V] | Area [Vs] | Lacula 4.0 54 del | AMP [V] | Area [Vs] |
| number | Compound | | | | | | | | | |
| 1 | iC5 | -27.7 | 7.5 | 24.2 | -27.5 | 5.6 | 19.0 | -27.6 | 4.6 | 15.4 |
| 2 | nC5 | -32.5 | 9.7 | 31.1 | -27.4 | 7.4 | 25.6 | -27.6 | 5.8 | 19.3 |
| 3 | 22DMC4 | | | | | | | | | |
| 4 | CYC5 | | | | | | | | | |
| 5 | 23DMC4 | -25.3 | 1.3 | 6.0 | -25.0 | 1.0 | 4.7 | -25.5 | 0.8 | 3.9 |
| 6 | 2MC5 | -28.0 | 5.2 | 19.3 | -27.8 | 4.0 | 15.4 | -27.8 | 3.3 | 12.6 |
| 7 | 3MC5 | -27.0 | 2.3 | 9.2 | -26.7 | 1.8 | 6.8 | -27.2 | 1.4 | 5.7 |
| 8 | nC6 | -27.1 | 8.6 | 31.0 | -27.8 | 6.5 | 24.7 | -27.9 | 5.1 | 19.8 |
| 9 | 22DMC5 | | | | | | | | | |
| 10 | MCYC5 | -24.2 | 4.3 | 15.5 | -23.8 | 3.3 | 12.2 | -23.7 | 2.7 | 10.2 |
| 11 | 24DMc5 | | | | | | | | | |
| 12 | 223TMC4 | | | | | | | | | |
| 13 | Benzene | -25.3 | 0.5 | 2.1 | -24.8 | 0.4 | 1.6 | -24.5 | 0.3 | 1.3 |
| 14 | 33DMC5 | | | | | | | | | |
| 15 | CYC6 | -26.0 | 3.7 | 14.6 | -25.9 | 2.8 | 11.6 | -25.9 | 2.4 | 9.8 |
| 16 | 2MC6 | -26.5 | 1.9 | 7.4 | -26.3 | 1.5 | 5.8 | -26.3 | 1.2 | 4.9 |
| 17 | 23DMC5 | -28.5 | 0.8 | 3.3 | -28.5 | 0.6 | 2.7 | -29.4 | 0.5 | 2.3 |
| 18 | 11DMCYC5 | -26.7 | 0.5 | 2.2 | -26.0 | 0.4 | 1.8 | -25.8 | 0.4 | 1.5 |
| 19 | 3McC6 | -27.0 | 2.3 | 9.4 | -26.8 | 1.7 | 7.4 | -26.8 | 1.5 | 6.3 |
| 20 | 1c3DMCYC5 | -23.0 | 1.2 | 5.0 | -22.7 | 1.0 | 3.9 | -23.3 | 0.8 | 3.3 |
| 21 | 1t3DMCYC5 | -22.7 | 1.2 | 5.4 | -22.5 | 0.9 | 4.3 | -22.8 | 0.8 | 3.6 |
| 22 | 1t2DMCYC5 | -24.2 | 2.6 | 10.5 | -23.8 | 2.0 | 8.6 | -23.9 | 1.7 | 7.2 |
| 23 | nC7 | -27.6 | 8.1 | 33.4 | -27.8 | 6.3 | 26.3 | -28.0 | 5.3 | 21.9 |
| 24 | 22DMC6 | | | | | | | | | |
| 25 | MCYC6 | -25.0 | 6.8 | 28.9 | -24.7 | 5.3 | 22.8 | -24.9 | 4.5 | 19.6 |
| 26 | 1c2DMCYC5 | -28.1 | 0.7 | 3.6 | -27.9 | 0.5 | 2.9 | -27.7 | 0.5 | 2.5 |
| 27 | EtCYC5 | -24.5 | 0.7 | 3.0 | -24.3 | 0.6 | 2.4 | -24.0 | 0.5 | 2.0 |
| 28 | 25DMC6 | -29.8 | 0.3 | 1.5 | -29.4 | 0.3 | 1.2 | -29.5 | 0.2 | 1.0 |
| 29 | 24DMC6 | -25.0 | 0.7 | 3.4 | -24.9 | 0.6 | 2.7 | -25.1 | 0.5 | 2.3 |
| 30 | 1t2c4TMCYC5 | -23.1 | 1.2 | 5.1 | -22.8 | 0.9 | 4.0 | -23.2 | 0.8 | 3.5 |
| 31 | 33DMC6 | | | | | | | | | |
| 32 | 1t2c3TMCYC5 | | | | | | | | | |
| 33 | 223TMCYC6 | | | | | | | | | |
| 34 | Toluene | -26.8 | 1.3 | 5.9 | -26.4 | 1.0 | 4.5 | -26.9 | 0.8 | 3.8 |
| 35 | 2MC7 | -27.6 | 3.2 | 13.4 | -27.1 | 2.5 | 10.5 | -27.2 | 2.2 | 9.2 |
| 36 | 3MC7 | -24.1 | 2.3 | 11.4 | -23.9 | 1.7 | 8.8 | -24.1 | 1.5 | 7.8 |
| 37 | 1c4DMCYC6 | -26.6 | 1.3 | 5.8 | -26.3 | 1.0 | 4.6 | -26.4 | 0.9 | 4.1 |
| 38 | nC8 | -26.8 | 6.7 | 29.1 | -26.4 | 5.4 | 22.8 | -26.8 | 4.8 | 20.4 |
| 39 | nC9 | -26.5 | 6.4 | 31.8 | -26.5 | 5.1 | 24.7 | -26.6 | 4.7 | 22.9 |

| LACULA 5 Hrs | | 990309.0 | | | 990309.0 | | | 990309.0 | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Lacula 5.0 50 del | AMP [V] | Area [Vs] | Lacula 5.0 47 del | AMP [V] | Area [Vs] | Lacula 5.0 47 del | AMP [V] | Area [Vs] |
| number | Compound | | | | | | | | | |
| 1 | iC5 | -27.5 | 4.5 | 15.1 | -27.7 | 5.8 | 18.7 | -27.9 | 4.8 | 15.8 |
| 2 | nC5 | -27.7 | 5.6 | 18.5 | -27.7 | 7.5 | 24.0 | -28.0 | 6.0 | 19.7 |
| 3 | 22DMC4 | | | | | | | | | |
| 4 | CYC5 | | | | | | | | | |
| 5 | 23DMC4 | -25.3 | 0.8 | 3.8 | -25.2 | 1.0 | 4.6 | -25.5 | 0.9 | 3.9 |
| 6 | 2MC5 | -28.0 | 3.2 | 12.3 | -27.9 | 3.9 | 14.2 | -28.2 | 3.4 | 12.5 |
| 7 | 3MC5 | -27.1 | 1.4 | 5.5 | -26.7 | 1.7 | 7.1 | -27.7 | 1.5 | 5.6 |
| 8 | nC6 | -28.0 | 4.9 | 18.9 | -28.0 | 6.3 | 23.6 | -28.3 | 5.2 | 19.9 |
| 9 | 22DMC5 | | | | | | | | | |
| 10 | MCYC5 | -23.7 | 2.6 | 10.0 | -23.6 | 3.2 | 11.9 | -24.3 | 2.8 | 10.3 |
| 11 | 24DMc5 | | | | | | | | | |
| 12 | 223TMC4 | | | | | | | | | |
| 13 | Benzene | -24.8 | 0.3 | 1.2 | -25.3 | 0.4 | 1.5 | -25.3 | 0.3 | 1.3 |
| 14 | 33DMC5 | | | | | | | | | |
| 15 | CYC6 | -25.9 | 2.3 | | -25.9 | 2.7 | 11.3 | -26.4 | 2.4 | 9.9 |
| 16 | 2MC6 | -26.0 | 1.1 | 4.7 | -27.0 | 1.4 | 5.6 | -26.2 | 1.2 | 4.9 |
| 17 | 23DMC5 | -30.3 | 0.5 | 2.2 | -27.7 | 0.6 | 2.6 | -30.3 | 0.5 | 2.2 |
| 18 | 11DMCYC5 | -27.1 | 0.4 | 1.5 | -26.2 | 0.4 | 1.7 | -27.2 | 0.4 | 1.5 |
| 19 | 3McC6 | -27.1 | 1.4 | 6.0 | -26.9 | 1.7 | 7.2 | -27.4 | 1.5 | 6.3 |
| 20 | 1c3DMCYC5 | -22.9 | 0.8 | 3.2 | -23.0 | 0.9 | 3.8 | -23.5 | 0.8 | 3.3 |
| 21 | 1t3DMCYC5 | -23.0 | 0.7 | 3.5 | -22.8 | 0.9 | 4.2 | -23.1 | 0.8 | 3.6 |
| 22 | 1t2DMCYC5 | -23.9 | 1.6 | 7.0 | -24.0 | 1.9 | 8.2 | -24.4 | 1.7 | 7.3 |
| 23 | nC7 | -28.1 | 4.9 | 20.6 | -27.9 | 6.1 | 25.3 | -28.3 | 5.2 | 21.7 |
| 24 | 22DMC6 | | | | | | | | | |
| 25 | MCYC6 | -25.2 | 4.4 | 19.1 | -24.8 | 5.1 | 22.2 | -25.4 | 4.6 | 19.6 |
| 26 | 1c2DMCYC5 | -28.5 | 0.4 | 2.5 | -27.3 | 0.5 | 2.8 | -29.2 | 0.5 | 2.5 |
| 27 | EtCYC5 | -23.9 | 0.5 | 1.9 | -24.3 | 0.5 | 2.3 | -25.2 | 0.5 | 2.0 |
| 28 | 25DMC6 | -29.7 | 0.2 | 1.0 | -29.5 | 0.3 | 1.2 | -30.3 | 0.2 | 1.0 |
| 29 | 24DMC6 | -25.4 | 0.5 | 2.2 | -25.6 | 0.5 | 2.6 | -25.8 | 0.5 | 2.3 |
| 30 | 1t2c4TMCYC5 | -23.2 | 0.8 | 3.4 | -22.9 | 0.9 | 4.0 | -23.3 | 0.8 | 3.5 |
| 31 | 33DMC6 | | | | | | | | | |
| 32 | 1t2c3TMCYC5 | | | | | | | | | |
| 33 | 223TMCYC6 | | | | | | | | | |
| 34 | Toluene | -27.0 | 0.7 | 3.5 | -26.6 | 0.9 | 4.3 | -27.0 | 0.8 | 3.7 |
| 35 | 2MC7 | -27.0 | 2.0 | 8.6 | -27.0 | 2.4 | 10.3 | -27.7 | 2.2 | 9.1 |
| 36 | 3MC7 | -24.5 | 1.5 | 7.4 | -24.5 | 1.7 | 8.8 | -24.4 | 1.5 | 7.8 |
| 37 | 1c4DMCYC6 | -26.9 | 0.9 | 3.9 | -26.4 | 1.0 | 4.5 | -27.1 | 0.9 | 4.1 |
| 38 | nC8 | -26.9 | 4.4 | 18.3 | -26.5 | 5.2 | 22.4 | -27.0 | 4.7 | 19.7 |
| 39 | nC9 | -26.9 | 4.4 | 21.1 | -26.6 | 5.1 | 24.5 | -27.8 | 4.8 | 23.0 |

| LACULA 6 Hrs | | 990309.0 | | | 990309.0 | | | 990309.0 | | | 990309.0 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Lacula 6.0 25 | AMP | Area | Lacula 6.0 50 | AMP | Area | Lacula 6.0 50 | AMP | Area | Lacula 6.0 50 | AMP | Area |
| | | del | [V] | [Vs] | del | [V] | [Vs] | del | [V] | [Vs] | del | [V] | [Vs] |
| number | Compound | | | | | | | | | | | | |
| 1 | iC5 | -28.4 | 9.5 | 32.1 | -28.7 | 5.3 | 17.4 | -27.8 | 4.9 | 15.9 | -27.8 | 4.8 | 16.9 |
| 2 | nC5 | -65.7 | 10.7 | 41.4 | -28.9 | 7.0 | 22.2 | -27.8 | 6.1 | 20.0 | -28.1 | 6.3 | 20.8 |
| 3 | 22DMC4 | | | | | | | | | | | | |
| 4 | CYC5 | | | | | | | | | | | | |
| 5 | 23DMC4 | -24.8 | 1.7 | 8.4 | -25.1 | 0.9 | 4.4 | -25.2 | 0.9 | 4.1 | -25.4 | 0.9 | 4.2 |
| 6 | 2MC5 | -27.9 | 7.1 | 27.0 | -28.6 | 3.8 | 14.4 | -27.9 | 3.5 | 13.1 | -28.3 | 3.5 | 13.0 |
| 7 | 3MC5 | -26.8 | 3.2 | 13.2 | -27.5 | 1.7 | 6.5 | -27.1 | 1.5 | 5.9 | -27.1 | 1.6 | 6.1 |
| 8 | nC6 | -62.3 | 10.7 | 42.3 | -28.8 | 6.1 | 22.6 | -28.1 | 5.4 | 20.6 | -28.2 | 5.6 | 21.3 |
| 9 | 22DMC5 | | | | | | | | | | | | |
| 10 | MCYC5 | -24.2 | 6.0 | 22.0 | -24.3 | 3.2 | 11.7 | -23.9 | 2.9 | 10.7 | -23.9 | 2.9 | 11.0 |
| 11 | 24DMc5 | | | | | | | | | | | | |
| 12 | 223TMC4 | | | | | | | | | | | | |
| 13 | Benzene | -25.2 | 0.7 | 2.9 | -24.4 | 0.4 | 1.5 | -25.0 | 0.3 | 1.3 | -24.8 | 0.3 | 1.4 |
| 14 | 33DMC5 | | | | | | | | | | | | |
| 15 | CYC6 | -25.6 | 5.2 | 21.1 | -26.1 | 2.8 | 11.1 | -26.1 | 2.5 | 10.2 | -26.1 | 2.5 | 10.5 |
| 16 | 2MC6 | -27.6 | 2.7 | 10.7 | -26.2 | 1.4 | 5.6 | -26.5 | 1.2 | 5.1 | -26.8 | 1.3 | 5.2 |
| 17 | 23DMC5 | -25.9 | 1.1 | 5.0 | -28.7 | 0.6 | 2.5 | -29.3 | 0.5 | 2.4 | -28.7 | 0.6 | 2.4 |
| 18 | 11DMCYC5 | -26.2 | 0.7 | 3.2 | -26.4 | 0.4 | 1.7 | -26.6 | 0.4 | 1.6 | -26.5 | 0.4 | 1.6 |
| 19 | 3McC6 | -26.8 | 3.3 | 13.7 | -27.1 | 1.7 | 7.1 | -27.0 | 1.5 | 6.5 | -27.1 | 1.5 | 6.7 |
| 20 | 1c3DMCYC5 | -22.1 | 1.8 | 7.2 | -22.5 | 0.9 | 3.7 | -23.6 | 0.9 | 3.4 | -23.4 | 0.9 | 3.5 |
| 21 | 1t3DMCYC5 | -23.1 | 1.7 | 8.0 | -22.9 | 0.9 | 4.1 | -23.3 | 0.8 | 3.8 | -23.1 | 0.8 | 3.9 |
| 22 | 1t2DMCYC5 | -23.4 | 3.8 | 15.9 | -24.0 | 1.9 | 8.1 | -24.4 | 1.7 | 7.5 | -24.2 | 1.8 | 7.6 |
| 23 | nC7 | -52.1 | 10.7 | 47.7 | -28.9 | 6.0 | 24.9 | -28.0 | 5.5 | 22.7 | -28.4 | 5.6 | 23.2 |
| 24 | 22DMC6 | | | | | | | | | | | | |
| 25 | MCYC6 | -23.8 | 9.6 | 42.4 | -25.6 | 5.1 | 22.2 | -25.1 | 4.7 | 20.3 | -25.5 | 4.8 | 20.9 |
| 26 | 1c2DMCYC5 | -26.6 | 1.0 | 5.3 | -28.0 | 0.5 | 2.8 | -29.1 | 0.5 | 2.6 | -26.8 | 0.5 | 2.7 |
| 27 | EtCYC5 | -24.0 | 1.0 | 4.5 | -23.8 | 0.5 | 2.3 | -25.1 | 0.5 | 2.1 | -24.2 | 0.5 | 2.1 |
| 28 | 25DMC6 | -29.2 | 0.5 | 2.2 | -29.2 | 0.3 | 1.1 | -30.9 | 0.2 | 1.1 | -29.9 | 0.2 | 1.1 |
| 29 | 24DMC6 | -25.3 | 1.0 | 5.1 | -24.4 | 0.5 | 2.6 | -25.2 | 0.5 | 2.4 | -25.5 | 0.5 | 2.4 |
| 30 | 1t2c4TMCYC5 | -22.7 | 1.7 | 7.7 | -22.9 | 0.9 | 3.9 | -23.2 | 0.8 | 3.7 | -23.2 | 0.9 | 3.7 |
| 31 | 33DMC6 | | | | | | | | | | | | |
| 32 | 1t2c3TMCYC5 | | | | | | | | | | | | |
| 33 | 223TMCYC6 | | | | | | | | | | | | |
| 34 | Toluene | -26.6 | 1.9 | 8.6 | -26.6 | 0.9 | 4.2 | -26.9 | 0.8 | 3.8 | -27.0 | 0.8 | 3.9 |
| 35 | 2MC7 | -28.0 | 4.7 | 20.2 | -27.7 | 2.4 | 10.0 | -27.2 | 2.2 | 9.4 | -27.7 | 2.2 | 9.6 |
| 36 | 3MC7 | -24.6 | 3.3 | 17.1 | -24.0 | 1.7 | 8.4 | -24.3 | 1.6 | 8.0 | -24.4 | 1.6 | 8.1 |
| 37 | 1c4DMCYC6 | -26.1 | 2.0 | 8.7 | -26.0 | 1.0 | 4.4 | -26.5 | 0.9 | 4.2 | -26.6 | 0.9 | 4.3 |
| 38 | nC8 | -23.9 | 9.5 | 43.7 | -27.3 | 5.1 | 21.5 | -26.8 | 4.7 | 20.0 | -26.8 | 4.9 | 21.0 |
| 39 | nC9 | -24.2 | 9.2 | 48.9 | -27.3 | 5.0 | 23.9 | -27.0 | 4.8 | 22.7 | -26.6 | 4.9 | 23.6 |

| LACULA 7 Hrs | | 990807.0 | | | 990807.0 | | |
|---|---|---|---|---|---|---|---|
| | | Lacula 7 35 del | AMP [V] | Area [Vs] | Lacula 7 20 del | AMP [V] | Area [Vs] |
| number | Compound | | | | | | |
| 1 | iC5 | -27.8 | 2.4 | 8.1 | -27.6 | 4.4 | 14.1 |
| 2 | nC5 | -27.9 | 2.9 | 9.7 | -27.7 | 5.4 | 16.9 |
| 3 | 22DMC4 | | | | | | |
| 4 | CYC5 | | | | | | |
| 5 | 23DMC4 | -25.3 | 0.5 | 2.1 | -25.7 | 0.8 | 3.7 |
| 6 | 2MC5 | -28.2 | 1.8 | 7.0 | -28.1 | 3.4 | 12.1 |
| 7 | 3MC5 | -27.4 | 0.8 | 3.1 | -27.4 | 1.5 | 5.5 |
| 8 | nC6 | -28.2 | 2.8 | 10.4 | -28.2 | 5.1 | 18.3 |
| 9 | 22DMC5 | | | | | | |
| 10 | MCYC5 | -24.5 | 1.5 | 5.8 | -24.3 | 2.8 | 10.0 |
| 11 | 24DMc5 | | | | | | |
| 12 | 223TMC4 | | | | | | |
| 13 | Benzene | -25.2 | 0.1 | 0.6 | -24.9 | 0.2 | 1.1 |
| 14 | 33DMC5 | | | | | | |
| 15 | CYC6 | -26.0 | 1.3 | 5.7 | -26.2 | 2.4 | 9.9 |
| 16 | 2MC6 | -26.2 | 0.7 | 2.7 | -25.7 | 1.2 | 5.0 |
| 17 | 23DMC5 | -31.5 | 0.3 | 1.3 | -30.1 | 0.5 | 2.2 |
| 18 | 11DMCYC5 | -27.7 | 0.2 | 0.9 | -26.3 | 0.4 | 1.5 |
| 19 | 3McC6 | -27.2 | 0.8 | 3.4 | -27.1 | 1.5 | 6.2 |
| 20 | 1c3DMCYC5 | -22.9 | 0.5 | 1.9 | -22.6 | 0.8 | 3.3 |
| 21 | 1t3DMCYC5 | -23.3 | 0.4 | 2.0 | -22.7 | 0.8 | 3.7 |
| 22 | 1t2DMCYC5 | -24.9 | 0.9 | 4.1 | -23.9 | 1.7 | 7.3 |
| 23 | nC7 | -28.9 | 2.7 | 11.7 | -28.3 | 4.8 | 21.0 |
| 24 | 22DMC6 | | | | | | |
| 25 | MCYC6 | -25.2 | 2.5 | 11.2 | -25.1 | 4.4 | 19.6 |
| 26 | 1c2DMCYC5 | -28.9 | 0.3 | 1.5 | -29.5 | 0.5 | 2.6 |
| 27 | EtCYC5 | -24.1 | 0.3 | 1.1 | -24.3 | 0.5 | 2.0 |
| 28 | 25DMC6 | -30.9 | 0.1 | 0.6 | -31.4 | 0.2 | 1.0 |
| 29 | 24DMC6 | -25.5 | 0.3 | 1.3 | -25.1 | 0.5 | 2.4 |
| 30 | 1t2c4TMCYC5 | -23.2 | 0.5 | 2.0 | -23.6 | 0.8 | 3.6 |
| 31 | 33DMC6 | | | | | | |
| 32 | 1t2c3TMCYC5 | | | | | | |
| 33 | 223TMCYC6 | | | | | | |
| 34 | Toluene | -26.7 | 0.3 | 1.7 | -26.6 | 0.6 | 3.3 |
| 35 | 2MC7 | -26.8 | 1.1 | 5.1 | -26.3 | 2.0 | 9.3 |
| 36 | 3MC7 | -24.6 | 0.8 | 4.4 | -24.1 | 1.4 | 7.8 |
| 37 | 1c4DMCYC6 | -26.9 | 0.5 | 2.3 | -26.7 | 0.9 | 4.1 |
| 38 | nC8 | -26.4 | 2.3 | 10.5 | -25.5 | 3.9 | 19.1 |
| 39 | nC9 | -27.2 | 2.2 | 11.4 | -26.3 | 3.7 | 20.4 |

| LACULA 8 Hrs | | 990808.0 | | | 990808.0 | | | 990808.0 | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Lacula 8 10 del | AMP [V] | Area [Vs] | Lacula 8 13 del | AMP [V] | Area [Vs] | Lacula 8 13 del | AMP [V] | Area [Vs] |
| number | Compound | | | | | | | | | |
| 1 | iC5 | -25.3 | 6.3 | 20.0 | -28.0 | 5.6 | 16.8 | -28.0 | 4.9 | 15.1 |
| 2 | nC5 | -23.6 | 7.5 | 23.8 | -27.9 | 6.5 | 19.5 | -27.6 | 5.7 | 18.1 |
| 3 | 22DMC4 | | | | | | | | | |
| 4 | CYC5 | | | | | | | | | |
| 5 | 23DMC4 | -25.0 | 1.1 | 5.3 | -25.6 | 1.0 | 4.6 | -25.6 | 0.9 | 4.2 |
| 6 | 2MC5 | -25.9 | 4.9 | 17.2 | -28.5 | 4.2 | 14.7 | -28.5 | 3.8 | 13.5 |
| 7 | 3MC5 | -25.7 | 2.2 | 8.4 | -27.7 | 1.9 | 7.2 | -27.4 | 1.7 | 6.2 |
| 8 | nC6 | -24.2 | 7.2 | 25.8 | -28.8 | 6.3 | 21.9 | -28.7 | 5.8 | 20.3 |
| 9 | 22DMC5 | | | | | | | | | |
| 10 | MCYC5 | -21.6 | 4.1 | 14.5 | -24.4 | 3.5 | 12.5 | -24.4 | 3.2 | 11.6 |
| 11 | 24DMc5 | | | | | | | | | |
| 12 | 223TMC4 | | | | | | | | | |
| 13 | Benzene | -23.8 | 0.4 | 1.6 | -25.5 | 0.3 | 1.4 | -24.7 | 0.3 | 1.3 |
| 14 | 33DMC5 | | | | | | | | | |
| 15 | CYC6 | -23.7 | 3.7 | 14.3 | -26.7 | 3.2 | 12.5 | -26.8 | 2.9 | 11.6 |
| 16 | 2MC6 | -24.2 | 1.8 | 7.2 | -26.4 | 1.5 | 6.2 | -26.4 | 1.4 | 5.8 |
| 17 | 23DMC5 | -28.3 | 0.8 | 3.2 | -31.0 | 0.7 | 2.8 | -30.5 | 0.6 | 2.6 |
| 18 | 11DMCYC5 | -25.2 | 0.5 | 2.2 | -26.9 | 0.5 | 1.9 | -27.0 | 0.4 | 1.8 |
| 19 | 3McC6 | -25.3 | 2.1 | 8.9 | -27.7 | 1.9 | 7.8 | -27.6 | 1.8 | 7.3 |
| 20 | 1c3DMCYC5 | -21.4 | 1.1 | 4.7 | -23.4 | 1.0 | 4.2 | -23.1 | 0.9 | 3.9 |
| 21 | 1t3DMCYC5 | -21.3 | 1.1 | 5.3 | -23.6 | 1.0 | 4.6 | -23.4 | 0.9 | 4.3 |
| 22 | 1t2DMCYC5 | -21.7 | 2.6 | 10.7 | -24.8 | 2.2 | 9.2 | -24.5 | 2.0 | 8.6 |
| 23 | nC7 | -24.3 | 6.2 | 30.3 | -29.0 | 5.7 | 26.0 | -29.0 | 5.4 | 24.2 |
| 24 | 22DMC6 | | | | | | | | | |
| 25 | MCYC6 | -21.2 | 6.0 | 29.1 | -26.0 | 5.4 | 25.1 | -26.0 | 5.1 | 23.4 |
| 26 | 1c2DMCYC5 | -26.8 | 0.7 | 3.8 | -28.9 | 0.6 | 3.4 | -28.9 | 0.6 | 3.2 |
| 27 | EtCYC5 | -22.1 | 0.7 | 3.0 | -25.1 | 0.6 | 2.6 | -24.7 | 0.6 | 2.4 |
| 28 | 25DMC6 | -28.8 | 0.3 | 1.5 | -32.4 | 0.3 | 1.3 | -30.7 | 0.3 | 1.2 |
| 29 | 24DMC6 | -23.8 | 0.7 | 3.5 | -25.8 | 0.6 | 3.0 | -25.8 | 0.6 | 2.8 |
| 30 | 1t2c4TMCYC5 | -21.2 | 1.2 | 5.3 | -24.0 | 1.0 | 4.6 | -24.0 | 0.9 | 4.3 |
| 31 | 33DMC6 | | | | | | | | | |
| 32 | 1t2c3TMCYC5 | | | | | | | | | |
| 33 | 223TMCYC6 | | | | | | | | | |
| 34 | Toluene | -25.0 | 0.9 | 4.9 | -27.4 | 0.8 | 4.3 | -27.1 | 0.8 | 3.9 |
| 35 | 2MC7 | -25.0 | 2.9 | 13.5 | -27.7 | 2.6 | 11.8 | -27.5 | 2.4 | 11.1 |
| 36 | 3MC7 | -21.7 | 2.1 | 11.7 | -25.0 | 1.8 | 10.2 | -25.3 | 1.7 | 9.5 |
| 37 | 1c4DMCYC6 | -24.5 | 1.3 | 6.0 | -27.6 | 1.1 | 5.3 | -27.5 | 1.0 | 5.0 |
| 38 | nC8 | -22.6 | 5.1 | 29.6 | -27.3 | 4.8 | 25.9 | -27.5 | 4.5 | 24.1 |
| 39 | nC9 | -22.0 | 4.9 | 31.2 | -27.2 | 4.5 | 27.0 | -27.3 | 4.4 | 25.5 |

| | LACULA 10Hrs | 990810.0 | | | 990811.0 | | | 990811.0 | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Lacula 10 10 del | AMP [V] | Area [Vs] | Lacula 10 15 del | AMP [V] | Area [Vs] | Lacula 10 20 del | AMP [V] | Area [Vs] |
| number | Compound | | | | | | | | | |
| 1 | iC5 | -27.1 | 8.5 | 26.0 | -29.0 | 6.4 | 19.3 | -28.2 | 4.1 | 12.5 |
| 2 | nC5 | -37.2 | 10.1 | 31.0 | -28.8 | 7.5 | 22.8 | -28.0 | 4.8 | 14.7 |
| 3 | 22DMC4 | | | | | | | | | |
| 4 | CYC5 | | | | | | | | | |
| 5 | 23DMC4 | -25.1 | 1.4 | 7.1 | -26.3 | 1.0 | 5.1 | -25.5 | 0.7 | 3.3 |
| 6 | 2MC5 | -28.1 | 6.5 | 22.6 | -29.2 | 4.8 | 16.4 | -28.5 | 3.0 | 10.7 |
| 7 | 3MC5 | -26.7 | 3.0 | 11.2 | -28.0 | 2.1 | 8.1 | -27.6 | 1.3 | 4.9 |
| 8 | nC6 | -25.8 | 9.4 | 33.9 | -29.6 | 7.0 | 24.4 | -28.9 | 4.5 | 15.9 |
| 9 | 22DMC5 | | | | | | | | | |
| 10 | MCYC5 | -23.6 | 5.4 | 19.0 | -25.3 | 3.9 | 13.7 | -24.6 | 2.5 | 8.9 |
| 11 | 24DMc5 | | | | | | | | | |
| 12 | 223TMC4 | | | | | | | | | |
| 13 | Benzene | -25.0 | 0.5 | 2.2 | -26.0 | 0.3 | 1.5 | -24.5 | 0.2 | 1.0 |
| 14 | 33DMC5 | | | | | | | | | |
| 15 | CYC6 | -25.6 | 4.8 | 19.0 | -27.1 | 3.5 | 13.6 | -26.4 | 2.2 | 8.9 |
| 16 | 2MC6 | -25.1 | 2.4 | 9.5 | -27.0 | 1.7 | 6.7 | -26.2 | 1.1 | 4.4 |
| 17 | 23DMC5 | -30.0 | 1.0 | 4.4 | -30.8 | 0.8 | 3.2 | -31.0 | 0.5 | 2.1 |
| 18 | 11DMCYC5 | -26.2 | 0.7 | 3.1 | -27.7 | 0.5 | 2.2 | -27.3 | 0.3 | 1.4 |
| 19 | 3McC6 | -26.5 | 3.0 | 12.4 | -28.3 | 2.1 | 8.8 | -27.9 | 1.3 | 5.6 |
| 20 | 1c3DMCYC5 | -22.4 | 1.6 | 6.5 | -24.0 | 1.1 | 4.6 | -23.4 | 0.7 | 3.0 |
| 21 | 1t3DMCYC5 | -22.4 | 1.5 | 7.3 | -24.2 | 1.1 | 5.2 | -23.6 | 0.7 | 3.3 |
| 22 | 1t2DMCYC5 | -23.5 | 3.5 | 14.7 | -25.3 | 2.5 | 10.6 | -25.0 | 1.5 | 6.6 |
| 23 | nC7 | -27.5 | 7.9 | 40.0 | -29.4 | 6.1 | 28.4 | -29.1 | 4.3 | 18.5 |
| 24 | 22DMC6 | | | | | | | | | |
| 25 | MCYC6 | -24.3 | 7.5 | 38.0 | -26.3 | 5.7 | 27.1 | -25.7 | 4.0 | 17.7 |
| 26 | 1c2DMCYC5 | -29.6 | 0.9 | 5.4 | -29.8 | 0.7 | 3.9 | -29.6 | 0.5 | 2.5 |
| 27 | EtCYC5 | -23.9 | 0.9 | 4.0 | -25.4 | 0.6 | 2.8 | -25.0 | 0.4 | 1.8 |
| 28 | 25DMC6 | -30.3 | 0.4 | 2.0 | -31.5 | 0.3 | 1.5 | -32.4 | 0.2 | 1.0 |
| 29 | 24DMC6 | -24.5 | 0.9 | 4.7 | -26.7 | 0.7 | 3.3 | -26.2 | 0.4 | 2.1 |
| 30 | 1t2c4TMCYC5 | -22.6 | 1.6 | 7.2 | -24.5 | 1.1 | | -23.8 | 0.7 | 3.3 |
| 31 | 33DMC6 | | | | | | | | | |
| 32 | 1t2c3TMCYC5 | | | | | | | | | |
| 33 | 223TMCYC6 | | | | | | | | | |
| 34 | Toluene | -26.6 | 1.4 | 6.9 | -27.7 | 0.9 | 4.6 | -27.0 | 0.6 | 2.9 |
| 35 | 2MC7 | -26.2 | 3.8 | 18.2 | -28.4 | 2.8 | 12.7 | -26.9 | 1.8 | 8.3 |
| 36 | 3MC7 | -23.4 | 2.8 | 15.6 | -25.3 | 2.0 | 11.0 | -24.9 | 1.3 | 7.1 |
| 37 | 1c4DMCYC6 | -26.2 | 1.8 | 8.2 | -28.0 | 1.2 | 5.7 | -27.3 | 0.8 | 3.7 |
| 38 | nC8 | -25.6 | 6.6 | 39.3 | -27.6 | 5.1 | 27.8 | -26.2 | 3.6 | 17.1 |
| 39 | nC9 | -25.2 | 6.2 | 41.2 | -27.4 | 4.8 | 29.1 | -27.1 | 3.4 | 18.8 |

| number | LACULA 12 Hrs<br>Compound | 990811.0 Lacula 12 10<br>del | AMP<br>[V] | Area<br>[Vs] | 990811.0 Lacula 12 8<br>del | AMP<br>[V] | Area<br>[Vs] | 990813.0 Lacula 12 20<br>del | AMP<br>[V] | Area<br>[Vs] | 990813.0 Lacula 12 20<br>del | AMP<br>[V] | Area<br>[Vs] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | iC5 | -26.6 | 0.5 | 1.6 | -26.4 | 0.7 | 2.3 | -27.6 | 5.0 | 15.5 | -27.3 | 4.3 | 13.9 |
| 2 | nC5 | -25.4 | 0.5 | 1.7 | -25.2 | 0.7 | 2.4 | -27.3 | 5.6 | 17.8 | -27.2 | 4.9 | 16.0 |
| 3 | 22DMC4 | | | | | | | | | | | | |
| 4 | CYC5 | | | | | | | | | | | | |
| 5 | 23DMC4 | -24.5 | 0.3 | 1.3 | -23.9 | 0.3 | 1.7 | -25.4 | 0.8 | 4.0 | -25.0 | 0.8 | 3.7 |
| 6 | 2MC5 | -27.4 | 1.2 | 4.4 | -27.1 | 1.6 | 6.0 | -28.2 | 3.7 | 13.2 | -27.9 | 3.2 | 11.7 |
| 7 | 3MC5 | -22.4 | 0.4 | 1.9 | -22.2 | 0.9 | 3.9 | -26.9 | 1.6 | 6.4 | -26.9 | 1.4 | 5.5 |
| 8 | nC6 | -26.3 | 0.7 | 3.1 | -25.6 | 0.9 | 4.3 | -28.2 | 5.5 | 19.3 | -28.0 | 4.8 | 17.6 |
| 9 | 22DMC5 | | | | | | | | | | | | |
| 10 | MCYC5 | -27.4 | 2.3 | 8.6 | -27.7 | 3.1 | 11.5 | -24.4 | 3.0 | 11.0 | -23.8 | 2.7 | 10.1 |
| 11 | 24DMc5 | | | | | | | | | | | | |
| 12 | 223TMC4 | | | | | | | | | | | | |
| 13 | Benzene | -23.6 | 1.6 | 6.3 | -23.8 | 2.2 | 8.5 | -24.9 | 0.2 | 1.1 | -24.3 | 0.2 | 1.1 |
| 14 | 33DMC5 | | | | | | | | | | | | |
| 15 | CYC6 | -25.6 | 1.9 | 8.1 | -25.4 | 2.6 | 10.8 | -26.4 | 2.8 | 11.1 | -25.8 | 2.5 | 10.3 |
| 16 | 2MC6 | -25.8 | 1.0 | 4.2 | -25.4 | 1.3 | 5.6 | -25.9 | 1.3 | 5.3 | -25.2 | 1.2 | 4.8 |
| 17 | 23DMC5 | -30.8 | 0.5 | 2.1 | -29.9 | 0.6 | 2.8 | -30.6 | 0.6 | 2.5 | -30.4 | 0.5 | 2.4 |
| 18 | 11DMCYC5 | -27.3 | 0.3 | 1.4 | -26.5 | 0.5 | 2.0 | -26.7 | 0.4 | 1.7 | -26.8 | 0.4 | 1.7 |
| 19 | 3McC6 | -27.5 | 1.3 | 5.6 | -26.9 | 1.7 | 7.8 | -27.2 | 1.6 | 6.8 | -26.9 | 1.5 | 6.5 |
| 20 | 1c3DMCYC5 | -23.0 | 0.7 | 3.0 | -22.7 | 0.9 | 4.0 | -22.9 | 0.8 | 3.5 | -22.6 | 0.8 | 3.4 |
| 21 | 1t3DMCYC5 | -23.0 | 0.7 | 3.4 | -22.8 | 0.9 | 4.6 | -23.1 | 0.8 | 4.0 | -22.4 | 0.8 | 3.8 |
| 22 | 1t2DMCYC5 | -24.5 | 1.6 | 7.0 | -24.3 | 2.2 | 9.4 | -24.4 | 1.9 | 8.2 | -23.7 | 1.7 | 7.9 |
| 23 | nC7 | -28.7 | 4.6 | 20.0 | -28.4 | 5.8 | 27.0 | -28.8 | 5.2 | 22.5 | -28.5 | 4.8 | 20.8 |
| 24 | 22DMC6 | | | | | | | | | | | | |
| 25 | MCYC6 | -25.4 | 4.6 | 20.9 | -25.2 | 5.9 | 28.0 | -25.6 | 5.0 | 22.2 | -24.7 | 4.6 | 20.6 |
| 26 | 1c2DMCYC5 | -29.4 | 0.5 | 3.1 | -29.3 | 0.7 | 4.1 | -29.3 | 0.6 | 3.1 | -29.3 | 0.5 | 2.9 |
| 27 | EtCYC5 | -24.0 | 0.5 | 2.2 | -24.4 | 0.7 | 3.0 | -23.9 | 0.5 | 2.2 | -23.6 | 0.5 | 2.0 |
| 28 | 25DMC6 | -30.8 | 0.3 | 1.2 | -31.1 | 0.3 | 1.6 | -30.7 | 0.2 | 1.2 | -30.9 | 0.2 | 1.1 |
| 29 | 24DMC6 | -25.4 | 0.5 | 2.7 | -25.6 | 0.7 | 3.7 | -25.7 | 0.5 | 2.6 | -24.6 | 0.5 | 2.5 |
| 30 | 1t2c4TMCYC5 | -23.4 | 0.9 | 4.2 | -23.3 | 1.2 | 5.7 | -23.4 | 0.9 | 4.0 | -23.0 | 0.8 | 3.8 |
| 31 | 33DMC6 | | | | | | | | | | | | |
| 32 | 1t2c3TMCYC5 | | | | | | | | | | | | |
| 33 | 223TMCYC6 | | | | | | | | | | | | |
| 34 | Toluene | -26.8 | 0.7 | 3.6 | -26.7 | 0.9 | 4.9 | -26.8 | 0.6 | 3.4 | -25.8 | 0.6 | 3.2 |
| 35 | 2MC7 | -27.1 | 2.4 | 10.9 | -27.8 | 3.2 | 14.9 | -26.8 | 2.3 | 10.1 | -26.1 | 2.1 | 9.5 |
| 36 | 3MC7 | -24.4 | 1.8 | 9.7 | -24.6 | 2.4 | 13.2 | -24.4 | 1.6 | 8.7 | -24.1 | 1.5 | 8.2 |
| 37 | 1c4DMCYC6 | -27.0 | 1.1 | 5.2 | -27.0 | 1.5 | 7.1 | -26.6 | 1.0 | 4.6 | -26.1 | 0.9 | 4.4 |
| 38 | nC8 | -27.0 | 4.6 | 24.5 | -26.7 | 5.9 | 33.8 | -26.3 | 4.4 | 20.6 | -25.5 | 4.1 | 19.5 |
| 39 | nC9 | -26.8 | 4.6 | 28.0 | -26.5 | 5.9 | 39.1 | -26.8 | 4.1 | 22.8 | -26.0 | 4.0 | 21.9 |

| | LACULA 16 Hrs | 990813.0 | | |
|---|---|---|---|---|
| | | Lacula 16 20 del | AMP [V] | Area [Vs] |
| number | Compound | | | |
| 1 | iC5 | -27.6 | 4.4 | 14.2 |
| 2 | nC5 | -27.4 | 4.9 | 15.7 |
| 3 | 22DMC4 | | | |
| 4 | CYC5 | | | |
| 5 | 23DMC4 | -25.2 | 0.8 | 3.7 |
| 6 | 2MC5 | -28.1 | 3.2 | 11.6 |
| 7 | 3MC5 | -26.7 | 1.4 | 6.0 |
| 8 | nC6 | -28.1 | 4.7 | 17.2 |
| 9 | 22DMC5 | | | |
| 10 | MCYC5 | -24.0 | 2.6 | 10.0 |
| 11 | 24DMc5 | | | |
| 12 | 223TMC4 | | | |
| 13 | Benzene | -24.8 | 0.2 | 1.0 |
| 14 | 33DMC5 | | | |
| 15 | CYC6 | -25.8 | 2.5 | 10.2 |
| 16 | 2MC6 | -25.6 | 1.1 | 4.8 |
| 17 | 23DMC5 | -30.8 | 0.5 | 2.3 |
| 18 | 11DMCYC5 | -26.9 | 0.4 | 1.6 |
| 19 | 3McC6 | -27.2 | 1.4 | 6.1 |
| 20 | 1c3DMCYC5 | -22.7 | 0.8 | 3.2 |
| 21 | 1t3DMCYC5 | -23.1 | 0.7 | 3.6 |
| 22 | 1t2DMCYC5 | -24.3 | 1.6 | 7.5 |
| 23 | nC7 | -28.4 | 4.6 | 19.9 |
| 24 | 22DMC6 | | | |
| 25 | MCYC6 | -25.3 | 4.5 | 20.1 |
| 26 | 1c2DMCYC5 | -29.0 | 0.5 | 2.8 |
| 27 | EtCYC5 | -23.6 | 0.4 | 2.0 |
| 28 | 25DMC6 | -31.6 | 0.2 | 1.1 |
| 29 | 24DMC6 | -24.9 | 0.5 | 2.4 |
| 30 | 1t2c4TMCYC5 | -23.6 | 0.8 | 3.7 |
| 31 | 33DMC6 | | | |
| 32 | 1t2c3TMCYC5 | | | |
| 33 | 223TMCYC6 | | | |
| 34 | Toluene | -25.7 | 0.6 | 3.0 |
| 35 | 2MC7 | -26.0 | 2.0 | 9.2 |
| 36 | 3MC7 | -24.3 | 1.4 | 8.0 |
| 37 | 1c4DMCYC6 | -26.3 | 0.9 | 4.2 |
| 38 | nC8 | -25.6 | 3.9 | 18.4 |
| 39 | nC9 | -26.0 | 3.8 | 20.7 |

| | LACULA 20 Hrs | 990813.0 | | | 990815.0 | | |
|---|---|---|---|---|---|---|---|
| | | Lacula 20 16 del | AMP [V] | Area [Vs] | Lacula 20 16 del | AMP [V] | Area [Vs] |
| number | Compound | | | | | | |
| 1 | iC5 | -27.6 | 5.1 | 16.5 | | 10.7 | |
| 2 | nC5 | -27.5 | 5.5 | 18.0 | | 10.7 | |
| 3 | 22DMC4 | | | | | | |
| 4 | CYC5 | | | | | | |
| 5 | 23DMC4 | -24.9 | 0.9 | 4.4 | -26.0 | 1.9 | 9.3 |
| 6 | 2MC5 | -28.2 | 3.8 | 13.9 | -28.0 | 8.2 | 28.9 |
| 7 | 3MC5 | -27.7 | 1.7 | 6.4 | -27.3 | 3.7 | 15.1 |
| 8 | nC6 | -28.2 | 5.6 | 20.0 | | 10.7 | |
| 9 | 22DMC5 | | | | | | |
| 10 | MCYC5 | -24.4 | 3.2 | 12.0 | -24.5 | 6.9 | 25.3 |
| 11 | 24DMc5 | | | | | | |
| 12 | 223TMC4 | | | | | | |
| 13 | Benzene | -25.0 | 0.2 | 1.2 | -25.7 | 0.5 | 2.4 |
| 14 | 33DMC5 | | | | | 0.5 | |
| 15 | CYC6 | -26.3 | 3.0 | 12.2 | -26.2 | 6.4 | 26.0 |
| 16 | 2MC6 | -25.8 | 1.3 | 5.7 | -25.9 | 3.0 | 12.0 |
| 17 | 23DMC5 | -30.5 | 0.6 | 2.8 | -31.3 | 1.4 | 6.2 |
| 18 | 11DMCYC5 | -27.2 | 0.5 | 1.9 | -27.3 | 1.0 | 4.4 |
| 19 | 3McC6 | -27.1 | 1.7 | 7.3 | -27.4 | 3.7 | 16.2 |
| 20 | 1c3DMCYC5 | -22.9 | 0.9 | 3.9 | -22.9 | 2.0 | 8.5 |
| 21 | 1t3DMCYC5 | -22.9 | 0.9 | 4.3 | -23.4 | 2.0 | 9.5 |
| 22 | 1t2DMCYC5 | -24.6 | 2.1 | 9.0 | -24.9 | 4.5 | 20.2 |
| 23 | nC7 | -28.5 | 5.3 | 23.2 | | 10.7 | |
| 24 | 22DMC6 | | | | | | |
| 25 | MCYC6 | -25.4 | 5.3 | 24.0 | | 10.7 | |
| 26 | 1c2DMCYC5 | -29.1 | 0.6 | 3.4 | -31.2 | 1.3 | 7.0 |
| 27 | EtCYC5 | -23.5 | 0.5 | 2.3 | -24.0 | 1.2 | 5.1 |
| 28 | 25DMC6 | -31.6 | 0.3 | 1.3 | -31.6 | 0.6 | 2.8 |
| 29 | 24DMC6 | -25.4 | 0.6 | 2.9 | -26.2 | 1.2 | 5.9 |
| 30 | 1t2c4TMCYC5 | -23.3 | 0.9 | 4.4 | -23.9 | 2.1 | 9.5 |
| 31 | 33DMC6 | | | | | | |
| 32 | 1t2c3TMCYC5 | | | | | | |
| 33 | 223TMCYC6 | | | | | | |
| 34 | Toluene | -26.0 | 0.7 | 3.4 | -27.6 | 1.5 | 7.6 |
| 35 | 2MC7 | -26.8 | 2.4 | 10.7 | -26.3 | 5.2 | 23.3 |
| 36 | 3MC7 | -24.2 | 1.7 | 9.5 | -24.4 | 3.9 | 20.7 |
| 37 | 1c4DMCYC6 | -26.7 | 1.0 | 5.0 | -27.1 | 2.4 | 11.0 |
| 38 | nC8 | -25.9 | 4.4 | 21.1 | -23.9 | 9.6 | 45.6 |
| 39 | nC9 | -26.2 | 4.2 | 23.0 | -23.8 | 9.4 | 52.8 |

| LOUIS 0 Hrs | | 990515.0 | | | 990516.0 | | | 990314.0 | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Lou 0 80 DEL | AMP [V] | Area [Vs] | Lou 0 75 DEL | AMP [V] | Area [Vs] | Lou 0 120 DEL | AMP [V] | Area [Vs] |
| number | Compound | | | | | | | | | |
| 1 | iC5 | -26.5 | 2.6 | 9.8 | -26.6 | 2.7 | 10.4 | -25.6 | 2.1 | 6.7 |
| 2 | nC5 | -26.0 | 2.7 | 10.6 | -26.1 | 2.8 | 11.2 | -25.2 | 2.1 | 6.6 |
| 3 | 22DMC4 | | | | | | | | | |
| 4 | CYC5 | | | | | | | | | |
| 5 | 23DMC4 | | | | | | | -25.5 | 0.4 | 2.0 |
| 6 | 2MC5 | -26.5 | 2.1 | 9.1 | -26.5 | 2.2 | 9.5 | -25.7 | 1.7 | 5.8 |
| 7 | 3MC5 | -26.6 | 1.5 | 6.3 | -26.3 | 1.5 | 6.6 | -25.7 | 1.2 | 4.5 |
| 8 | nC6 | -26.4 | 3.4 | 13.4 | -26.1 | 3.5 | 13.7 | -26.0 | 2.4 | 8.7 |
| 9 | 22DMC5 | | | | | | | | | |
| 10 | MCYC5 | -24.8 | 1.3 | 5.7 | -24.6 | 1.4 | 5.9 | -24.7 | 1.1 | 3.8 |
| 11 | 24DMC5 | | | | | | | | | |
| 12 | 223TMC4 | | | | | | | | | |
| 13 | Benzene | -27.7 | 0.7 | 3.1 | -27.2 | 0.7 | 3.5 | -26.9 | 0.5 | 1.9 |
| 14 | 33DMC5 | | | | | | | | | |
| 15 | CYC6 | -26.3 | 1.6 | 7.5 | -26.1 | 1.6 | 7.8 | -26.4 | 1.3 | 4.9 |
| 16 | 2MC6 | -24.4 | 1.4 | 6.5 | -24.8 | 1.4 | 6.7 | -23.9 | 1.2 | 4.2 |
| 17 | 23DMC5 | -27.7 | 0.7 | 3.1 | -26.5 | 0.7 | 3.2 | -29.0 | 0.5 | 2.0 |
| 18 | 11DMCYC5 | -27.1 | 0.3 | 1.4 | -26.6 | 0.3 | 1.4 | -26.0 | 0.2 | 0.9 |
| 19 | 3MC6 | -26.3 | 1.6 | 7.8 | -26.5 | 1.6 | 7.8 | -25.9 | 1.3 | 5.2 |
| 20 | 1c3DMCYC5 | -24.5 | 0.5 | 1.8 | -24.9 | 0.5 | 10.8 | -24.8 | 0.3 | 1.1 |
| 21 | 1t3DMCYC5 | -24.2 | 0.4 | 2.4 | -24.5 | 0.5 | 2.4 | -24.3 | 0.3 | 1.5 |
| 22 | 1t2DMCYC5 | -26.0 | 0.7 | 3.1 | -26.5 | 0.7 | 3.0 | -26.4 | 0.5 | 2.0 |
| 23 | nC7 | -27.1 | 3.5 | 15.2 | -26.5 | 3.6 | 15.5 | -26.5 | 2.5 | 9.8 |
| 24 | 22DMC6 | | | | | | | | | |
| 25 | MCYC6 | -25.2 | 4.4 | 19.6 | -24.2 | 4.4 | 20.0 | -25.2 | 3.2 | 13.4 |
| 26 | 1c2DMCYC5 | -31.7 | 0.3 | 2.4 | -30.5 | 0.4 | 2.4 | | | |
| 27 | EtCYC5 | -25.3 | 0.5 | 2.5 | -25.0 | 0.5 | 2.6 | -24.8 | 0.4 | 1.6 |
| 28 | 25DMC6 | -28.0 | 0.5 | 2.0 | -27.6 | 0.5 | 2.1 | -27.8 | 0.3 | 1.4 |
| 29 | 24DMC6 | -17.3 | 0.3 | 1.2 | -17.5 | 0.3 | 1.3 | | | |
| 30 | 1t2c4TMCYC5 | -25.0 | 0.3 | 1.3 | -24.9 | 0.3 | 1.3 | | | |
| 31 | 33DMC6 | | | | | | | | | |
| 32 | 1t2c3TMCYC5 | | | | | | | | | |
| 33 | 223TMCYC6 | | | | | | | | | |
| 34 | Toluene | -26.2 | 1.9 | 9.5 | -26.2 | 2.0 | 9.9 | -26.0 | 1.3 | 6.0 |
| 35 | 2MC7 | -24.9 | 1.5 | 7.3 | -24.7 | 1.6 | 7.6 | -24.2 | 1.2 | 4.8 |
| 36 | 3MC7 | -25.4 | 1.1 | 5.8 | -25.0 | 1.0 | 6.0 | -25.0 | 0.8 | 3.9 |
| 37 | 1c4DMCYC6 | -26.3 | 0.6 | 3.0 | -26.2 | 0.7 | 3.1 | -26.9 | 0.5 | 2.0 |
| 38 | nC8 | -26.1 | 2.8 | 13.3 | -25.9 | 2.9 | 13.9 | -25.6 | 2.1 | 8.5 |
| 39 | nC9 | -26.7 | 2.5 | 12.6 | -26.3 | 2.4 | 12.7 | -26.1 | 1.7 | 8.2 |

| LOUIS 0.5 Hrs | | 990516.0 | | | 990516.0 | | | 990315.0 | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Lou 0.5 40 DEL | AMP [V] | Area [Vs] | Lou 0.5 37 DEL | AMP [V] | Area [Vs] | Lou 0.5 45 DEL | AMP [V] | Area [Vs] |
| number | Compound | | | | | | | | | |
| 1 | iC5 | -25.4 | 1.5 | 5.5 | -25.4 | 1.4 | 5.4 | -25.1 | 0.8 | 2.5 |
| 2 | nC5 | -25.1 | 1.4 | 5.3 | -25.5 | 1.5 | 5.4 | -24.5 | 0.8 | 2.3 |
| 3 | 22DMC4 | | | | | | | | | |
| 4 | CYC5 | | | | | | | | | |
| 5 | 23DMC4 | -25.1 | 0.5 | 2.5 | -25.2 | 0.5 | 2.6 | -24.9 | 0.3 | 1.3 |
| 6 | 2MC5 | -25.5 | 1.6 | 7.6 | -25.9 | 1.7 | 7.8 | -25.1 | 1.1 | 3.8 |
| 7 | 3MC5 | -25.8 | 1.3 | 5.6 | -26.2 | 1.3 | 5.9 | -25.3 | 0.8 | 3.0 |
| 8 | nC6 | -25.8 | 3.0 | 12.0 | -26.1 | 3.2 | 12.5 | -25.1 | 1.7 | 6.2 |
| 9 | 22DMC5 | | | | | | | | | |
| 10 | MCYC5 | -24.4 | 1.3 | 5.9 | -24.7 | 1.4 | 6.5 | -24.5 | 0.9 | 3.3 |
| 11 | 24DMc5 | | | | | | | | | |
| 12 | 223TMC4 | | | | | | | | | |
| 13 | Benzene | -26.8 | 0.7 | 3.1 | -26.8 | 0.7 | 3.3 | -26.4 | 0.4 | 1.5 |
| 14 | 33DMC5 | | | | | | | | | |
| 15 | CYC6 | -25.6 | 1.8 | 8.7 | -25.9 | 2.0 | 9.2 | -25.7 | 1.4 | 5.3 |
| 16 | 2MC6 | -25.2 | 1.7 | 7.8 | -25.7 | 1.9 | 8.2 | -23.4 | 1.3 | 4.9 |
| 17 | 23DMC5 | -24.3 | 0.8 | 3.9 | -24.4 | 0.8 | 4.1 | -25.6 | 0.6 | 2.4 |
| 18 | 11DMCYC5 | -26.6 | 0.4 | 1.8 | -26.6 | 0.4 | 1.8 | -26.0 | 0.3 | 1.1 |
| 19 | 3MC6 | -26.1 | 2.1 | 9.8 | -26.3 | 2.3 | 10.3 | -25.3 | 1.5 | 6.2 |
| 20 | 1c3DMCYC5 | -24.7 | 0.5 | 2.2 | -24.6 | 0.6 | 2.4 | -23.9 | 0.3 | 1.4 |
| 21 | 1t3DMCYC5 | -24.1 | 0.5 | 3.0 | -24.3 | 0.6 | 3.3 | -24.3 | 0.4 | 1.9 |
| 22 | 1t2DMCYC5 | -26.9 | 0.8 | 3.6 | -26.0 | 0.9 | 4.3 | -26.0 | 0.6 | 2.5 |
| 23 | nC7 | -25.2 | 4.5 | 19.7 | -25.2 | 4.7 | 20.5 | -25.9 | 3.2 | 12.8 |
| 24 | 22DMC6 | | | | | | | | | |
| 25 | MCYC6 | -22.4 | 5.6 | 26.4 | -22.3 | 5.9 | 27.7 | -25.0 | 4.5 | 18.9 |
| 26 | 1c2DMCYC5 | -29.5 | 0.5 | 3.4 | -29.3 | 0.5 | 3.4 | -29.6 | 0.3 | 1.8 |
| 27 | EtCYC5 | -24.9 | 0.6 | 3.6 | -25.0 | 0.7 | 3.9 | -24.4 | 0.6 | 2.4 |
| 28 | 25DMC6 | -27.3 | 0.6 | 3.0 | -27.6 | 0.7 | 3.2 | -26.9 | 0.5 | 2.1 |
| 29 | 24DMC6 | -17.0 | 0.4 | 1.8 | -17.4 | 0.5 | 2.0 | -15.7 | 0.3 | 1.2 |
| 30 | 1t2c4TMCYC5 | -24.7 | 0.4 | 1.9 | -24.8 | 0.5 | 2.0 | -24.2 | 0.3 | 1.3 |
| 31 | 33DMC6 | | | | | | | | | |
| 32 | 1t2c3TMCYC5 | | | | | | | | | |
| 33 | 223TMCYC6 | | | | | | | | | |
| 34 | Toluene | -25.8 | 2.9 | 14.0 | -26.2 | 3.1 | 14.7 | -25.6 | 2.0 | 9.0 |
| 35 | 2MC7 | -27.0 | 2.5 | 11.5 | -27.1 | 2.7 | 12.3 | -24.1 | 2.0 | 8.3 |
| 36 | 3MC7 | -26.0 | 1.6 | 9.3 | -26.4 | 1.8 | 9.8 | -24.3 | 1.4 | 6.8 |
| 37 | 1c4DMCYC6 | -26.0 | 1.0 | 4.9 | -26.1 | 1.0 | 5.3 | -25.9 | 0.8 | 3.6 |
| 38 | nC8 | -25.1 | 4.7 | 22.1 | -25.0 | 5.0 | 23.7 | -24.8 | 3.8 | 15.8 |
| 39 | nC9 | -25.9 | 4.6 | 22.7 | -26.2 | 4.8 | 23.7 | -25.9 | 3.6 | 17.3 |

| LOUIS 1 Hrs | | 990516.0 | | | 990516.0 | | | 990517.0 | | | 990517.0 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Lou 1.0 10 | AMP | Area | Lou 1.0 10 | AMP | Area | Lou 1.0 25 | AMP | Area | Lou 1.0 25 | AMP | Area |
| | | DEL | [V] | [Vs] | DEL | [V] | [Vs] | DEL | [V] | [Vs] | DEL | [V] | [Vs] |
| number | Compound | | | | | | | | | | | | |
| 1 | iC5 | -25.1 | 0.8 | 2.7 | -25.0 | 0.9 | 3.2 | -24.8 | 0.4 | 1.3 | -24.9 | 0.4 | 1.4 |
| 2 | nC5 | -24.0 | 0.8 | 2.5 | -23.9 | 0.9 | 3.0 | -23.6 | 0.4 | 1.2 | -24.3 | 0.4 | 1.3 |
| 3 | 22DMC4 | | | | | | | | | | | | |
| 4 | CYC5 | | | | | | | | | | | | |
| 5 | 23DMC4 | -24.8 | 0.5 | 2.2 | -24.6 | 0.5 | 2.5 | | | | | | |
| 6 | 2MC5 | -25.0 | 1.4 | 6.4 | -25.0 | 1.6 | 7.2 | -24.3 | 0.7 | 3.0 | -25.1 | 0.8 | 3.3 |
| 7 | 3MC5 | -25.3 | 1.2 | 5.3 | -24.8 | 1.4 | 6.7 | -25.1 | 0.6 | 2.5 | -24.9 | 0.7 | 3.0 |
| 8 | nC6 | -25.3 | 2.7 | 11.2 | -25.4 | 3.2 | 13.2 | -24.7 | 1.2 | 5.3 | -25.2 | 1.3 | 6.0 |
| 9 | 22DMC5 | | | | | | | | | | | | |
| 10 | MCYC5 | -24.1 | 1.5 | 6.8 | -24.0 | 1.7 | 7.9 | -24.1 | 0.8 | 3.3 | -24.0 | 0.8 | 3.6 |
| 11 | 24DMc5 | | | | | | | | | | | | |
| 12 | 223TMC4 | | | | | | | | | | | | |
| 13 | Benzene | -26.4 | 0.8 | 3.5 | -26.2 | 0.9 | 4.1 | -25.9 | 0.4 | 1.6 | -26.2 | 0.5 | 1.8 |
| 14 | 33DMC5 | | | | | | | | | | | | |
| 15 | CYC6 | -25.5 | 2.8 | 12.6 | -25.8 | 3.2 | 14.2 | -25.4 | 1.2 | 6.0 | -25.5 | 1.3 | 6.5 |
| 16 | 2MC6 | -26.4 | 2.8 | 11.5 | -26.7 | 3.2 | 13.3 | -24.4 | 1.2 | 5.6 | -24.8 | 1.3 | 6.0 |
| 17 | 23DMC5 | -22.1 | 1.2 | 6.4 | -21.1 | 1.4 | 7.2 | -25.7 | 0.7 | 3.0 | -25.2 | 0.7 | 3.3 |
| 18 | 11DMCYC5 | -25.6 | 0.6 | 3.1 | -26.0 | 0.7 | 3.6 | -25.6 | 0.3 | 1.4 | -26.3 | 0.3 | 1.5 |
| 19 | 3MC6 | -25.0 | 3.5 | 15.7 | -25.0 | 4.0 | 17.5 | -25.3 | 1.5 | 7.5 | -25.6 | 1.6 | 8.1 |
| 20 | 1c3DMCYC5 | -23.9 | 0.8 | 3.9 | -23.6 | 0.9 | 4.2 | -23.3 | 0.4 | 1.7 | -23.8 | 0.5 | 1.9 |
| 21 | 1t3DMCYC5 | -23.8 | 0.8 | 5.3 | -23.2 | 0.9 | 5.8 | -23.1 | 0.4 | 2.4 | -23.3 | 0.5 | 2.6 |
| 22 | 1t2DMCYC5 | -25.5 | 1.3 | 7.6 | -25.6 | 1.5 | 7.7 | -25.0 | 0.7 | 3.3 | -25.6 | 0.7 | 3.6 |
| 23 | nC7 | -23.8 | 7.0 | 31.9 | -23.7 | 8.1 | 37.5 | -26.2 | 3.8 | 16.4 | -26.5 | 4.1 | 17.8 |
| 24 | 22DMC6 | | | | | | | | | | | | |
| 25 | MCYC6 | x | 9.3 | 46.9 | | 10.7 | 55.0 | -24.9 | 5.5 | 24.7 | -25.0 | 5.9 | 26.6 |
| 26 | 1c2DMCYC5 | -22.8 | 0.9 | 6.5 | -20.3 | 1.0 | 7.6 | -29.8 | 0.5 | 3.2 | -29.8 | 0.5 | 3.4 |
| 27 | EtCYC5 | -23.8 | 1.1 | 7.4 | -24.1 | 1.3 | 8.2 | -24.4 | 0.6 | 3.4 | -24.4 | 0.6 | 3.7 |
| 28 | 25DMC6 | -27.0 | 1.2 | 6.9 | -27.1 | 1.3 | 7.1 | -27.4 | 0.6 | 3.0 | -27.8 | 0.7 | 3.2 |
| 29 | 24DMC6 | -18.1 | 0.8 | 3.7 | -16.9 | 0.9 | 4.4 | -16.3 | 0.4 | 1.8 | -16.8 | 0.4 | 1.9 |
| 30 | 1t2c4TMCYC5 | -24.2 | 0.8 | 4.0 | -23.9 | 0.9 | 4.6 | -24.0 | 0.4 | 1.9 | -24.1 | 0.5 | 2.1 |
| 31 | 33DMC6 | | | | | | | | | | | | |
| 32 | 1t2c3TMCYC5 | | | | | | | | | | | | |
| 33 | 223TMCYC6 | | | | | | | | | | | | |
| 34 | Toluene | -25.6 | 5.9 | 26.9 | -25.1 | 6.8 | 31.1 | -25.7 | 2.8 | 12.9 | -25.8 | 3.0 | 13.8 |
| 35 | 2MC7 | -25.8 | 5.5 | 26.0 | -26.3 | 6.2 | 25.0 | -27.0 | 2.8 | 12.6 | -26.9 | 2.9 | 13.8 |
| 36 | 3MC7 | -24.6 | 4.8 | 21.9 | -23.8 | 4.5 | 25.3 | -25.1 | 1.9 | 10.4 | -24.4 | 2.1 | 14.0 |
| 37 | 1c4DMCYC6 | -25.8 | 2.4 | 11.5 | -25.1 | 2.9 | 13.7 | -25.7 | 1.1 | 5.8 | -25.8 | 1.2 | 6.1 |
| 38 | nC8 | | 9.7 | 53.0 | | 10.6 | 61.5 | -25.1 | 5.7 | 27.0 | -25.6 | 6.0 | 28.6 |
| 39 | nC9 | | 10.4 | 65.5 | | 10.7 | 73.6 | -25.6 | 6.5 | 33.2 | -26.0 | 6.7 | 34.8 |

| LOUIS 2HRS | | 990518.0 | | | 990316.0 | | | 990316.0 | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Lou 2 25 | AMP | Area | Lou 2b 30 | AMP | Area | Lou 2a 30 | AMP | Area |
| | | DEL | [V] | [Vs] | DEL | [V] | [Vs] | DEL | [V] | [Vs] |
| number | Compound | | | | | | | | | |
| 1 | iC5 | | | | -23.5 | 0.1 | 0.3 | | | |
| 2 | nC5 | | | | -24.2 | 0.1 | 0.3 | | | |
| 3 | 22DMC4 | | | | | | | | | |
| 4 | CYC5 | | | | | | | | | |
| 5 | 23DMC4 | | | | | | | | | |
| 6 | 2MC5 | -26.3 | 0.1 | 0.3 | -25.1 | 0.3 | 0.9 | -24.7 | 0.2 | 0.6 |
| 7 | 3MC5 | -24.9 | 0.1 | 0.2 | -25.5 | 0.2 | 0.8 | -24.9 | 0.2 | 0.6 |
| 8 | nC6 | -25.2 | 0.2 | 0.7 | -24.6 | 0.5 | 1.7 | -23.7 | 0.3 | 1.3 |
| 9 | 22DMC5 | | | | | | | | | |
| 10 | MCYC5 | -24.9 | 0.2 | 0.6 | -24.4 | 0.4 | 1.3 | -25.1 | 0.3 | 1.0 |
| 11 | 24DMc5 | | | | | | | | | |
| 12 | 223TMC4 | | | | | | | | | |
| 13 | Benzene | -26.1 | 0.1 | 0.3 | -25.7 | 0.1 | 0.6 | -31.8 | 0.1 | 0.3 |
| 14 | 33DMC5 | | | | | | | | | |
| 15 | CYC6 | -25.5 | 0.4 | 1.6 | -26.1 | 0.7 | 2.7 | -25.3 | 0.6 | 2.4 |
| 16 | 2MC6 | -23.2 | 0.4 | 1.7 | -23.2 | 0.7 | 2.6 | -23.3 | 0.7 | 2.4 |
| 17 | 23DMC5 | -28.7 | 0.2 | 0.9 | -28.8 | 0.3 | 1.4 | -28.4 | 0.3 | 1.3 |
| 18 | 11DMCYC5 | -26.2 | 0.1 | 0.5 | -24.7 | 0.2 | 0.7 | -25.8 | 0.1 | 0.6 |
| 19 | 3McC6 | -25.2 | 0.6 | 2.4 | -25.6 | 0.9 | 3.5 | -25.1 | 0.8 | 3.3 |
| 20 | 1c3DMCYC5 | -24.5 | 0.1 | 0.5 | -24.2 | 0.2 | 0.8 | -23.3 | 0.2 | 0.8 |
| 21 | 1t3DMCYC5 | -23.5 | 0.1 | 0.8 | -23.5 | 0.2 | 1.2 | -23.6 | 0.2 | 1.1 |
| 22 | 1t2DMCYC5 | -26.2 | 0.3 | 1.1 | -25.9 | 0.4 | 1.6 | -25.5 | 0.4 | 1.5 |
| 23 | nC7 | -26.0 | 1.2 | 6.2 | -26.0 | 2.1 | 8.4 | -25.3 | 2.0 | 8.2 |
| 24 | 22DMC6 | | | | | | | | | |
| 25 | MCYC6 | -25.2 | 2.3 | 11.4 | -24.9 | 3.4 | 14.5 | -24.5 | 3.4 | -30.4 |
| 26 | 1c2DMCYC5 | -31.1 | 0.2 | 1.5 | -30.7 | 0.3 | 1.5 | -30.4 | 0.3 | 1.4 |
| 27 | EtCYC5 | -24.6 | 0.3 | 1.7 | -24.3 | 0.5 | 2.0 | -23.8 | 0.5 | 2.0 |
| 28 | 25DMC6 | -27.4 | 0.3 | 1.6 | -26.6 | 0.4 | 1.9 | -26.5 | 0.4 | 1.9 |
| 29 | 24DMC6 | | | | -15.4 | 0.3 | 1.1 | -14.8 | 0.3 | 1.1 |
| 30 | 1t2c4TMCYC5 | -24.1 | 0.2 | 1.1 | -24.7 | 0.3 | 1.2 | -24.2 | 0.3 | 1.3 |
| 31 | 33DMC6 | | | | | | | | | |
| 32 | 1t2c3TMCYC5 | | | | | | | | | |
| 33 | 223TMCYC6 | | | | | | | | | |
| 34 | Toluene | -25.5 | 1.4 | 6.5 | -25.7 | 1.6 | 7.5 | -24.9 | 1.7 | 7.6 |
| 35 | 2MC7 | -25.2 | 1.7 | 8.0 | -23.6 | 2.1 | 8.7 | -23.5 | 2.2 | 8.9 |
| 36 | 3MC7 | -22.4 | 1.4 | 7.0 | -21.1 | 1.8 | 7.4 | -24.5 | 1.6 | 7.5 |
| 37 | 1c4DMCYC6 | -25.8 | 0.8 | 4.1 | -26.3 | 1.0 | 4.2 | -25.2 | 1.0 | 4.3 |
| 38 | nC8 | -26.1 | 4.4 | 20.4 | -25.3 | 4.5 | 19.1 | -24.5 | 4.7 | 19.9 |
| 39 | nC9 | -26.4 | 6.9 | 34.1 | -25.9 | 5.8 | 28.7 | -24.9 | 6.0 | 29.6 |

| Con't | LOUIS 2HRS | 990517.0 | | | 990517.0 | | | 990518.0 | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Lou 2 0 DEL | AMP [V] | Area [Vs] | Lou 2 0 DEL | AMP [V] | Area [Vs] | Lou 2 25 DEL | AMP [V] | Area [Vs] |
| number | Compound | | | | | | | | | |
| 1 | iC5 | -24.4 | 0.3 | 0.9 | | | | | | |
| 2 | nC5 | -23.2 | 0.2 | 0.7 | | | | | | |
| 3 | 22DMC4 | | | | | | | | | |
| 4 | CYC5 | | | | | | | | | |
| 5 | 23DMC4 | | | | | | | | | |
| 6 | 2MC5 | -24.4 | 1.0 | 4.5 | -24.2 | 0.8 | 3.2 | | | |
| 7 | 3MC5 | -21.7 | 1.0 | 4.3 | -22.0 | 0.6 | 2.8 | | | |
| 8 | nC6 | -24.2 | 1.0 | 5.2 | -24.1 | 0.8 | 3.7 | | | |
| 9 | 22DMC5 | | | | | | | | | |
| 10 | MCYC5 | -24.5 | 2.0 | 9.7 | -23.9 | 1.6 | 6.9 | | | |
| 11 | 24DMc5 | | | | | | | | | |
| 12 | 223TMC4 | | | | | | | | | |
| 13 | Benzene | -23.7 | 1.7 | 8.1 | -23.1 | 1.4 | 6.1 | | | |
| 14 | 33DMC5 | | | | | | | | | |
| 15 | CYC6 | -25.1 | 4.1 | 20.1 | -24.6 | 4.3 | 16.1 | -24.5 | 0.5 | 2.0 |
| 16 | 2MC6 | -24.9 | 4.4 | 19.9 | -21.9 | 5.0 | 16.8 | -22.5 | 0.5 | 2.1 |
| 17 | 23DMC5 | -24.2 | 2.2 | 12.0 | -28.9 | 2.7 | 10.2 | | | |
| 18 | 11DMCYC5 | -25.5 | 1.0 | 5.8 | -25.5 | 1.3 | 5.2 | | | |
| 19 | 3McC6 | -25.1 | 6.0 | 29.7 | -24.8 | 7.0 | 26.4 | -24.8 | 0.7 | 2.8 |
| 20 | 1c3DMCYC5 | -23.0 | 1.4 | 7.3 | -22.4 | 1.8 | 6.9 | | | |
| 21 | 1t3DMCYC5 | -22.5 | 1.4 | 10.3 | -22.0 | 2.0 | 9.7 | | | |
| 22 | 1t2DMCYC5 | -25.4 | 2.5 | 16.2 | | | | | | |
| 23 | nC7 | | | | | | | -25.8 | 1.4 | 7.3 |
| 24 | 22DMC6 | | | | | | | | | |
| 25 | MCYC6 | | | | | | | -24.6 | 2.6 | 12.9 |
| 26 | 1c2DMCYC5 | -25.8 | 2.4 | 17.8 | | | | | | |
| 27 | EtCYC5 | -22.9 | 2.9 | 19.9 | | | | | | |
| 28 | 25DMC6 | -26.7 | 3.3 | 19.7 | | | | | | |
| 29 | 24DMC6 | -14.4 | 2.1 | 10.4 | | | | | | |
| 30 | 1t2c4TMCYC5 | -40.1 | 1.2 | 7.5 | | | | | | |
| 31 | 33DMC6 | | | | | | | | | |
| 32 | 1t2c3TMCYC5 | | | | | | | | | |
| 33 | 223TMCYC6 | | | | | | | | | |
| 34 | Toluene | | | | | | | -25.1 | 1.5 | 7.3 |
| 35 | 2MC7 | | | | | | | -24.9 | 1.8 | 8.6 |
| 36 | 3MC7 | | | | | | | -25.2 | 1.4 | 7.4 |
| 37 | 1c4DMCYC6 | | | | | | | -25.1 | 0.9 | 4.3 |
| 38 | nC8 | | | | | | | -25.4 | 4.5 | 21.1 |
| 39 | nC9 | | | | | | | -25.7 | 6.7 | 33.1 |

| LOUIS 3Hrs | | 990519.0 | | | 990521.0 | | | 990522.0 | | | 990522.0 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Lou 3 0 | AMP | Area | Lou 3 25 | AMP | Area | Lou 3 10 | AMP | Area | Lou 3 10 | AMP | Area |
| | | DEL | [V] | [Vs] | DEL | [V] | [Vs] | DEL | [V] | [Vs] | DEL | [V] | [Vs] |
| number | Compound | | | | | | | | | | | | |
| 1 | iC5 | | | | | | | | | | -26.5 | 0.1 | 0.4 |
| 2 | nC5 | | | | | | | | | | -26.8 | 0.1 | 0.3 |
| 3 | 22DMC4 | | | | | | | | | | | | |
| 4 | CYC5 | | | | | | | | | | | | |
| 5 | 23DMC4 | | | | | | | | | | | | |
| 6 | 2MC5 | -25.1 | 0.4 | 1.8 | | | | | | | -25.8 | 0.2 | 1.2 |
| 7 | 3MC5 | -25.1 | 0.4 | 1.8 | | | | | | | -25.5 | 0.2 | 1.1 |
| 8 | nC6 | -24.6 | 0.8 | 3.7 | | | | | | | -26.0 | 0.5 | 2.5 |
| 9 | 22DMC5 | | | | | | | | | | | | |
| 10 | MCYC5 | -23.7 | 0.9 | 3.8 | | | | | | | -23.4 | 0.6 | 2.3 |
| 11 | 24DMc5 | | | | | | | | | | | | |
| 12 | 223TMC4 | | | | | | | | | | | | |
| 13 | Benzene | -25.5 | 0.5 | 2.2 | | | | | | | -26.1 | 0.3 | 1.5 |
| 14 | 33DMC5 | | | | | | | -25.3 | | | | | |
| 15 | CYC6 | -25.6 | 2.0 | 10.6 | -25.4 | 0.1 | 0.6 | -22.7 | 0.3 | 1.3 | -25.0 | 1.3 | 6.7 |
| 16 | 2MC6 | -23.4 | 2.2 | 10.8 | -22.1 | 0.2 | 0.6 | -28.5 | 0.3 | 1.4 | -22.0 | 1.4 | 6.9 |
| 17 | 23DMC5 | -26.3 | 1.2 | 6.5 | | | | -26.7 | 0.2 | 0.8 | -29.2 | 0.8 | 4.1 |
| 18 | 11DMCYC5 | -25.8 | 0..607 | 3.2 | -25.0 | 0.2 | 0.9 | -25.6 | 0.5 | 0.4 | -26.3 | 0.4 | 2.1 |
| 19 | 3McC6 | -25.5 | 3.2 | 16.5 | -25.0 | 0.2 | 0.9 | -23.7 | 0.5 | 2.0 | -25.1 | 1.9 | 10.6 |
| 20 | 1c3DMCYC5 | -23.2 | 0.8 | 4.0 | -24.3 | 0.1 | 0.2 | -23.2 | 0.1 | 0.5 | -24.1 | 0.5 | 2.3 |
| 21 | 1t3DMCYC5 | -22.7 | 0.8 | 5.8 | -25.8 | 0.1 | 0.3 | -25.6 | 0.1 | 0.7 | -23.3 | 0.6 | 3.6 |
| 22 | 1t2DMCYC5 | -25.7 | 1.5 | 9.2 | -27.4 | 0.1 | 0.4 | -25.7 | 0.2 | 1.0 | -27.3 | 1.0 | 5.2 |
| 23 | nC7 | | | | -25.0 | 0.6 | 2.5 | | 1.1 | 5.6 | -25.6 | 5.9 | 28.8 |
| 24 | 22DMC6 | | | | | | | -24.3 | | | | | |
| 25 | MCYC6 | | | | -24.1 | 1.1 | 5.0 | | 2.3 | 11.7 | | | |
| 26 | 1c2DMCYC5 | -25.3 | 1.5 | 12.5 | | | | -24.7 | | | -28.0 | 1.1 | 9.1 |
| 27 | EtCYC5 | -23.2 | 2.0 | 13.5 | | | | -27.6 | 0.4 | 1.8 | -23.9 | 1.5 | 9.1 |
| 28 | 25DMC6 | -27.0 | 2.2 | 14.0 | -26.4 | 0.2 | 0.8 | | 0.4 | 1.8 | -28.1 | 1.6 | 8.9 |
| 29 | 24DMC6 | -24.8 | 1.5 | 12.8 | | | | | | | | 1.1 | 5.3 |
| 30 | 1t2c4TMCYC5 | -23.6 | 1.5 | 8.9 | | | | | | | -24.0 | 1.2 | 6.3 |
| 31 | 33DMC6 | | | | | | | | | | | | |
| 32 | 1t2c3TMCYC5 | | | | | | | | | | | | |
| 33 | 223TMCYC6 | | | | | | | | | | | | |
| 34 | Toluene | | | | -25.1 | 0.6 | 3.0 | -25.1 | 1.4 | 6.8 | -25.0 | 7.0 | 34.4 |
| 35 | 2MC7 | | | | -23.5 | 1.0 | 4.5 | -24.0 | 2.1 | 10.0 | -21.5 | 8.8 | 50.0 |
| 36 | 3MC7 | | | | -25.5 | 0.8 | 4.0 | -25.2 | 1.7 | 9.0 | -24.9 | 6.8 | 56.5 |
| 37 | 1c4DMCYC6 | | | | -26.1 | 0.5 | 2.5 | -26.1 | 1.2 | 5.6 | -25.1 | 5.5 | 28.9 |
| 38 | nC8 | | | | -24.9 | 2.6 | 12.6 | -25.1 | 5.8 | 27.6 | | | |
| 39 | nC9 | | | | -25.0 | 5.5 | 26.9 | | | | | | |

# APPENDIX B

Appendix B contains the normalized abundance and corrected $\delta^{13}C$ data for the 21 gasoline-range compounds used for final discussion and statistical treatment.

ALB – Alberta Sweet Mixed Blend

LAC – Lacula

LOU - Louisiana

| Compound | ALB 0hrs Cx/nC9 **ABUN.** | ALB 0.5hrs Cx/nC9 **ABUN.** | ALB 1hrs Cx/nC9 **ABUN.** | ALB 2hrs Cx/nC9 **ABUN.** | ALB 3hrs Cx/nC9 **ABUN.** | ALB 4hrs Cx/nC9 **ABUN.** | ALB 6hrs Cx/nC9 **ABUN.** | ALB 9hrs Cx/nC9 **ABUN.** | ALB 10hrs Cx/nC9 **ABUN.** | ALB 12hrs Cx/nC9 **ABUN.** | ALB 14hrs Cx/nC9 **ABUN.** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| iC5 | 1.4 | 0.5 | 0.3 | 0.2 | 0.1 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| nC5 | 1.7 | 0.6 | 0.4 | 0.2 | 0.1 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 2MC5 | 0.9 | 0.5 | 0.4 | 0.2 | 0.1 | 0.1 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 |
| 3MC5 | 0.6 | 0.3 | 0.3 | 0.1 | 0.1 | 0.1 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 |
| nC6 | 1.5 | 0.8 | 0.7 | 0.3 | 0.2 | 0.2 | 0.1 | 0.1 | 0.0 | 0.1 | 0.1 |
| MCYC5 | 0.9 | 0.6 | 0.5 | 0.3 | 0.2 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 |
| CYC6 | 0.7 | 0.5 | 0.4 | 0.3 | 0.2 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 |
| 11DMCYC5 | 0.1 | 0.1 | 0.1 | 0.1 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 3MC6 | 0.5 | 0.4 | 0.3 | 0.2 | 0.2 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 |
| 1c3DMCYC5 | 0.4 | 0.3 | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 | 0.0 | 0.0 | 0.1 | 0.1 |
| 1t3DMCYC5 | 0.4 | 0.3 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 | 0.0 | 0.1 | 0.1 | 0.1 |
| 1t2DMCYC5 | 0.7 | 0.5 | 0.4 | 0.3 | 0.2 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 |
| nC7 | 1.4 | 1.0 | 0.9 | 0.6 | 0.4 | 0.5 | 0.4 | 0.2 | 0.2 | 0.2 | 0.2 |
| MCYC6 | 1.5 | 1.1 | 1.1 | 0.7 | 0.6 | 0.6 | 0.6 | 0.3 | 0.3 | 0.3 | 0.4 |
| EtCYC5 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.0 | 0.0 | 0.0 | 0.1 |
| 25DMC6 | 0.1 | 0.1 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Toluene | 0.9 | 0.7 | 0.7 | 0.5 | 0.4 | 0.4 | 0.3 | 0.1 | 0.1 | 0.1 | 0.2 |
| 2MC7 | 0.6 | 0.5 | 0.5 | 0.4 | 0.3 | 0.3 | 0.3 | 0.2 | 0.2 | 0.2 | 0.2 |
| 1c4DMCYC6 | 0.2 | 0.2 | 0.2 | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| nC8 | 1.1 | 1.0 | 1.0 | 0.8 | 0.7 | 0.7 | 0.7 | 0.4 | 0.4 | 0.4 | 0.5 |
| nC9 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |

| Compound | CORR **ALB** 0hrs **$\delta^{13}C$ ‰** | CORR **ALB** 0.5hrs **$\delta^{13}C$ ‰** | CORR **ALB** 1hrs **$\delta^{13}C$ ‰** | CORR **ALB** 2hrs **$\delta^{13}C$ ‰** | CORR **ALB** 3hrs **$\delta^{13}C$ ‰** | CORR **ALB** 4hrs **$\delta^{13}C$ ‰** | CORR **ALB** 6hrs **$\delta^{13}C$ ‰** | CORR **ALB** 9hrs **$\delta^{13}C$ ‰** | CORR **ALB** 10hrs **$\delta^{13}C$ ‰** | CORR **ALB** 12hrs **$\delta^{13}C$ ‰** | CORR **ALB** 14hrs **$\delta^{13}C$ ‰** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| iC5 | -28.5 | -28.8 | -28.8 | -28.6 | -27.5 | -27.9 | -27.4 | -25.4 | -26.4 | | |
| nC5 | -29.2 | -29.2 | -29.1 | -28.9 | -28.1 | -27.8 | -27.8 | -26.2 | -27.0 | | |
| 2MC5 | -28.5 | -28.6 | -28.5 | -28.3 | -27.6 | -27.9 | -27.3 | -26.2 | -26.9 | -27.0 | -27.1 |
| 3MC5 | -27.5 | -27.7 | -27.5 | -27.2 | -26.8 | -27.2 | -26.6 | -26.8 | -26.2 | -25.8 | -25.2 |
| nC6 | -29.9 | -30.0 | -29.8 | -29.6 | -29.0 | -29.4 | -28.6 | -27.6 | -27.6 | -27.8 | -28.1 |
| MCYC5 | -26.3 | -26.9 | -26.8 | -26.5 | -25.8 | -25.9 | -25.5 | -23.8 | -24.4 | -24.7 | -24.8 |
| CYC6 | -29.8 | -29.9 | -29.8 | -29.6 | -29.4 | -29.2 | -28.9 | -28.1 | -28.4 | -28.2 | -28.9 |
| 11DMCYC5 | -27.3 | -27.5 | -27.5 | -27.3 | -27.3 | -26.7 | -26.6 | -26.7 | -26.5 | -25.2 | -26.5 |
| 3MC6 | -28.0 | -28.1 | -28.0 | -27.8 | -27.2 | -27.5 | -27.2 | -26.2 | -26.5 | -26.1 | -26.4 |
| 1c3DMCYC5 | -25.5 | -25.7 | -25.7 | -25.3 | -24.8 | -24.8 | -24.0 | -23.5 | -23.3 | -23.2 | -23.8 |
| 1t3DMCYC5 | -25.2 | -25.3 | -25.3 | -24.8 | -24.5 | -25.1 | -24.6 | -23.4 | -23.5 | -23.3 | -23.7 |
| 1t2DMCYC5 | -25.9 | -25.9 | -26.0 | -25.6 | -25.7 | -25.5 | -24.5 | -25.3 | -25.4 | -25.1 | -25.8 |
| nC7 | -30.0 | -30.0 | -30.1 | -29.5 | -30.0 | -30.2 | -29.4 | -28.7 | -29.0 | -28.6 | -29.0 |
| MCYC6 | -27.9 | -28.5 | -28.3 | -28.2 | -26.9 | -26.9 | -25.2 | -26.2 | -26.4 | -26.2 | -26.1 |
| EtCYC5 | -27.5 | -27.8 | -27.3 | -27.1 | -26.2 | -26.6 | -26.1 | -25.4 | -25.2 | -24.7 | -25.0 |
| 25DMC6 | -31.5 | -32.0 | -32.2 | -31.7 | -32.0 | -31.7 | -30.6 | -32.2 | -32.2 | -30.6 | -31.3 |
| Toluene | | -29.6 | -29.9 | -29.1 | -28.7 | -29.3 | -28.5 | -27.9 | -27.7 | -28.4 | -27.8 |
| 2MC7 | -28.0 | -28.4 | -28.4 | -27.9 | -28.0 | -28.3 | -27.4 | -27.9 | -27.5 | -27.4 | -27.2 |
| 1c4DMCYC6 | -28.3 | -28.5 | -28.1 | -27.5 | -27.4 | -27.5 | -27.1 | -26.7 | -26.9 | -26.9 | -26.9 |
| nC8 | -29.5 | -29.2 | -28.6 | -28.4 | -28.4 | -27.6 | -27.3 | -28.2 | -27.7 | -28.0 | -27.0 |
| nC9 | -30.0 | -29.5 | -29.2 | -28.4 | -28.8 | -30.0 | | | | -27.6 | -27.4 |

| | LAC 0hrs Cx/nC9 ABUN. | LAC 0.5hrs Cx/nC9 ABUN. | LAC 1hrs Cx/nC9 ABUN. | LAC 2hrs Cx/nC9 ABUN. | LAC 3hrs Cx/nC9 ABUN. | LAC 4hrs Cx/nC9 ABUN. | LAC 5hrs Cx/nC9 ABUN. | LAC 6hrs Cx/nC9 ABUN. | LAC 7hrs Cx/nC9 ABUN. | LAC 8hrs Cx/nC9 ABUN. | LAC 10hrs Cx/nC9 ABUN. | LAC 12hrs Cx/nC9 ABUN. | LAC 16hrs Cx/nC9 ABUN. | LAC 20hrs Cx/nC9 ABUN. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | | | | | | | | | | | | | | |
| iC5 | 0.9 | 0.9 | 0.7 | 0.8 | 0.7 | 0.7 | 0.7 | 0.7 | 0.7 | 0.6 | 0.6 | 0.7 | 0.7 | 0.7 |
| nC5 | 1.3 | 1.3 | 1.0 | 1.1 | 0.8 | 1.0 | 0.9 | 0.9 | 0.8 | 0.7 | 0.8 | 0.8 | 0.8 | 0.8 |
| 2MC5 | 0.7 | 0.7 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.5 | 0.6 | 0.6 | 0.6 | 0.6 |
| 3MC5 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 |
| nC6 | 1.2 | 1.2 | 1.0 | 1.0 | 1.0 | 0.9 | 0.9 | 0.9 | 0.9 | 0.8 | 0.8 | 0.8 | 0.8 | 0.9 |
| MCYC5 | 0.6 | 0.6 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| CYC6 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.4 | 0.4 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| 11DMCYC5 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| 3MC6 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 |
| 1c3DMCYC5 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| 1t3DMCYC5 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| 1t2DMCYC5 | 0.4 | 0.4 | 0.4 | 0.4 | 0.3 | 0.3 | 0.3 | 0.3 | 0.4 | 0.3 | 0.4 | 0.4 | 0.4 | 0.4 |
| nC7 | 1.3 | 1.3 | 1.1 | 1.1 | 1.1 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| MCYC6 | 1.0 | 1.0 | 0.9 | 1.0 | 0.9 | 0.9 | 0.9 | 0.9 | 1.0 | 0.9 | 0.9 | 1.0 | 1.0 | 1.0 |
| EtCYC5 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| 25DMC6 | 0.1 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.1 | 0.1 | 0.1 |
| Toluene | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 |
| 2MC7 | 0.5 | 0.5 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.5 | 0.4 | 0.4 | 0.4 | 0.4 | 0.5 |
| 1c4DMCYC6 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| nC8 | 1.0 | 1.0 | 1.0 | 1.0 | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 | 1.0 | 0.9 | 0.9 | 0.9 | 0.9 |
| nC9 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |

| | CORR LAC 0hrs $\delta^{13}C$ ‰ | CORR LAC 0.5hrs $\delta^{13}C$ ‰ | CORR LAC 1hrs $\delta^{13}C$ ‰ | CORR LAC 2hrs $\delta^{13}C$ ‰ | CORR LAC 3hrs $\delta^{13}C$ ‰ | CORR LAC 4hrs $\delta^{13}C$ ‰ | CORR LAC 5hrs $\delta^{13}C$ ‰ | CORR LAC 6hrs $\delta^{13}C$ ‰ | CORR LAC 7hrs $\delta^{13}C$ ‰ | CORR LAC 8hrs $\delta^{13}C$ ‰ | CORR LAC 10hrs $\delta^{13}C$ ‰ | CORR LAC 12hrs $\delta^{13}C$ ‰ | CORR LAC 16hrs $\delta^{13}C$ ‰ | CORR LAC 20hrs $\delta^{13}C$ ‰ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | | | | | | | | | | | | | | |
| iC5 | -27.9 | -28.4 | -27.4 | -27.4 | -27.4 | -27.6 | -27.8 | -28.2 | -27.1 | -26.2 | -27.8 | -26.6 | -26.6 | -26.7 |
| nC5 | -28.3 | -27.8 | -27.7 | -27.5 | -27.2 | -29.3 | -27.8 | -28.3 | -27.2 | -25.4 | -28.0 | -25.9 | -26.8 | -26.8 |
| 2MC5 | -28.1 | -28.6 | -27.9 | -27.8 | -27.8 | -27.7 | -28.0 | -28.3 | -27.1 | -26.7 | -27.8 | -27.0 | -27.3 | -27.2 |
| 3MC5 | -27.3 | -27.6 | -27.8 | -26.6 | -27.4 | -27.4 | -27.2 | -27.3 | -26.7 | -26.2 | -26.5 | -23.9 | -26.1 | -26.6 |
| nC6 | -28.5 | -28.8 | -28.3 | -27.8 | -28.1 | -27.7 | -28.1 | -28.3 | -27.2 | -26.1 | -27.4 | -26.4 | -27.3 | -27.4 |
| MCYC5 | -24.2 | -24.2 | -24.0 | -23.7 | -24.0 | -24.1 | -23.2 | -23.4 | -23.4 | -21.7 | -23.2 | -23.4 | -22.6 | -23.3 |
| CYC6 | -26.0 | -25.9 | -25.9 | -25.4 | -25.6 | -25.7 | -26.0 | -26.1 | -25.3 | -24.6 | -25.7 | -25.2 | -25.2 | -25.5 |
| 11DMCYC5 | -27.0 | -26.3 | -25.9 | -25.5 | -26.5 | -26.2 | -26.9 | -26.6 | -26.1 | -25.8 | -25.7 | -25.7 | -25.9 | -26.1 |
| 3McC6 | -27.1 | -27.4 | -26.8 | -26.4 | -27.0 | -26.9 | -27.2 | -27.2 | -26.4 | -25.9 | -26.7 | -26.4 | -26.5 | -26.4 |
| 1c3DMCYC5 | -22.8 | -23.3 | -22.6 | -22.3 | -23.0 | -23.1 | -23.1 | -23.2 | -22.2 | -21.9 | -22.4 | -22.2 | -22.3 | -22.0 |
| 1t3DMCYC5 | -22.6 | -23.1 | -22.6 | -22.2 | -22.9 | -22.9 | -22.8 | -22.9 | -22.7 | -22.1 | -22.6 | -22.1 | -22.3 | -22.1 |
| 1t2DMCYC5 | -24.5 | -24.3 | -23.9 | -23.4 | -23.9 | -24.1 | -24.3 | -24.3 | -24.1 | -23.0 | -23.7 | -23.6 | -23.8 | -23.7 |
| nC7 | -28.7 | -28.6 | -28.1 | -27.7 | -27.5 | -27.8 | -28.2 | -28.5 | -27.5 | -26.4 | -27.8 | -27.8 | -27.9 | -28.0 |
| MCYC6 | -25.0 | -24.8 | -23.5 | -23.0 | -24.3 | -24.5 | -24.4 | -24.7 | -23.5 | -23.5 | -24.7 | -24.6 | -24.7 | -24.7 |
| EtCYC5 | -24.0 | -24.6 | -23.8 | -23.9 | -24.8 | -24.7 | -24.5 | -24.4 | -24.5 | -23.3 | -23.8 | -23.3 | -23.3 | -23.0 |
| 25DMC6 | -30.5 | -29.8 | -30.0 | -30.1 | -30.0 | -29.8 | -30.1 | -30.3 | -30.5 | -29.7 | -29.6 | -29.5 | -30.6 | -30.2 |
| Toluene | -26.9 | -26.8 | -26.7 | -26.0 | -27.0 | -26.9 | -27.4 | -27.4 | -25.8 | -25.7 | -26.7 | -26.2 | -25.0 | -25.3 |
| 2MC7 | -27.4 | -27.6 | -26.7 | -26.3 | -27.3 | -27.4 | -26.9 | -27.2 | -27.1 | -27.3 | -27.8 | -27.4 | -26.8 | -27.3 |
| 1c4DMCYC6 | -26.2 | -26.8 | -26.8 | -26.2 | -26.1 | -26.2 | -27.2 | -26.7 | -25.8 | -25.4 | -26.0 | -25.7 | -25.2 | -25.8 |
| nC8 | -26.2 | -27.2 | -26.1 | -25.7 | -26.2 | -26.5 | -27.4 | -27.5 | -25.4 | -26.3 | -26.8 | -26.6 | -25.8 | -25.1 |
| nC9 | -26.5 | -27.5 | -27.3 | -26.9 | -27.2 | -27.0 | -27.1 | -27.0 | -24.4 | -26.6 | -26.4 | -26.4 | -25.6 | -25.0 |

| compound | LOU 0hrs Cx/nC9 **ABUND.** | LOU 0.5hrs Cx/nC9 **ABUND.** | LOU 1hrs Cx/nC9 **ABUND.** | LOU 2hrs Cx/nC9 **ABUND.** | LOU 3hrs Cx/nC9 **ABUND.** | CORR LOU 0hrs **$\delta^{13}C$ ‰** | CORR LOU 0.5hrs **$\delta^{13}C$ ‰** | CORR LOU 1hrs **$\delta^{13}C$ ‰** | CORR LOU 2hrs **$\delta^{13}C$ ‰** | CORR LOU 3hrs **$\delta^{13}C$ ‰** |
|---|---|---|---|---|---|---|---|---|---|---|
| iC5 | 0.8 | 0.2 | 0.0 | 0.0 | 0.0 | -25.6 | -24.9 | -24.2 | | |
| nC5 | 0.8 | 0.2 | 0.0 | 0.0 | 0.0 | -24.9 | -24.6 | -23.3 | | |
| 2MC5 | 0.7 | 0.3 | 0.1 | 0.0 | 0.0 | -25.5 | -25.0 | -24.2 | -24.3 | |
| 3MC5 | 0.5 | 0.2 | 0.1 | 0.0 | 0.0 | -25.5 | -25.6 | -24.5 | -23.4 | |
| nC6 | 1.1 | 0.5 | 0.2 | 0.1 | 0.0 | -25.8 | -25.2 | -24.5 | -23.8 | |
| MCYC5 | 0.5 | 0.2 | 0.1 | 0.0 | 0.0 | -24.5 | -24.6 | -23.8 | -24.1 | -23.4 |
| CYC6 | 0.6 | 0.4 | 0.2 | 0.1 | 0.0 | -26.4 | -25.9 | -25.5 | -24.8 | -24.6 |
| 11DMCYC5 | 0.1 | 0.1 | 0.0 | 0.0 | 0.0 | -26.3 | -26.3 | -25.6 | -25.3 | -25.2 |
| 3MC6 | 0.6 | 0.4 | 0.2 | 0.1 | 0.0 | -25.8 | -25.6 | -24.6 | -24.6 | -24.5 |
| 1c3DMCYC5 | 0.1 | 0.1 | 0.1 | 0.0 | 0.0 | -24.6 | -24.6 | -23.7 | -23.2 | -23.5 |
| 1t3DMCYC5 | 0.2 | 0.1 | 0.1 | 0.0 | 0.0 | -23.6 | -24.6 | -23.9 | -23.1 | -24.3 |
| 1t2DMCYC5 | 0.2 | 0.2 | 0.1 | 0.1 | 0.0 | -26.3 | -26.3 | -25.3 | -25.6 | -26.4 |
| nC7 | 1.2 | 0.8 | 0.5 | 0.3 | 0.1 | -25.4 | -25.5 | -24.4 | -25.3 | -24.9 |
| MCYC6 | 1.6 | 1.1 | 0.7 | 0.5 | 0.2 | -24.6 | -24.4 | -23.6 | -24.7 | -23.9 |
| EtCYC5 | 0.2 | 0.2 | 0.1 | 0.1 | 0.0 | -24.6 | -24.6 | -23.6 | -23.6 | -24.7 |
| 25DMC6 | 0.2 | 0.1 | 0.1 | 0.1 | 0.0 | -28.1 | -26.9 | -26.6 | -25.8 | -27.1 |
| Toluene | 0.7 | 0.6 | 0.4 | 0.3 | 0.1 | -26.2 | -26.1 | -25.5 | -25.3 | -23.4 |
| 2MC7 | 0.6 | 0.5 | 0.4 | 0.3 | 0.2 | -24.7 | -25.9 | -25.1 | -24.3 | -24.3 |
| 1c4DMCYC6 | 0.2 | 0.2 | 0.2 | 0.1 | 0.1 | -26.2 | -26.1 | -25.3 | -25.4 | -24.9 |
| nC8 | 1.0 | 1.0 | 0.8 | 0.7 | 0.5 | -25.7 | -25.4 | -25.2 | -25.5 | -26.0 |
| nC9 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | -26.4 | -26.1 | -25.1 | -25.6 | -25.1 |