

EVALUATION OF TIERED ENVIRONMENTAL FORENSIC METHODS FOR  
PETROLEUM DERIVED LIGHT AND MIDDLE RANGE DISTILLATES

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By

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## ABSTRACT

Environmental forensics of crude oil releases to the environment has been a topic of considerable research in recent years. However, less study has been conducted to develop and employ environmental forensic strategies for light and middle range distillates released to the environment. Complex molecular structures allow certain petroleum biomarkers to be quite recalcitrant to changes in their molecular structure from environmental processes such as weathering, making these biomarkers common target analytes for crude oil environmental forensics studies. However, refining and weathering processes remove a significant amount of commonly analyzed biomarkers from light and middle range distillates, presenting challenges for environmental forensic studies.

A tiered environmental forensics strategy was developed to attempt to identify diagnostic compounds and ratios that are most beneficial for application in light and middle distillate chemical fingerprinting. Samples were collected from a Study Site that was evidently contaminated by multiple sources. Contaminated groundwater and light non-aqueous phase liquid (LNAPL) samples were collected for laboratory analysis from various areas of the Study Site. Additionally, fresh gasoline and diesel samples were collected directly from the on-site fuel dispensers and analyzed as reference samples.

Distribution patterns of C3-alkylbenzene compounds proved valuable for linking the light distillate contaminant plume at the Study Site to the reference sample. C3-alkylbenzenes were found to be a beneficial target analyte compound group for environmental forensics studies on sites contaminated by light distillates due to the recalcitrant nature of this compound group. Further, analysis of diagnostic ratios of certain analyte pairs with similar solubility and chemical properties was sufficient to confirm the source of light distillate contamination across the Study Site, supporting the defensibility of the light distillate study methodology. The distinct distribution and diagnostic ratios of the biomarker sesquiterpanes compound group and alkylated PAHs were used to differentiate LNAPL collected from a contaminated portion of the Study Site to the fresh diesel reference sample. The LNAPL collected at the Study Site was determined to have originated from a different crude oil feedstock source and/or refining process than the fresh diesel reference sample.

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## LIST OF ABBREVIATIONS

<b>API</b>	American Petroleum Institute
<b>AST</b>	Aboveground Storage Tank
<b>BTEX</b>	Benzene, Toluene, Ethylbenzene, Xylenes
<b>CCME</b>	Canadian Council of Ministers of the Environment
<b>CSA</b>	Canadian Standards Association
<b>DCM</b>	Dichloromethane
<b>DIPE</b>	Di-isopropyl ether
<b>EIA</b>	Energy Information Administration
<b>EPA</b>	Energy Protection Agency
<b>ESA</b>	Environmental Site Assessment
<b>ETBE</b>	Ethyl-tertiary-butyl-ether
<b>FID</b>	Flame Ionization Detector
<b>FOI</b>	Freedom of Information
<b>GC</b>	Gas Chromatography
<b>GPS</b>	Global Positioning System
<b>gpl</b>	grams lead per litre
<b>HDPE</b>	high density polyethylene
<b>kPa</b>	kilopascal
<b>L</b>	litre
<b>LNAPL</b>	Light Non-Aqueous Phase Liquid
<b>MAC</b>	Maximum Allowable Concentrations
<b>mBGL</b>	Meter Below Ground Level
<b>MS</b>	Mass Spectrometry
<b>MSD</b>	Mass Selective Detector
<b>MTBE</b>	methyl-tert-butyl ether
<b>MW</b>	Monitoring Well
<b>NIST</b>	National Institute of Standards and Technology
<b>NEB</b>	National Energy Board

<b>OPEC</b>	Organization of the Petroleum Exporting Countries
<b>PAH</b>	Polycyclic Aromatic Hydrocarbon
<b>PHC</b>	Petroleum Hydrocarbon
<b>PHC F1</b>	Volatile Petroleum Hydrocarbons Fraction C <sub>6</sub> -C <sub>10</sub>
<b>PHC F2</b>	Volatile Petroleum Hydrocarbons Fraction > C <sub>6</sub> -C <sub>10</sub>
<b>PHC F3</b>	Volatile Petroleum Hydrocarbons Fraction > C <sub>16</sub> -C <sub>34</sub>
<b>PHC F4</b>	Volatile Petroleum Hydrocarbons Fraction > C <sub>34</sub> -C <sub>50</sub>
<b>PIANO</b>	Paraffins, Iso-Paraffins, Aromatics, Napthenes, Olefins
<b>RAP</b>	Remedial Action Plan
<b>RW</b>	Recovery Well
<b>SIM</b>	Selected Ion Monitoring
<b>TAME</b>	Tertiary-amyl-methyl-ether
<b>TBA</b>	Tertiary-butyl alcohol
<b>TEL</b>	Tetraethyl lead
<b>TIC</b>	Total Ion Chromatogram
<b>TPH</b>	Total Petroleum Hydrocarbons
<b>UCM</b>	Universal Complex Mixture
<b>US</b>	United States of America
<b>UST</b>	Underground Storage Tank
<b>UTM</b>	Universal Transverse Mercator (UTM)
<b>VOC</b>	Volatile Organic Compound

# CHAPTER 1

## INTRODUCTION AND OBJECTIVES

### 1.1 Background

The need for source identification and differentiation of petroleum-derived contaminants resulting from leaking storage tanks, pipelines, or following a release of fuel during transportation and distribution is a challenging aspect of site assessment and remedial design. Liability allocation is the primary driver behind the development of environmental forensics studies. Significant advances have been made in recent years regarding detailed compositional analysis of petroleum in the environment. Some of the earliest applications of environmental forensics were related to marine oil spills. An example is the 1989 Exxon Valdez crude oil spill, in which knowledge of crude oil or residual fuel geochemistry was applied to identify and differentiate the spilled oil in Prince William Sound and assess its environmental impacts (Bence et al. 1996).

Environmental forensic investigations are often conducted when legal disputes have developed, and often when multiple property owners or insurers are involved and there is no conclusive evidence linking individual parties to the environmental liabilities at a site (Oudijk 2005). Environmental forensic investigations typically address questions aimed at identifying the nature of contamination, contaminant source, and the timing of contaminant release to the environment to attempt to determine the responsible parties. Definitive answers to these questions are not always achieved through forensic investigations, but combining detailed compositional analysis, often referred to as chemical fingerprinting with other types of forensic data, including an understanding of the site-specific geologic and hydrogeologic conditions and operational and regulatory histories for the site, can produce highly effective and defensible arguments (Stout et al. 1998; Morrison 2000).

A significant portion of the published body of knowledge in the field of environmental forensics of petroleum hydrocarbon (PHC) releases has been conducted on crude oil releases specific to marine environments (Peters et al. 2005a). A limited number of real world cases studies that develop and employ environmental forensic strategies for light and middle range distillates have been conducted in Canada (Wang and Stout 2007) and the United States (US) (Oudijk 2005). A study of this nature has not been completed in Western Canada. Geography is



an important consideration for environmental forensics of petroleum product releases as the crude oil source and refining processes differ across geographic locations and can provide some of the leading indicators for source identification and differentiation.

The chemical composition of middle and light distillates are primarily influenced by three factors: crude oil parentage, the effects of petroleum refining and the effects of weathering processes. The chemical composition of petroleum products (e.g., asphalt, heating oil, jet fuel, diesel fuel and gasoline) is largely altered during the refining process. Many aliphatic hydrocarbons that comprise the bulk of most crude oils are removed during the refining process; essentially removing many of the traditional target analytes that are commonly detected in oil spill environmental forensics (Lentini 2013). The availability of target analytes or biomarkers for chemical fingerprinting decreases in relation to the extent of refining processes required for a petroleum product. For example, heating oil requires less refining processes than gasoline; therefore, heating oil would have more target analytes available for fingerprinting purposes than a more refined petroleum product such as gasoline. One of the primary knowledge gaps that leads to the avoidance of employing environmental forensics studies at sites contaminated by light and middle range distillates is the lack of information of chemical compounds that are recalcitrant to refining and weathering processes that could be quantified and be defensible.

A novel tiered environmental forensics strategy for light and middle distillates that could be implemented by an environmental practitioner in this field of study does not exist, or is at least not well known. However, such a strategy could be beneficial for the following applications (Uhler et. al. 2002).

- Differentiating and allocating proportional amounts of contamination at sites that have been impacted by multiple sources;
- Determining sources of contamination that has adversely impacted the environment;
- Linking a specific source or multiple sources to a hydrocarbon plume by identifying select target compounds or compound diagnostic ratios and fragmentation patterns as source indicators; and,
- Determining legal liability and proportional legal liabilities in the event of multiple sources.

## **1.2 Research Objectives**

There is potential that a novel environmental forensics strategy for light and middle distillates could speed up litigation, in turn this could mitigate contamination exposure risk to the environment and to human health by identifying responsible parties and thereby expediting remedial actions at contaminated sites. Therefore, the overall objective of this study is to develop a defensible tiered environmental forensics strategy that can be effectively replicated to differentiate and identify the source of light middle range distillates.

The overall objective of this study was divided into the following sub-objectives:

- i. To identify technique(s) that can be effectively used onsite;
- ii. To identify diagnostic compounds and ratios that are most beneficial to target for application in light and middle distillate chemical fingerprinting; and,
- iii. To determine if the proposed tiered approach can be defensible (e.g., do the individual tiers of the study support each other).

The hypotheses for this study are that alternative residual biomarkers will be identified which persist in light and middle distillates following refining and weathering processes. These identified analytes could be consistently selected for analysis for application in light and middle distillate chemical fingerprinting. The study will further identify residual compounds and isomers that could be valuable for chemical fingerprinting light and middle distillates by calculating and analyzing diagnostic ratios and normalized distributions of selected residual compounds and compound pairs.

## **1.3 Scope of Study**

This study was conducted to identify valuable target biomarkers, diagnostic analytes and diagnostic ratios of analyte pairs that could have value for conducting environmental forensics studies of sites contaminated by light and middle distillate petroleum products. Samples were collected from a Study Site that was evidently contaminated by multiple sources. Contaminated groundwater and light non-aqueous phase liquid (LNAPL) samples were collected for laboratory analysis from various areas of the Study Site. A gasoline sample, collected directly from the on-site fuel dispenser, and LNAPL samples (i.e., suspected diesel fuel) were collected for laboratory analysis as reference samples. Unique analytical methodologies were developed to analyze non-

traditional diagnostic compounds that could be integrated into a reproducible tiered environmental forensics strategy that includes collecting information regarding site operational history and geology/hydrogeology, as well as collecting and interpreting data from gas chromatography (GC)/flame ionization detector (FID) pre-screening, volatile GC/mass spectrometry (MS), semi-volatile GC/MS, and GC/MS selected ion monitoring (SIM) chromatograms.

#### **1.4 Thesis Organization**

Chapter 1 was the introduction of the thesis, which provided background information to the field of study of environmental forensics of light and middle range distillates. Chapter 2 presents a literature review which describes the significant global issue of light and middle distillate spills to the environment, discusses theoretical background and an overview of research conducted in this field, and methods which can be adapted to achieve the objectives of this study. Chapter 3 describes the methodology of the sampling and laboratory procedures conducted for this study to satisfy the objectives. Chapter 4 describes the fundamentals of the Study Site that was used for the basis of this thesis. The presentation of data and results is included in Chapter 4, along with critical discussion. Chapter 5 draws together the conclusions of the study and provides recommendations for future work.

## **CHAPTER 2**

### **BACKGROUND AND LITERATURE REVIEW**

A significant body of work has been established exploring the benefits of modern environmental forensic strategies for petroleum product identification sourced from heavy petroleum fractions, specifically unrefined crude oil. However, chemical fingerprinting of light and middle range distillates has received much less focus for research (Uhler et al. 1999). The application of a novel tiered environmental forensics approach for light and middle range distillates for the purpose of remediation design and risk management has significant potential and importance for soils and groundwater contaminated by the unplanned release of these products. A thorough consideration of environmental assessments of spill sites, analytical methodologies, and chemical fingerprinting strategies of petroleum derived products is required to understand this potential. This information must be understood in the context of light and middle range distillate releases to the environment and the resulting subsequent impact to the environment and human health.

This background information provides the foundation of knowledge for how the remediation of sites contaminated by light and middle range distillates can be delayed due to liability allocation. The significance of this problem in North America is put into perspective in this chapter. The adverse environmental legacy of a contaminated site escalates with time when the environmental liability ownership is not clear. The current body of knowledge on environmental forensic methods specific to differentiation and source identification of light and middle range distillates, while limited, provides a foundation for this study and is presented and summarized in this chapter. Finally, methods which can be adapted to achieve the objectives of this study are discussed.

## **2.1 A Case for Environmental Forensics of Light and Middle Range Distillates**

### **2.1.1 Crude Oil Releases to the Environment**

Crude oil is extracted from underground reservoirs around the world and refined to produce a variety of petroleum products including gasoline, diesel, jet fuels, lubricants, and heating oils. The United States (US) Energy Information Administration (EIA) (2012) estimates that the worldwide consumption of crude oil per year has grown by approximately 25% over the past 20 years. Predictably, the increase in global demand for petroleum and petroleum-derived products has resulted in more frequent involuntary PHC releases to natural environments and this adversely impacts soil, surface water and groundwater resources, and has become a significant global environmental problem (Fingas 2013). Crude oil undergoes a significant amount of handling, refining, transportation, and storage prior to consumption as a light or middle-range distillate. An accidental release during each one of these phases of the cycle can lead to an anthropogenic release of petroleum-derived product to the environment.

A common source of crude oil releases during transportation is caused by pipeline incidents resulting in a spill. Pipeline spills have recently received a considerable amount of media coverage, largely attributed to stakeholder protests and political interests associated with pipeline projects. Pipelines transporting crude oil in Canada, regulated by the National Energy Board (NEB), released to the environment an average of approximately 1,084 barrels (172,342 L) per year between 2011 and 2014 (Gov. Can. 2015). An average of 12 petroleum spills per day of more than 4,000 L are reported in Canada, where the United States reports more than 25 spills per day of similar volume (Morrison and Murphy 2006).

The BP Deepwater Horizon blowout in the Gulf of Mexico is an example of a catastrophic crude oil spill. The increase in public awareness and concern for crude oil spills is largely attributed to increased media coverage of catastrophic oil spills such as the BP Deepwater Horizon blowout. The BP Deepwater Horizon oil spill directly impacted approximately 180,000 km<sup>2</sup> of ocean (Minchew et al. 2012). However, since baseline marine conditions were not known at all coastal areas that the BP Deepwater Horizon oil spill impacted, it is possible that some areas classified as impacted by the BP oil spill could actually have been impacted by an alternate source (Stout and Wang 2017). Large financial penalties were paid by companies involved with

the oil spill, and such penalties are a strong motivator to engage experts in environmental forensics for source identification studies (Etkin 2009).

Public perception is important for companies operating in the petroleum industry, as current regulatory environment requires proposed development projects be put through rigorous project permitting and approval processes prior to approval to develop the resource. Many of the large companies are publicly-owned and to continue to operate and expand they must remain within regulatory compliance, or risk facing large financial penalties and operational restrictions. Hence, this is a strong driver for more research in the field of environmental forensics associated with crude oil spills, primarily within marine environments, and occurring during the upstream and middle stream components of the petroleum product life cycle (Peters et al. 2005). However, Etkin (2009) estimates only 4% of total annual petroleum spilled in the US can be attributed to extraction and production sources, while 92% of petroleum product spills that occur inland result from transportation, storage, distribution and consumption. These statistics indicate that the petroleum product spills associated with the downstream components of the petroleum life cycle represent a major environmental concern and an area of study that requires more research (Uhler et al. 2002).

### **2.1.2 The Importance of Light and Middle Range Distillates**

Canadians consumed 40,907,329 litres of gasoline fuel and 17,655,729 litres of diesel fuel in 2014 (Statistics Canada 2015). The potential for contaminating a groundwater source is dependant on several variables; however, statistics show that gasoline releases are a significant concern for preserving drinking water resources in Canada. Gasoline is the most widely-distributed petroleum product and is stored and sold at more than 14,000 operating retail fuel facilities across Canada (2011 estimate). Gasoline and diesel fuels are also stored and distributed at a large number of locations in the US; with more than 170,000 retail fuel facilities across the US in 2002 (Stout et al. 2006). All gasoline and diesel fuel purchased by consumers from retail fuel facilities, which accounts for the majority of fuel sales in Canada, is transported to retail fuel facilities by highway truck tankers from terminals or refinery truck loading facilities (Gov. Can. 2015).

There are numerous steps between initially recovering crude oil from the subsurface during production to the point where it is used during consumption stages of the petroleum life cycle. Petroleum-derived light and middle range distillates, commonly gasoline and diesel fuels, respectively, are typically stored at retail fuel facilities in aboveground storage tanks (ASTs) or underground storage tanks (USTs), prior to distribution to the end user. The primary sources of light and middle range distillates released to the environment include releases during transportation from the production facility to the retail downstream fuel facility and during storage of the products at both the production and retail facilities (Peters et al. 2005a). Surface spills are often acute incidents and are typically easier to control and therefore easier to remediate than a spill that occurs underground. Aboveground releases are typically controlled by surficial environmental conditions (e.g., topography, land use, vegetation, presence of surface water). Subsurface spills typically occur when buried pipelines or USTs are compromised and as a result, release their contents into the subsurface environment, contaminating intercepting soils and groundwater (Peters et al. 2005a).

One of the primary differences between surface spill and subsurface spill remediation activities appears to be petroleum source age dating. The timing of a surface spill occurrence can often be narrowed to a smaller time gap and is more likely to be associated with an acute or catastrophic incident (e.g., tanker truck accident). Alternatively, subsurface releases often occur slowly (i.e., chronic leaks); therefore, relatively small volumes of product can be released to the environment over extended periods of time. It is not unusual for a subsurface spill to take several years to be identified or acknowledged and subsequently assessed (Oudijk 2005). Chronic subsurface leaks can impact large volumes of groundwater. Peters et al. (2005a) reports that a chronically leaking UST, releasing a light or middle range distillate at a rate of 1 millilitre per minute (ml/min), has the potential to release over 500 litres (L) of fuel to the subsurface environment over the course of one year. A 500 L petroleum spill has the potential to contaminate approximately  $5 \times 10^8$  L of groundwater to the point where aesthetic objectives for drinking water can no longer be achieved (Peters et al. 2005a). Releases from USTs can cause considerable environmental impact, particularly in locations where groundwater is used as a potable water supply (Oudijk 2005).

Numerous USTs were installed in North America during the boom years following World War II and impacts from chronic leakage in the subsurface are still being discovered at sites across North America (Pearson and Oudijk 1993). Prior to the early 1980s, USTs were primarily manufactured of steel and installed without adequate corrosion protection. Robinson et al. (1988) reported findings that indicated the typical non-leaking lifespan for a steel UST is in the range of 15 to 20 years. Fiberglass tanks have a longer lifespan; however, fittings and connections still provide opportunity for system failures. Government of Canada (2010) report estimated that up to 50% of steel USTs leak within 15 years of being installed.

Many sites across Canada containing steel USTs are still yet to be decommissioned or replaced with fiberglass USTs (Gov. Can. 2013). An understanding of the problems associated with leaking petroleum USTs has been known since the 1950s. However, Government intervention only began to be phased in throughout North America in the late 1970s. Canadian regulations introduced in the 1990s require that USTs older than 25 years must be removed (Oudijk 2007). US Environmental Protection Agency (EPA) reports that there are over one million federally regulated USTs in the USA that contain petroleum or similar hazardous material. An estimated 500,000 of the one million federally regulated USTs were estimated to have experienced some degree of leakage as of 2008 (US EIA 2015). This data represents a very significant environmental concern when the cumulative impacts of over one million USTs with potential for leaking and contaminating potable aquifers is considered.

A surface spill often poses a more significant risk to surface water bodies and a subsurface spill often poses a more significant risk to groundwater aquifers. However, the environmental receptors of both surface and subsurface are similar, especially in regards to freshwater environments since surface water bodies are often connected to unconfined groundwater aquifers. The source of potable water for residents of the USA is approximately 50% from groundwater aquifer reserves and 50% from freshwater surface bodies (Todd and Mays 2005). Therefore, while contamination of surface water bodies is more evident and visual to the general public, it is equally important that groundwater aquifer reserves be protected. The underground spills are less apparent to the general public and therefore appear to pose less of a risk; however, it appears that surface and subsurface spills pose a near equal risk to both the environment and human health.



Gasoline and diesel fuel released to the subsurface are typically distributed among five primary phases: soil gas vapour; hydrocarbons adsorbed to soil and/or sediment particles; free-phase hydrocarbons in soil pore spaces; light non-aqueous phase liquid (LNAPL) floating on the groundwater table; and dissolved phase hydrocarbons in groundwater (Kaplan et al. 1997). There are many physical processes in the subsurface that will influence the transportation and fate of the product constituents as they reside in the subsurface. The partitioning of individual hydrocarbon chemical constituents will constantly change because individual hydrocarbon chemicals will move between the five primary phases at various rates under different controlling physical, chemical, and biological processes. Weathering processes are discussed in further detail in Section 2.7.

### **2.1.3 Overview of Canadian Environmental Law and Regulatory Considerations**

The Canadian Council of Ministers of the Environment (CCME) (Gov. Can. 2013) reports that prior to the late 1980s Canada did not have a code that incorporated an environmental perspective on the management of storage tanks containing petroleum and allied petroleum products. Historically, the installation and operation of USTs were solely governed by fire prevention and fire safety until CCME published the *“Environmental Code of Practice for Underground Storage Tank Systems Containing Petroleum Products and Allied Petroleum Products”* in 1988. This meant that when owners of USTs (e.g., retail fuel facility operators) experienced issues with USTs or pumps, operational issues often associated with petroleum products being released to the environment, the local fire department was the responsible party for which these releases to the surrounding environment were reported. Therefore, documentation of spills from USTs was not typically conducted by persons with relevant education or training to understand the complex processes that occur when petroleum products are released to the subsurface.

The development of CCME (1988) was a positive move for UST system management; however, USTs have been installed and operated across Canada since the early 1900s. A lack of a consistent registry and historical data make it difficult to develop an estimate of how many PHC contaminated sites are present across Canada. As a benchmark, the US EPA estimates there are approximately 225,000 PHC contaminated sites across the US. The PHC contamination at

many of these sites is attributed to leaking USTs associated with retail fuel facility operations (US EPA 2017).

Canada has established environmental standards for addressing environmental contamination which are mandated at the various levels of Canadian government; municipal, provincial/territorial, and federal. The Canadian federal government's environmental regulatory body is led by the CCME task group which established the Interim Canadian Environmental Quality Criteria for Contaminated Sites (CCME EPC-CS43) in 1998 with a mandate to protect ecological and human health. CCME used this document as a foundation for developing the CCME Canada-wide Environmental Standards between 2000 and 2006. Revisions have been published; however, these guidelines are currently applicable (Gov. Can. 2015).

The federal Government of Canada established the Environmental Protection Act in 1999 which detailed mandatory standards for protection of the environment and human health. The Government of Canada's Environmental Protection Act adopted the "polluter pays" principle which assigns the companies or individuals responsible for the contamination fiscal responsibility for managing the costs of preventing damage to human health or the environment. Pollution is often defined in environmental law as contamination of the land, water or air by harmful or potentially harmful substances (Gov. Can. 1999). Gov. Can. (1999) indicates that not adequately addressing environmental contamination of which the polluter is aware is considered an offence that could result in financial penalty.

#### **2.1.4 Contaminated Sites with Multiple Source Candidates**

There are many scenarios which lead to sites becoming initially contaminated and subsequently contaminated by multiple sources. The following section will use three hypothetical scenarios to describe how sites often become contaminated. The examples also illustrate how this is a common problem that could often lead to litigation disputes, particularly for retail fuel operations.

A simple case of the polluter pays scenario is if an operator of an environmentally-hazardous substance (e.g., gasoline and diesel fuels) contaminates their own property. Here the contaminant source is clearly from the owner's operations and the contamination is discovered while the operator still maintains control of the property in good financial standing. The risk to human

health and the environment is mitigated by the property owner as they are evidently responsible. To avoid financial penalty or other adverse impacts to their business, such as negative stakeholder and public relations within their local community, the owner will bear the cost of ensuring that the contamination is remediated to levels in accordance with applicable environmental regulations.

However, the polluter pays scenario can quickly become complicated. A common scenario across North American cities is having competing fuel retailers located at opposite corners of a busy intersection, across the street, or within close proximity, particularly in high traffic areas. As fuel leaks from USTs, the product will eventually encounter the shallow groundwater table and potentially migrate with the direction of groundwater flow. The liability allocation for cleanup can be complex if source identification is not clear. An example could be that as the contaminated groundwater plume progresses downgradient it moves in the direction of a competing retail fuel facility across the intersection and then further downgradient to eventually impact a residential property. It is evident that the residential property owner is not responsible for the contamination as they do not or never have maintained a contaminant source on their property. The property owner would naturally be tempted to look to the nearest fuel facility as a source of impacts on their property and suggest that this operator should bear the cost of cleanup. However, that fuel facility owner is not likely to cover the cost of remediation without contest, especially knowing additional potential contaminant sources are located up-gradient in proximity to their property.

A third hypothetical example scenario is where a new fuel release occurs by an overland release from a tanker truck while unloading fuel on a contaminated site which had been previously contaminated by an underground release from a corroding UST. This event adds a new additional contaminant source to the site. The newly-spilled substance will potentially impact the site in three primary ways if introduced to the subsurface; migrating to a different vertical stratigraphic zone in the subsurface, migrating laterally to a different horizontal area of the site, or potentially co-mingling with the substance released at an earlier time. The latter of the three migration scenarios would of course be the most difficult to differentiate to what extent each of the two responsible parties impacted the site; however, all three scenarios would benefit from a novel approach to chemical fingerprinting light and middle distillate fuels. Being able to

determine who the polluter is and therefore who is tied to the environment liability is of critical importance to this area of study. There is potential that a novel environmental forensics strategy for light and middle distillates could determine that a liability allocation could be feasible at the site. The allocation of liability when supported by scientific methods could speed up litigation and thereby mitigate contaminant exposure risk to human health and the environment by expediting remedial actions.

## **2.2 Review of Environmental Forensics Processes and Procedures**

Wang and Stout (2007) indicate that successful chemical fingerprinting typically employs a variety of analytical techniques to allow for both quantitative and qualitative interpretations of data. Employing multiple environmental forensic methods can provide a more defensible conclusion; therefore, methods employed should be distinct and independent from one another. Independent methods are preferable in the event that one method does not provide sufficient, defensible data, it does not invalidate the other methods employed (Oudijk 2005). A combined analytical approach could allow for the ability to initially collect qualitative data based on the interpretation of patterns in resulting chromatogram data and subsequently collect quantitative data based on a variety of statistical and numerical methods (Wang and Stout 2007).

### **2.2.1 Environmental Site Assessment and Characterization**

Environmental forensics methods for studying PHC contaminated sites can be benefited from compiling and reviewing relevant current and historical property documents Relevant property documents should include current and historical records for the subject property and surrounding lands as well as available surface geology, bedrock geology and hydrogeology records.

The Canadian National Energy Board suggests that an appropriate level of Environmental Site Assessment (ESA) needs to be completed to first determine whether remediation is required and subsequently to provide adequate site information to develop an effective Remedial Action Plan (RAP) for the contaminated portion(s) of the subject property (CCME 2008). The Canadian Standards Association (CSA) has developed standards to help ensure ESAs are being completed with a consistent level of integrity across Canada (CSA 2013; 2016). A Phase I ESA typically consists of a desktop screening study of current and historical property records which might be associated with environmental risk as well as non-obtrusive site reconnaissance. The Phase I

ESA is completed with the intent of determining if potential risk of environmental contamination is present at the subject property. A critical component of a Phase I ESA is aerial photography review. Aerial photographs provide an established practice to identify historical information related to waste handling practices at subject properties. Further aerial photography reviews can potentially age date a contaminant release or establish an approximate timeframe for which a contaminant source was present (Morrison 1999).

A properly completed Phase I ESA should recommend a Phase II ESA be completed at the subject property, in the event that the initial assessment finds reasonable cause to suspect environmental contamination at a source within the subject property boundaries or from a neighbouring property, as per CSA Standard Z768 (R2016) (CSA 2016).

A Phase II ESA typically consists of developing an effective sampling plan, collecting soil and groundwater data and samples for interpretation and analysis. The results of an adequately completed Phase II ESA should be able to provide an estimated extent of contamination across the subject property, potential for offsite contaminant migration and estimated calculated volume of impacted soil and groundwater. Phase II ESAs should also be able to provide baseline hydrogeology data including general groundwater flow direction, hydraulic conductivity, and hydraulic gradients across the Study Site. The data should be reported in the context of the local applicable regulatory framework and remediation objectives for the site as per CSA Standard Z769-00 (R2013) (CSA 2013).

### **2.2.2 Review of Analytical Methods for Environmental Forensics**

Chemical fingerprinting data must provide sufficient specificity to recognize the particular PHC compounds present at a site, characterize the effects of weathering on selected chemical characteristics, and provide the diagnostic information necessary to distinguish and perhaps allocate between multiple sources of petroleum and potentially determine approximate age of release. For this reason, an analytical program that uses standard regulatory methods for chemical analysis (e.g., US EPA Methods 8015, 8020, 8260 and 8270) does not produce sufficient chemical details required to defensibly resolve environmental forensic questions. Conventional lists of chemicals measured to demonstrate regulatory compliance do not include many potential valuable biomarkers and chemicals that comprise light and middle range distillate products. For example, the polycyclic aromatic hydrocarbons (PAH) and benzene, toluene,

ethylbenzene, and xylenes (BTEX) compounds measured using standard US EPA methods (i.e., methods 8270 and 8260) measure concentrations of 16 priority PAH compounds considered most toxic to the environment by the EPA. However, there could be more than one thousand alkylated forms of PAHs that are not measured by US EPA methods 8270 and 8260 present in a hydrocarbon sample (Stout and Wang 2016). Therefore, modified analytical methods must be developed to measure specific suites of chemical compounds that could be used for diagnostic purposes and that could be found within spilled light and middle range distillates.

The initial phase of an environmental forensics program would typically consist of conducting analyses to obtain qualitative data which could be interpreted to determine the general hydrocarbon composition of the sample containing the petroleum contaminants of concern (i.e., is the sample gasoline or diesel?). GC/FID analysis can provide sufficient datasets to satisfy the initial stages of an environmental forensics program (Uhler et al., 1999) in that GC/FID data can provide initial qualifying data to potentially differentiate between different fuel types. However, GC/FID data alone can often be inconclusive and subsequent analysis is often required to obtain more quantitative data to determine concentrations and distribution patterns of targeted chemical analytes to differentiate contaminant plumes. Therefore, GC/FID data can be useful to indicate the presence of different fuel types present at a site; however, further analysis is required to obtain further data for source differentiation (Wang and Stout 2007).

The following sections will detail the fundamental laboratory analytical principals that can be employed to obtain concentrations and distribution patterns for target analytes that are most beneficial to chemical fingerprinting light and middle range distillates.

### **2.2.2.1 Gas Chromatography**

GC is a common and favoured method for measurement of TPHs. The primary reasons for the popularity of GC in this application is that it can be used to detect a broad range of hydrocarbon compounds and both sensitivity and selectivity can be reported to the user. GC is the analytical foundation for both identifying and quantifying individual hydrocarbon compound constituents within a sample (Speight 2005).

Significant advancements in laboratory analytical methods used for PHC analysis have been achieved in the past two decades. Various adsorbents, including silica gel, alumina, florisil, and

various eluting solvents are commonly used to fractionate hydrocarbons into saturated, aromatic, and polar groups. The hydrocarbon fractions are then analyzed using instruments including FID and MS (Wang and Fingas 2003).

The high-resolution capillary GC analytical technique is considered the most widely-accepted technique for the molecular characterization of contamination derived from light and middle range distillates (Uhler et al. 2010). The principal concept of high resolution capillary GC is that as the temperature increases, compounds that have low boiling points elute from the column sooner than those that have higher boiling points. As the compounds are separated, they elute from the column and enter a detector. The detector is capable of creating an electronic signal whenever the presence of a compound is detected, and the greater the concentration in the sample, the greater the signal that is produced. The signal is then processed by a computer. The time from when the injection of the sample into the GC is made (time zero) to when elution occurs is referred to as the retention time (Jennings 1997).

The US EPA has developed and published methods standards for the characterization of hydrocarbons using GC instruments including; US EPA Method 8015 (TPH by GC-FID), US EPA Method 8020 (Aromatic Volatile Organics by GC), and US EPA Method 8260 (Volatile Organic Compounds by GC/MS).

#### **2.2.2.2 Gas Chromatograph – Flame Ionization Detection**

High resolution capillary GC coupled with FID (GC/FID) has commonly been employed in oil spill studies for the determination of normal alkanes (*n*-alkanes), isoprenoids, and TPHs. GC/FID pattern matching techniques provide valuable analytical data pertaining to the boiling point range of the chemical constituents comprising an analyzed sample (Peters et. al. 2005b).

The primary principal behind FID is that burning carbon compounds produces ions, which can be detected and measured. Combustion of hydrogen does not produce ions; however, the combustion of organic compounds does produce ions. As carbon compounds are eluted from the GC column, they are released into the hydrogen flame of the detector, as the hydrogen flame of the detector current passes between electrodes, placed near the flame, a recordable signal is produced and detected (Jennings 1997). Holm (1999) describes the FID system as a carbon counting device, as hydrocarbons give equal responses in proportion to the equal number of

carbon atoms. FIDs are designed to collect 100 percent of the ions produced. This is facilitated by the high sensitivity of the detector, which results from the absence of the charge carriers (e.g. hydrogen) in the flame, as well as the relative ease with which the ions produced by the combustion of the organic compounds can be collected and counted by the detector. There are several advantages to utilizing FID methods including high sensitivity, low noise level, linear response over a wide range, and high reliability.

The FID is considered a non-selective detector as the signal response is essentially of the same order of magnitude for all organic compounds. Since the quantitative response of the FID is approximately the same for equal weights of most hydrocarbon compounds, relative peak areas can be used directly for the approximate determination of weight percent values (Zhao et al. 2014). Zhao et al. (2014) suggests that utilizing GC-FID for detecting PAH compounds can produce erroneous results due to the non-specific nature of FID analysis and associated factors such as analyte coelution and matrix interference. Further, quantification of aromatic compounds can be only partially achieved, and identification and quantification of petroleum biomarker compounds is not accurate also due to the non-specific nature of the FID method (Peters et al. 2005b).

Data derived from GC-FID analysis can often provide sufficient evidence to initially characterize a primary contaminant source in a sample and provide initial data on the extent of weathering of a sample. However, GC-FID application in light and middle distillates environmental forensic investigations can be limited and often further analysis will be required to determine differentiation of contaminants in multiple samples.

### **2.2.2.3 Gas Chromatograph – Mass Spectrometry**

Detailed and specific chemical composition data is required for source differentiation. The detection technique most commonly used for modern environmental forensics in conjunction with GC for determining the concentrations of individual compound classes within a sample is MS (Bouchonnet 2013). The combined analytical and detection techniques of GC/MS, allow for both qualitative and quantitative evaluations of a sample that may contain hundreds of individual compounds. The primary benefits to employing MS analysis in an environmental forensics study, in addition to FID analysis, is the ability to individually characterize each chemical compound within a sample. Bouchonnet (2013) reported advantages of GC/MS over GC/FID



pertain primarily to the valuable additional compound specific information (e.g., alkylated PAHs) that can be derived from the MS data, as well as the opportunity to obtain unique hydrocarbon distribution patterns.

When a GC is produced for a sample each peak should be identified or classified, in accordance with the chemical group to which it belongs. Coupling the MS detector with GC allows for peak identification in a chromatogram, based on retention time. Therefore, GC/MS system can be used to separate and identify individual components of a complex hydrocarbon sample. The GC/MS is a valuable tool to determine the concentrations of each of the individual compounds within a sample that can be used for calculating diagnostic ratios of chemical constituents of interest. It is possible to obtain biomarker compound information as well as both parent and alkylated PAH data during the same analytical run (Stout and Wang 2016).

A GC/MS system works similar to the GC/FID system in that compounds are eluted from the GC column, and subsequently the compounds enter the MS component, which is also an electron ionization detector. However, it is different in that once the compound groups enter the MS, the compounds are introduced to a stream of electrons which causes the compound groups to further separate into fragments, which can still be large or small fragmentations of the original compound molecules. The fragments of these compounds are charged ions, and each with a specific mass. The mass of the fragment divided by the charge is called the mass to charge ratio ( $m/z$ ). Since most fragments have a charge of  $+1$ , the  $m/z$  ratio typically represents the molecular weight of the fragment (Wang and Stout 2007). Selected ion monitoring (SIM) is the typical mode of GC/MS data acquisition for biomarker analysis.

The mass spectrum produced by a given chemical compound is essentially the same every time. Therefore, the mass spectrum is essentially a fingerprint for the molecule. This fingerprint can be used to identify the compound. One ion of a given  $m/z$  ratio together with the gas chromatographic retention time is often diagnostic of the structure of the biomarker compounds being studied (Peters et al. 2006). Computers connected to GC/MS instruments typically maintain a library of spectra that can be used to identify an unknown chemical in a sample mixture. The mass spectrum from a sample component is compared to the mass spectra in the library to obtain a list of potential compound identifications.

Use of GC/MS analysis to evaluate extracted ion chromatograms and profiles is of high value for application in environmental forensics of light and middle range distillates. Biomarkers can be selected or targeted for analysis based primarily on their boiling point during GC/MS extraction (Lentini 2013). The high sensitivity of GC/MS allows the user to zoom in on target analytes, such as biomarkers terpanes and steranes, that produce peaks too small to individually identify and quantify using only GC/FID (Peters et al. 2005a). The use of PAH diagnostic ratios to interpret PAH sources is based on the relative stability of the PAH isomers, which have been evaluated from the relative heat of formation of the compounds. Ratios based on isomers with the highest heat of formation difference provide the highest discrimination capacity (Wang and Fingas 2003). When used in conjunction with GC/FID analysis, GC/MS analysis appears to be a critical tool for developing a novel tiered environmental forensics method for light and middle range distillates.

### **2.3 Review of Crude Oil Characteristics for Environmental Forensics**

The previous sections detailed why environmental forensic investigations on light and middle range distillate contaminated sites are of academic importance. This section will explore the current body of knowledge in the field of crude oil environmental forensic procedures and the pre-release factors (e.g., crude oil feedstock genesis and refining processes) and post-release factors (e.g., weathering processes and contaminant mixing) that affect our ability to identify, characterize, and differentiate light and middle range distillates.

Stout and Wang (2016) indicate that the most frequently measured compound classes for quantitative oil spill environmental forensic studies include n-alkanes, acyclic isoprenoids, polycyclic aromatic hydrocarbons (PAHs), alkylated PAHs, and triterpene and sterane biomarkers. Differentiating fuel sources in an environment is challenging due to the overlap of n-alkane, alkylbenzene and alkyl naphthalene chromatographic patterns in light and middle range distillate products with similar boiling ranges (Kaplan et al. 1997).

#### **2.3.1 Chemical Composition of Crude Oil**

Crude oil is a liquid form of petroleum that was formed as the result of burial of once living organisms (e.g., algae, plants) in organic rich geological strata. The organisms were buried with

sediments during geological processes through time. As the organic rich strata was buried it was submitted to significant pressure, intense thermal conditions, and lack of oxygen over the course of millions of years resulting in the formation of kerogen (Peters et al. 2005a). Kerogen is particulate organic matter that is distributed throughout PHC-bearing sedimentary rock formations and continues to form as pressure and temperature increase with burial depth. The breakdown of organic kerogens, primarily catalyzed by thermal degradation processes, is referred to as catagenesis. Catagenesis results in hydrocarbon rich material that forms petroleum contained within fine grained sedimentary rock formations, referred to as source rock (Peters et al. 2005a). Crude oil is often described as being light or heavy, based on the product density and specific gravity. The product is visually differentiated by a wide range of colours; ranging from black to dark brown and can consist of yellowish, reddish, and greenish tints. The observed color variations are a result of the varied chemical compositions of the different crude oil sources from around the world (Morrison 1999; Morrison and Murphy 2006).

In the simplest form, hydrocarbons consist of only hydrogen and carbon atoms, joined by covalent bonds. Crude oil is a complex mixture of hundreds of hydrocarbons; primarily carbon and hydrocarbons typically comprising more than 90% of the mixture with some commonly-occurring Earth elements such as nitrogen, sulfur, and oxygen accounting for the remainder (Demirbas 2008). Hydrocarbons are characterized and classified by their chemical structures, including alkanes (commonly referred to as saturates), alkenes (commonly referred to as olefins), aromatics, polar compounds (e.g., nitrogen, sulfur, and oxygen), and asphaltenes (Morrison 2000).

Wang et al. (1994) identified more than 300 individual hydrocarbon compounds within one crude oil sample of Alberta Sweet Mixed Blend. GC/MS analysis was used to identify the individual compounds by comparison of GC retention data with authentic standards and calculation of retention index values. The average composition of classes of hydrocarbons that comprise crude oil is approximately 57% alkanes hydrocarbons, 29% aromatic hydrocarbons and 14% polar compounds (Wang and Stout 2007).

The group of hydrocarbons classified as alkanes are composed of hydrogen and carbon atoms with no carbon-carbon bonds. Alkanes can be further sub-classified as normal alkanes (commonly referred to as normal paraffins) which are straight-chain alkanes ranging from  $n$ -C<sub>5</sub>

to *n*-C<sub>40</sub>, branched-chain alkanes (saturated hydrocarbons with straight and branched chain alkanes (isoparaffins contain both straight and branched carbon chains)), and cycloalkanes which are carbon atoms joined by single bonds in a ring structure (Morrison and Murphy 2006).

The range of aromatic content in naturally-occurring crude oil ranges from approximately 10% to 50% of the mixture by volume (Schobert 2013). A crude oil feedstock sourced from oil sands productions in Northeastern Alberta (i.e., heavy crude oil or bitumen) will exhibit notably different ratios of saturate and aromatic components comprising the hydrocarbon mixture than crude oil sourced from the Bakken Formation in Southern Saskatchewan (i.e., conventional light or medium crude oil). Additionally, the concentration of aromatic compounds and parent and alkylated PAHs will vary between various crude oil sources (Hollebone 2015). These varied characteristics facilitate the ability to chemically fingerprint different products.

An inventory of target analytes of saturated hydrocarbons, PAHs, and biomarkers conventionally analyzed for crude oil environmental forensics studies is presented in Table A.1 (Appendix A).

### **2.3.2 Petroleum Biomarkers**

PHC biomarkers represent components of complex molecules derived from organic particles of the formerly-living organisms that comprised the organic kerogen, which eventually formed crude oil. The manner in which molecules are organized in the hydrocarbon mixture is a result of the original composition of the ancient organic strata (Schobert 2013).

Catagenesis is the complex result of combined physical, biochemical, and geological processes that were detailed in Section 2.3.1. Peters et al. (2005a) describes this chemical reaction as a time, temperature and pressure dependent process. The chemical reaction process which creates PHCs from kerogen (X) and can be summarized using the following equation:

$$X_0 \rightarrow \text{PHC} + X(t) \quad (2.1)$$

where  $X_0$  is the initial kerogen concentration and  $X(t)$  is the kerogen concentration at time  $t$ .

This process would have varied vastly across the Earth, even within the same oil reserve fields, as different formations would result in different chemical fingerprints. The amount of heat and pressure that the ancient organic stratum was exposed to also contributes to variations in hydrocarbon composition. The complex structure of petroleum biomarkers reveal more about the origins of the source crude oil than other compounds comprising crude oil (Morrison and Murphy 2006). At the molecular level it is unlikely that two crude oils could be identical due to the numerous variables in the formation processes of crude oil, including organic matter input, thermal maturation, and weathering (Wang and Stout 2007).

Biomarkers in crude oil, source rocks, and sediments show little and often no changes in structures from their parent organic molecules precursors (e.g., hopanoids and sterols) in living organisms. Biomarker concentrations observed in crude oil are low when compared to the concentrations of the parent organic molecules. However, biomarkers are beneficial to environmental forensic assessments because they often retain significant portions of the original carbon skeleton of the parent organism, which is universal for all naturally-occurring crude oils. The molecular structure similarities can provide critical information about the petroleum source (Morrison and Murphy 2006).

Petroleum biomarkers that are conventionally targeted for chemical fingerprinting crude oil spills include pentacyclic triterpanes (e.g., hopanes), regular and rearranged steranes, and mono-aromatic and tri-aromatic steranes (Gaines et al. 2006; Yang et al. 2012). However, steranes and terpanes are often partially or well removed during refining processes, because these compounds consist of five or six carbon rings, which need to be broken down for light and middle distillates. A list of classes of petroleum biomarker parameters used in crude oil environmental forensics studies adapted from Wang et al. (1999) and Stout and Wang (2016) is included in Table A.1 (Appendix A). A list of common biomarker compound classes showing approximate relative carbon boiling ranges and target ions are presented in Table 2.1.

**Table 2.1** - Biomarker classes showing approximate relative carbon boiling ranges and target ions (dominant mass/charge ratio (m/z)) (adapted from Wang et al. 1999; Stout and Wang 2016)

<b>Compound Class Name</b>	<b>Approximate Carbon Boiling Range</b>	<b>Target Ions - Mass Spectral Fragment Ions (dominant mass/charge ratio (m/z))</b>
<i>n</i> -alkanes	C1 – C45	85
Diamondoids (Adamantanes)	C10 - C13	136, 150, 164, 178, 192
Diamondoids (Diamantanes)	C10 - C13	188, 202, 216, 230
Acyclic isoprenoids	C12 - C19	123
Sesquiterpanes	C13 - C16	123, 179, 193, 207
Terpanes	C22 – C34	163, 177, 191
Steranes	C25 – C29	217, 218, 259

#### **2.4 Source of Petroleum Derived Products in Canada**

The Canadian Association of Petroleum Producers (2015) reports that the total capacity of Canadian refineries in 2015 was used to produce 35.7% gasoline, 23.9% diesel, 12.8% fuel oil, 4.6% petrochemical feedstock, and 4.2% was used to produce aviation fuel. There are currently 19 oil refineries operating across Canada (Table 2.2).

**Table 2.2** - Canadian refineries showing production capacity (BBL/day and L/day) (adapted from Crawford 2011)

Refinery Operator	Location	Capacity (BBL/day)	Capacity (L/day)
North Atlantic Refining	Come By Chance, NL	115,000	18,283,505
Imperial Oil	Dartmouth, NS	89,000	14,149,843
Irving Oil	Saint John, NB	300,000	47,696,100
Ultramar	Levis, QC	265,000	42,131,555
Suncor	Montreal, QC	130,000	20,668,310
Suncor	Mississauga, ON	15,600	2,480,197
Imperial Oil	Nanticoke, ON	120,000	19,078,440
Imperial Oil	Sarnia, ON	120,000	19,078,440
Suncor	Sarnia, ON	85,000	13,513,895
Nova	Sarnia, ON	78,000	12,400,986
Shell	Sarnia, ON	75,000	11,924,025
Consumers Co-op	Regina, SK	145,000	23,100,000
Moose Jaw Refining	Moose Jaw, SK	14,000	2,225,818
Husky	Lloydminster, AB	29,000	4,610,623
Shell	Scotford, AB	100,000	15,898,700
Suncor	Edmonton, AB	135,000	21,463,245
Imperial Oil	Edmonton, AB	185,000	29,412,595
Husky	Prince George, BC	12,000	1,907,844
Chevron	Burnaby, BC	55,000	8,744,285

In 2014, over 300,000 barrels (BBL)/day (95,400,000 l/day) of crude oil was imported to feed Canadian oil refineries. Oil is imported into Canada, primarily from countries that are members of the Organization of the Petroleum Exporting Countries (OPEC), including the United Kingdom, Algeria, Saudi Arabia, Nigeria, Angola, Iraq, and Venezuela (Crawford 2011; NEB 2014). Canada has increased their crude oil imports from the United States (not a member of OPEC) from less than 50,000 BBL/day (7,950,000 l/day) in 2010 to more than 300,000 BBL/day in 2014 (NEB 2014). The data presented in Table 2.2 indicates that less than one third of crude oil refined in Canada are confirmed to be sourced from Canadian oil reserves. The high number of various crude oil feedstocks being processed in Canadian refineries present the variety for different chemical and molecular characteristics and biomarkers to be present within distilled petroleum products following refinery processing.

## **2.5 Effects of Refinery Processes on the Chemical Composition of Crude Oil**

Complex molecular structures allow certain petroleum biomarkers to be quite recalcitrant to biodegradation processes and experience limited change to their molecular structure from that of their biogenic precursors over time (Yang et al. 2012). However, refining crude oil to middle distillate products and gasoline presents a challenge for environmental fingerprinting as the refining processes remove a significant amount of the valuable higher molecular weight biomarkers including terpanes and steranes (Wang et al. 2005). Biomarkers are removed from the hydrocarbon mixture as the crude oil feedstock progresses through the various stages of the refining process (Wang and Stout 2007). The concentration and distribution of residual biomarker parameters in light and middle range distillates following the refining processes are controlled by factors including the initial presence of biomarkers in the crude oil feedstock, volatility and thermal stability of present biomarkers, and the effects of catalysts and hydrogen pressure employed during refining (Peters et al. 2005a).

### **2.5.1 Refining Processes**

Crude oil is a complex mixture of PHCs and the overall objective of the refining process is to separate the complex mixture into groups of compounds specific to distinct boiling ranges (Peters et al. 2005a). The compounds present within the distillates are commonly referred to as fractions and each fraction is characteristic of specific carbon numbers and distillation boiling ranges (Demirbas 2008). Crude oil is first heated and then transferred into a distillation column, where different products boil off and are recovered at specific increasing temperatures ranges (Peters et al. 2005a). Table 2.3 presents a breakdown of the distillation process correlating carbon and distillation boiling range with the main constituents of crude oil.



**Table 2.3** - Carbon and distillation boiling range of common crude oil distillation products (compiled from Demirbas 2003, 2008)

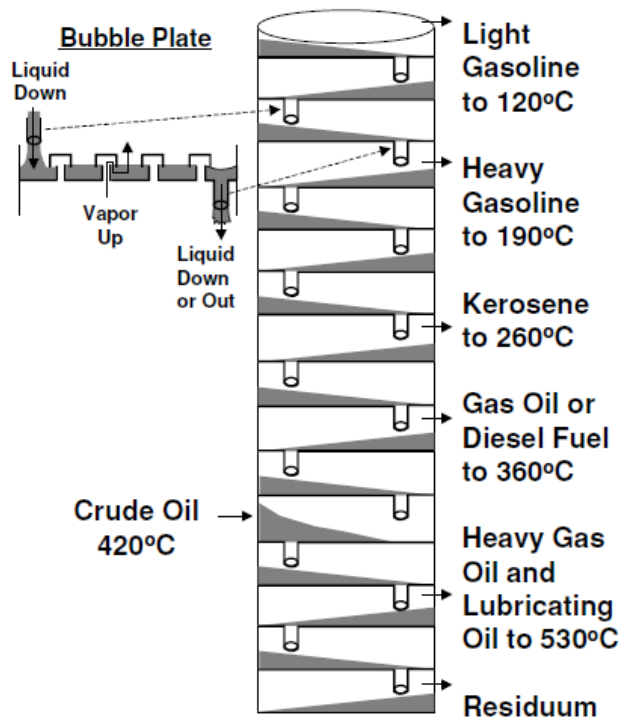
<b>Fraction</b>	<b>Carbon Boiling Range</b>	<b>Distillation Range (Kelvin (K))</b>
Natural gas	1 - 4	< 293
Petroleum ether	5 - 6	293 - 333
Ligroin (light naphtha)	5 - 8	333 - 373
Gasoline	5 - 10	313 - 478
Kerosene	10 - 16	433 - 578
Diesel fuel	10 - 25	448 - 613
Lubricant oil	20 - 50	635 - 875
Fuel Oil	20 - 70	> 610

**Distillation:** The initial major refining process is distillation; where vapours and liquids are separated off based on the temperature (Peters et al. 2005a). This process is often also referred to as fractionation. A vertical distillation tower is essentially a series of distillation sieve trays to separate vapors and liquids. The temperature at each sieve tray is controlled to match the temperature where the hydrocarbons will condense to a liquid (Peters et al. 2005a).

The various distillates liquify from the vapour when the rising vapour drops below their specific boiling point. The higher the vapour rises in the tower the lower the temperature becomes. The distilled liquid from each tray level within the distillation tower will contain a specific mixture of alkanes, alkenes, and aromatic hydrocarbon compounds with similar properties (Stout and Wang 2016). The condensed hydrocarbon mixtures will then require further processing to tailor the mixture to specific regulatory and industry standards for middle distillates and gasoline (Demirbas 2008).

The most significant impact that the distillation process has on the chemical characteristics of light and middle range distillates is that the compound distributions within the products will be altered, depending upon the volatility of specific compounds (Stout and Wang 2016). Therefore, a gradual decrease in the abundance of select biomarker compounds, such as terpanes, will occur with increasing molecular weight (i.e., decreasing volatility) in the light and middle distillate products (Stout and Wang 2016). The altering of compound distributions also causes altering

ratios between compounds with varying volatility, providing an opportunity for comparing ratios of diagnostic compounds that may still be present in light and middle distillate products (Stout and Wang 2016, Wang and Stout 2007). Therefore, an environmental forensics assessment should initially focus on diagnostic analytes that would potentially be present near the higher end of the boiling ranges for both light and middle distillate fuels. An illustration of a distillation tower is shown in Figure 2.2.



**Figure 2.1** - Illustration of a distillation tower in a crude oil refinery (from Peters et al. 2005a)

The condensed hydrocarbon compound mixtures resulting from the distillation process will contain heavier fraction molecules and longer chain alkane hydrocarbons in correlation to the lower distillation ranges (Peters et al. 2005a). Further refining processes are required to break longer chain molecules and create more usable short chain molecules for consumer fuel products (Stout and Wang 2016). The additional refining processes for gasoline and diesel fuels include cracking, reforming, isomerization, alkylation and dealkylation. These processes effectively remove many residual biomarkers and diagnostic ratios as detailed below.

**Cracking:** Depending on the crude oil field stock, a large portion of the feedstock may remain as heavy crude oil fractions following distillation, referred to as residuum. Cracking processes are

required to break longer carbon chain alkane molecules. Carbon chain cracking produces both shorter chain alkane and alkene molecules. The development of a double covalent bond forms alkene molecules (i.e., an unsaturated hydrocarbon molecule) (Olah and Molnar 2003). There are various forms of cracking processes conducted at different refineries. Thermal cracking was the initial cracking method developed in refineries. This process consists of heating the residual hydrocarbon mixture to temperatures greater than 900 degrees Celsius (°C) and increasing pressure to greater than 700 kilopascal (kPa). Thermal cracking has largely been replaced with fluid catalytic cracking processes in modern refineries (Schobert 2013). Fluid catalytic cracking consists of creating a cracking reaction by introducing a catalyst to the feedstock mixture (Peters et al. 2005a; Schobert 2013). The objective of all cracking methods is break carbon-carbon bonds, resulting in shorter chain molecules. As a result of this process, aromatic rings are saturated, carbon-carbon bonds are broken and hydrogen is added (Olah and Molnar 2003). Cracking processes are a major contributor to removal of biomarkers that might have remained in the product following distillation.

Most heteroatomic molecules that might have been remaining in the compound mixtures, that could be valuable biomarkers, will be destroyed during the cracking processes. Polar heteroatomic molecules, including alkylated carbazole, pyridine, quinoline, acridine, thiophene, and dibenzothiophene, are commonly identified in many crude oil feedstocks and are typically used for crude oil environmental forensics studies (Morrison and Murphy 2006). The cracking process will destroy most of these heteroatomic molecules. Further, catalytic cracking processes can also decrease the proportion of less stable compounds (such as selected less stable PAH  $\alpha$ -type isomers) and produce isomers that are not typically present in crude oil feedstocks (Schobert 2013; Stout and Wang 2016).

**Reforming and Blending:** Gasoline, and to a lesser extent middle distillates, require additional blending, additives, and removal of residual impurities following cracking processes, referred to as the reforming process. The reforming process results in break-down of straight-chain alkanes into branched-chain alkanes, cyclohexanes and aromatic hydrocarbons, (e.g., hexane is broken down into cyclohexane + hydrogen), forming a compound mixture referred to as reformate. Reforming processes largely consist of dehydrogenation reactions which result in an increased concentration of monoaromatic compounds (e.g., toluene) in the reformate mixture. Reformate is

then blended with light distillates to enhance the octane rating in the derived fuel products (Schobert 2013). The process converts saturated ring compounds (e.g., naphthenes) into higher octane aromatic hydrocarbons including BTEX compounds. Naphthalene compounds may also be present as a result of the reactions during the reforming process (Beall et al. 2002). Proportions of *n*-alkanes to isoprenoids (e.g., *n*-C17/Pristane, *n*-C18/Phytane) can be altered from the crude oil feedstock during the addition of the reformate blending stocks to the mixture to produce higher octane fuels, because they may be from a different source. This process may increase the proportion of *n*-alkanes in the distillate product relative to isoprenoids (Stout and Wang 2016, Wang and Stout 2007).

C<sub>3</sub>- and C<sub>4</sub>-alkylbenzenes, naphthalenes, and C<sub>1</sub>-alkylnaphthalenes are examples of compounds that are characteristic of relatively higher boiling aromatic compounds introduced into a gasoline blend during reforming processes. These could potentially be beneficial for source differentiation (Morrison and Murphy 2006). Normal alkylcyclohexanes (CH-1 to CH-18) are also good examples of these compounds since the refinery blends various reformates to meet desired specifications and octane ratings using distinct blending stocks, distillate fuels with distinctive *n*-alkylcyclohexane distributions will be produced (Kaplan 1997). Therefore, the characteristics of a reformate, once blended with a light or middle distillate, could provide valuable diagnostic information.

**Alkylation and isomerization:** These processes essentially consist of combining residual compounds that are less than C<sub>5</sub> (e.g., 2-methylpropene (isobutene)) to build molecules within the C<sub>5</sub> to C<sub>12</sub> range for gasoline. This is completed through an acid-catalyzed reaction of olefins with normal hydrocarbons to yield branched chain alkanes (iso-alkanes), predominately 2,2,4-trimethylpentane (isooctane) or one of three 2,2,4-trimethylpentane isomers (i.e., 2,2,3-, 2,3,4- and 2,3,3-trimethylpentane) (Morrison and Murphy 2006). Isooctane is valuable to refineries for the high octane characteristic of the compound. Of 2,2,4-trimethylpentane and the three trimethylpentane isomers, 2,2,4-trimethylpentane predominates, typically ranging between 60% and 80% of the total trimethylpentanes in gasoline products (Morrison and Murphy 2006; Schobert 2013). The three trimethylpentane isomers would react similarly to 2,2,4-trimethylpentane due to their chemical structure (Morrison and Murphy 2006). Beall et al. (2002) indicates that alkylation and polymerization processes will vary by refinery because

different acidic compounds may be used as catalysts, therefore, trimethylpentanes could be potentially be used to develop a diagnostic ratio calculation of the concentration of 2,2,4-trimethylpentane relative to the total concentration of the four combined trimethylpentane compounds.

### **2.5.1 Chemical Characteristics of Light Distillates**

Gasoline is the most popular product derived from petroleum and constitutes the largest fraction of product obtained per barrel of crude oil (i.e., typically greater than 42%) (US EIA, 2012). Gasolines are blended from a variety of intermediate refinery streams, which results in differing physical and chemical properties for gasoline fuels around the world (Uhler et al., 2002). Whittmore (1979) resolved and identified 361 individual chemical compounds in gasoline using GC-FID analysis.

Gasoline is a light distillate product that is comprised of a complex mixture of hundreds of different hydrocarbons. The hydrocarbons have a chain length that is typically between 5 and 10 carbon atoms but could potentially range between 3 and 12 carbon atoms (Demirbas 2008; Kaplan et al. 1996). A typical GC-FID chromatogram of a non-weathered gasoline sample will be dominated by light-end resolved hydrocarbons (Mudge 2009; Wang et al. 2002;). The predominant hydrocarbon compound classes that comprise gasoline are straight chain alkanes (i.e., paraffins), branched chain alkanes (i.e., iso-paraffins), aromatics, cyclo-alkanes (i.e., naphthenes), and alkenes (i.e., olefins). These five compound classes are commonly referred to by the acronym PIANO, and this is a common laboratory analytical package used to characterize gasoline-range distribution using GC-FID (Uhler et al. 1999). An inventory of PIANO analytes and the associated mass spectral quantification ions used in characterization of gasoline in environmental samples adapted from Uhler et al. (2002) is included in Table A.2 (Appendix A). The major non-hydrocarbon classes in gasolines could include oxygen-containing ethers (e.g., oxygenates including methyl-tert-butyl ether (MTBE)), alcohols (e.g., ethanol), sulfur (e.g., mercaptans, thiophenes, disulfides, thiolanes, thlanes)) (Morrison and Murphy 2006). Alkenes and alkynes do not occur naturally in crude oil; therefore, the alkenes and alkynes present within gasoline are the result of various refinery processes conducted to improve the quality of gasoline as previously detailed in Section 2.5.

The formulation of gasoline has evolved to improve the performance of the product since it was first used in the automotive industry in 1876. Initially gasoline formulation evolved to address the continual advancing performance requirements of gasoline powered automobiles. The chemical composition of gasoline required improved combustibility, increased product octane ( $C_8H_{18}$ ) rating, reduced gum formation potential, and the addition of performance-enhancing additives such as tetraethyl lead (TEL). TEL is an important gasoline additive for environmental forensics, as it was first used in gasoline in 1923 and was not completely eliminated from gasoline blends until the 1990s. It appears that lead toxicity was a concern even at the time TEL was first introduced as an effective gasoline additive, as the US implemented maximum allowable concentrations (MAC) of TEL in gasoline in 1926 (i.e., 0.84 grams lead per litre (gpl)) (Morrison and Murphy 2006; Dickson et al. 1987). Dickson et al. (1987) reported that the average level of TEL in regular grade gasoline sold in the US was 0.66 gpl between 1926 and 1970.

Changes in the formulation of gasoline blends since the 1970s have addressed evolving regulatory standards to lessen the adverse impact on environment and human health. Regulations and Acts introduced throughout the 1970s (such as the 1977 Clean Air Act) forced refineries to systematically reduce TEL concentrations in refined gasoline products until eventually less than 2% of gasoline sold in the US in 1992 contained TEL, and 0% in 1996 (Morrison and Murphy 2006). Amendments to the 1977 Clean Air Act in 1990 required refineries to add oxygen-containing additives to gasoline sold in the US. Therefore, in the early 1990s many US refineries began adding or increasing the amount of oxygenates in their gasoline (e.g., Methyl tert-butyl ether (MTBE)). Several environmental concerns have developed with the increased use of oxygenates, including MTBE, in gasoline and the introduction of oxygenates to soil and groundwater resources through surface spills and leaking USTs. As a result, certain US States banned the use of MTBE as a gasoline additive in the mid-2000s (Morrison and Murphy 2006).

Domask (1984) provided compositional data for a gasoline test mixture formulated by the American Petroleum Institute (API), intended to represent the typical gasoline formulation at the time in the US. The formulation was reported, in percent by volume, to contain 11.4% paraffins, 46.5% isoparaffins, 4.7% naphthenes, 9.0% olefins, and 28.4% aromatics. Benzene accounted for 1.6% of the total mixture of the 1984 API gasoline sample. The typical modern gasoline

formulation has changed from the sample discussed in Domask (1984), in that percent by weight of certain compound classes have changed to address demands for improved fuel economy, increased engine performance and more stringent emissions regulations. Regulations have become more stringent regarding the total aromatics content in gasoline. The US EPA (2008b) specified that modern gasoline must contain less than 25% aromatic compounds by volume, including less than 1% benzene. Refining processes typically remove all PAH compounds in gasoline, with the exception of naphthalenes (Peters et al. 2005a).

A fresh gasoline sample collected in 2001 contained 2-methylbutane, toluene, p-,m-xylene, MTBE and 2,2,4-trimethylpentane as the five most prevalent chemical compounds, accounting for 31% by volume of the sample (Harley and Kean 2004). Chin and Batterman (2012) found in a study of fresh gasoline from California that toluene, n-heptane, 1,2,4-trimethylbenzene, cyclohexane and p-,m-xylene were the five most prevalent compounds, accounting for 51% by volume of the sample. The octane rating refers to the anti-knock characteristic of a specific gasoline blend. To maintain a desired octane rating of gasoline blends (i.e., 87 to 93), in response to the need to reduce aromatics and alkenes, refineries increased the volume of isoalkanes (specifically, highly branched alkanes (e.g., 2,2,4-trimethylpentane) and also increased the proportion of additives such as oxygenates (e.g., MTBE).

The modern refining procedures used to produce high quality gasolines can result in a significant difference in the total number and distribution of individual chemical compounds in a gasoline blend. Gasolines that are blended at the refinery to contain higher percentages of alkylate could potentially have less than half the number of hydrocarbon chemical compounds detectable in a GC/MS scan than in gasolines blended to contain more cracked naphthas (Stout and Wang 2016). One of the primary reasons that refineries will employ different refining processes for their gasoline blends is that they will start with different crude oil feedstocks. The refineries are also required to meet government regulations for MACs of select chemicals (e.g., benzene) and so must change their process to accomplish these goals. Benzene concentrations can notably vary between different crude oil feedstocks, thereby warranting varied refining processes to produce a gasoline blend with the desired components (e.g., low benzene concentrations and high octane ratings).

Many common biomarkers conventionally used for environmental forensics studies are removed during the refining process; however, various refinery processes, including reforming and alkylation, impart specific chemical characteristics on gasoline products that can provide alternatives to characterize and potentially differentiate gasolines that have been released to the environment (Beall et al. 2002).

### **2.5.2 Chemical Characteristics of Middle Distillates**

The middle range distillates include products such as diesel fuel, heating oils, kerosene and jet fuels. Middle range distillate fuels are used throughout the world to power motors, heat residences, fuel jet engines and propel ships, among many other uses. Diesel fuel constitutes the second largest fraction of product obtained per barrel of crude oil (i.e., typically greater than 22%) (US EIA 2012).

Middle range distillates are characteristic of a more broad carbon boiling range than their light distillate counterparts. They include hydrocarbons with a chain length primarily between 8 and 28 carbon atoms. Fresh (non-weathered) diesel fuel typically consists of normal alkanes (*n*-alkanes), alkyl-cyclohexane, and PAHs. In comparisons with gasoline, the chemical composition of diesel fuel is more dependent on the crude oil feedstock composition. Diesel consists of higher concentrations of *n*-alkanes, alkyl-cyclohexanes, and PAH compounds than gasoline. Diesel is typically comprised of approximately 75% saturated hydrocarbons (primarily alkanes), and 25% aromatic hydrocarbons (including naphthalenes and alkylbenzenes) (Mudge 2009). Straight chain *n*-alkanes are the most prevalent chemical compound in diesel fuel and aromatics and branched chain alkanes are still present; however, *n*-alkanes are less required in diesel fuel than in gasoline (Stout and Wang 2016).

A universal complex mixture (UCM) hump is evident in most GC analyses of weathered diesel fuel, whereas a UCM hump will not be evident in a GC analysis from a fresh or weathered gasoline product sample due to the distribution of chemical compounds (Yang et al. 2012). The hydrocarbons that comprise diesel fuel are molecularly heavier than those in gasoline; making them essentially less volatile and therefore, less susceptible to most predominant weathering processes (Wang and Stout 2007).



Diesel fuels historically contained a high amount of sulfur because diesel fuel and sulfur are removed from crude during the refining process at a similar time interval in the distillation process (Wang and Stout 2007). Regulations introduced throughout the 1990s (e.g., 1997 Diesel Fuel Regulations Act (SOR/97-110)) mandated strict MACs of sulfur content in diesel fuel to 500 mg/kg (Gov. Can. 1999). Ultra-low sulfur diesel, introduced in 2009, and now produced and sold across North America and Europe contains a maximum sulfur content of 10 mg/kg. The evolving regulations regarding sulfur in diesel fuel provides an opportunity to identify variations in sulfur distribution patterns in diesel fuel products from different time periods.

## **2.6 Effects of Weathering Processes on Crude Oil Chemical Composition**

Weathering processes can have a significant effect on chemical characteristics within light and middle distillates. Alteration of the chemical composition of petroleum products in the environment is caused by physical, chemical, and biological factors collectively referred to as weathering. The predominant biological weathering process that will alter the chemical characteristics of light and middle range distillates is biodegradation. Additional physical and chemical weathering processes that have a large influence in altering the chemical fingerprint of distillates in the environment include evaporation, dissolution, solubilization, adsorption, sequestration, chemical precipitation, and advection (Morrison 2000; Mudge 2009).

Biodegradation of petroleum products in the subsurface is a complex process and requires a specific suite of conditions in order to degrade substantial amounts of gasoline or diesel fuel. The rate and effects of biodegradation on light and middle range distillates depend not only on the properties of the released distillate but also on environmental variables that affect growth of PHC-degrading microbial communities (Morrison and Murphy 2006). The primary geochemical factors influencing the rate and extent of petroleum biodegradation include the availability of oxygen (or other suitable electron acceptors; e.g., nitrogen, iron), available nutrients, pH levels, and the moisture content and temperature of the subsurface environment. Additionally, the volume of distillate product released to the environment is a key variable influencing the level of toxicity of the release product to the hydrocarbon-degrading microbes in the subsurface. For example, a slow product leak from a UST over an extended timeframe might encourage an acceleration of microbial growth and accelerate biodegradation. Alternatively, a large volume of product released in an acute event might limit the number of suitable electron acceptors (e.g.,

reduce oxygen concentrations in the subsurface), creating an environment that is too toxic for microbial biodegradation to occur (Stout and Lundegard 1998).

When a light distillate is released to the environment, the released product is subject to rapid evaporation and biodegradation due to the low carbon boiling range characteristic of light distillates. This can rapidly remove many potentially valuable diagnostic features from the product. The influence of weathering on the chemical composition of a spilled petroleum product is a direct function of the rate of weathering and the residence time in the environment (Mulroy and Ou 1998). Therefore, the longer the residence time of the product in the subsurface and the greater the distance from the source the distillate travels, the more difficult the distillate will become to fingerprint. For a surface release of light or middle range distillates, evaporation could contribute up to a 70% loss of chemical compounds within a matter of days (Morrison and Murphy 2006; Madge 2009).

Examining weathering patterns in sample analytical results is beneficial to an environmental forensics program. It may provide a basis to associate petroleum products originating from a common source and a qualitative foundation for age dating. A typical analysis run during standard Phase II ESAs will not produce sufficient chemical information for a quantitative chemical fingerprinting study. The PAH and BTEX compounds measured using standard EPA 8270 and 8260, respectively, typically make up less than 5% to 8% of the total aromatic compounds in most light and middle range distillate petroleum products by volume; therefore, the typical analytical dataset obtained from a Phase II ESA it is unlikely to provide sufficient diagnostic characteristics to permit source differentiation (McCarthy et al. 1998; Kaplan et al. 1997).

In contrast, qualitative forensic data can often be obtained from a standardized PHC analytical dataset (e.g., using EPA 8270 and 8260 analytical methods) and could help build the foundation for an environmental forensics study. For example, toluene is generally considered to be more biodegradable than other hydrocarbon chemicals in gasoline (e.g., benzene) and can therefore indicate microbial degradation when preferentially removed relative to benzene and the remaining C<sub>8</sub> aromatic compounds (Morrison 2000). The sequence of BTEX loss in groundwater generally begins with benzene because it diffuses rapidly from phase-separated gasoline and partitions into groundwater, followed by toluene, ethylbenzene and xylenes. The reverse

sequence occurs with BTEX in soils; toluene, ethylbenzene, and xylenes are preferentially retained by soils relative to benzene. Ethylbenzene and xylenes are more resistant to degradation than benzene or toluene and alkylbenzene compounds are more resistant than BTEX compounds (Morrison 2006).

Mudge (2009) describes three classes for defining the extent of weathering of a released crude oil or distillate product; lightly weathered (less than 15% weathered), moderately weathered (15% to 30%), and severely weathered (greater than 30% weathered). In a lightly weathered scenario, short chain *n*-alkanes decrease significantly and BTEX and C<sub>3</sub>-benzene compounds also decrease in abundance. However, isoprenoids may be largely unaltered and abundant two-ring alkylated naphthalene compounds can become more prominent. In a moderately weathered scenario, further significant reductions of *n*-alkanes and aromatic compounds. Certain biomarker compounds in crude oil and potentially diesel fuel products may become more prominent. As a released crude oil or distilled product becomes severely weathered, alkanes (including *n*-alkanes, branched-chain alkanes and cyclo-alkanes) and aromatics (including BTEX compounds) will be reduced and eventually completely degraded. As the extent of weathering becomes more severe, the concentrations of alkylated naphthalene compounds will decrease relative to other alkylated PAH homologous compounds. The alkylated chrysene series will become more concentrated relative to other PAH series hydrocarbons. Hydrocarbon biomarker compounds are concentrated because of their refractory nature and high resistance to biodegradation (Kaplan et al. 1997).

Kaplan et al. (1997) summarized the weathering process of light and middle range distillates; these occur in seven notable stages (Table 2.4).

**Table 2.4** - Alterations in the Chemical Composition of Light and Middle Range Distillates in Relation to the Extent of Weathering (adapted from Kaplan et al. 1997)

<b>Distillate Product Type</b>	<b>Extent of Weathering</b>	<b>Chemical Composition</b>
Light and Middle Distillates	1 (fresh, non-weathered)	Abundant <i>n</i> -alkanes
Light and Middle Distillates	2 (lightly weathered)	Low carbon range <i>n</i> -alkanes removed, benzene & toluene degraded or removed
Light and Middle Distillates	3 (lightly weathered)	Middle carbon range <i>n</i> -alkanes removed, ethylbenzene and xylenes degraded or removed
Light and Middle Distillates	4 (moderately weathered)	More than 50% of <i>n</i> -alkanes removed
Light and Middle Distillates	5 (moderately weathered)	More than 90% of <i>n</i> -alkanes removed, alkylbenzenes and alkylcyclohexanes degraded
Middle Distillates	6 (severely weathered)	All <i>n</i> -alkanes removed, alkylbenzenes & alkylcyclohexanes removed by 50%
Middle Distillates	7 (severely weathered)	Isoprenoids considerably removed

The susceptibility of alkanes (considering both normal and branched chain alkanes) to weathering processes can be directly correlated to the carbon number or chain length of the chemical compounds in light or middle distillates. The shorter or more simple the chemical structure, the more easily the compound can be weathered. As the more simple compounds in the released fuel blend become weathered and essentially disappear, more complex compounds will become more prevalent in the product.

The degradation order of key compound classes is expected to be similar in both aerobic and anaerobic conditions (for example, *n*-alkanes will be typically be degraded first followed by isoprenoids) (Hostettler and Kvenvolden 2002). Degradation of *n*-alkanes up to compounds in the C<sub>28</sub> range is possible under anaerobic conditions and more so under aerobic conditions. The compound degradation order can be influenced by numerous factors under both aerobic and anaerobic conditions. For example, the degradation order of key compound classes would likely be different if the same product were released to the sub-surface in sulfate-reducing conditions compared to nitrate-reducing conditions (Hostettler and Kvenvolden 2002; Onojake 2015). The

potential for numerous variations influencing redox reactions suggests that employing diagnostic ratios (e.g., *n*-alkane/isoprenoid), as a measure of degree of weathering could result in inconclusive data (Onojake 2015).

## **2.7 Recalcitrant Characteristics of Light and Middle Range Distillates**

Conventional target analytes for crude oil environmental forensics investigations include *n*-alkanes, acyclic isoprenoids, PAHs, alkylated PAHs, and triterpane and sterane biomarkers (Sauer and Costa 1993; Wang and Stout 2007; Stout and Wang 2016). This section will summarize the findings of this literature review for recalcitrant compounds in light and middle distillates. These compounds could provide value as target diagnostic analytes for environmental forensics studies.

### **2.7.1 Biomarkers**

Refining and weathering processes remove many valuable high molecular weight biomarkers, such as terpanes and steranes, from light and middle distillate products due to the lower boiling ranges of these products. However, there is potential that selected recalcitrant biomarker parameters, including sesquiterpanes and diamondoids, are not removed through the refining process of selected distillate products. Refinery processes could also cause these molecularly smaller biomarker compounds to become more concentrated in distillate products (Yang et al. 2012). Stout et al. (2005) observed that lower molecular weight biomarker compounds, including bi-cyclic sesquiterpanes and diamondoid hydrocarbons are present at detectable concentrations in GC/MS analysis of middle distillate samples. Yang et al. (2005, 2012) observed variations in absolute concentrations and relative distribution patterns of bi-cyclic sesquiterpanes in case studies analyzing middle range distillate samples.

Adamantanes and diamantanes are low boiling diamondoids that elute in the C<sub>10</sub> to C<sub>13</sub> and C<sub>15</sub> to C<sub>17</sub> boiling ranges, respectively. Therefore, there is potential that adamantanes could be present in gasoline samples and both biomarker compounds could be present in middle distillates. Diamondoids would be valuable biomarkers as they would retain the carbon skeleton from their crude oil feedstock and are also highly resistant to weathering (Yang et al. 2012; Stout and Wang 2016).

### 2.7.1.1 Normal Alkanes and Isoprenoids

Selected branched-chain alkanes that may be present in middle distillate fuels and biomarkers including 2,6,10,14-tetramethylpentadecane (pristane) and 3,5,11,15-tetramethylhexadecane (phytane) have the potential to remain largely chemically unaltered throughout the refinery process.

Alkyl-cyclohexane compounds can be more recalcitrant to weathering than *n*-alkanes and are also valuable because the distribution patterns of alkyl-cyclohexanes are highly varied due to the reforming and blending processes during refining. Kaplan et al. (1997) suggested that alkyl-cyclohexanes are highly resistant to chemical alteration due to weathering and could potentially be identified in samples where all or most *n*-alkanes, iso-alkanes and alkylbenzenes have been degraded. Therefore, comparing alkyl-cyclohexane distribution patterns to reference samples could provide valuable diagnostic data in products where diagnostic features, such as *n*-alkanes, iso-alkanes and to a lesser extent alkylbenzenes, can be more quickly degraded.

Iso-alkanes, formed during the alkylation process, such as 2,2,4-trimethylpentane (iso-octane) could be a valuable diagnostic feature. Different acids are used during the alkylation processes that would contribute to altering the chemical fingerprint and these would be specific to different refineries. Different proportions of isooctane could be expected in different refineries due to the proprietary processes they each use. Iso-octane isomers from two different products would be expected to react similarly to environmental weathering as they are highly resistant to biodegradation (Peters et al 2005a). Therefore, the iso-octane ratios could be valuable for product differentiation purposes.

### 2.7.1.2 Alkylbenzenes

Various practices employed by a refinery during the reforming process will result in varied proportions of BTEX compounds in gasoline blends, resulting in an opportunity to differentiate gasoline products. However, as detailed in Section 2.6, weathering processes can also have a significant impact on BTEX compound proportions, limiting the defensibility of this method (Beall et al. 2002).

The major hydrocarbon compounds present in light distillates that are of current environmental concern, as mandated by regulatory criterion, include monoaromatic hydrocarbons such as BTEX chemical compounds and certain compound classes of alkylbenzenes (e.g., C<sub>3</sub>-alkylbenzenes and C<sub>4</sub>-alkylbenzenes). In a recent forensics study conducted on fire debris for the purpose of arson investigation, Lentini (2013) considers the C<sub>3</sub>-alkylbenzene group of particular importance when analyzing datasets for evidence of gasoline. This could be one of the more important patterns to detect in a light distillate sample as C<sub>3</sub>-alkylbenzenes are found in all petroleum products where the aromatics have not been completely removed or degraded, and unless evaporation has decreased the concentration of the lighter compounds, the GC peak ratios will always be the same (Peters et al. 2005a). Wang et al (1998) found that when studying analytical results from samples collected from a crude oil spill site that alkylbenzenes had been substantially degraded in near-surface samples (i.e., less than 40 cm). However, the alkylbenzene distribution pattern was comparable in reference samples and in samples collected from greater than 40 cm depth. This evidence suggests that alkylbenzenes may be more resilient to weathering processes in the subsurface.

### **2.7.1.3 Polycyclic Aromatic Hydrocarbons**

PAHs refer to a large group of persistent organic compounds consisting of hundreds of individual homologues and isomers that contain at least two fused aromatic benzene rings (Jiang et al., 2009). PAHs are formed during the thermal decomposition of organic molecules and their subsequent recombination (Haritash and Kaushik 2009). Alkylated PAHs are fundamentally the parent PAH compound with at least one hydrogen atom substituted with an alkyl group (e.g., 2,3,5-trimethylnaphthalene is a C<sub>3</sub> alkyl homolog of the parent PAH compound naphthalene). Alkylated PAHs are characterized by the total number of alkyl carbon atoms present on the parent PAH compound. Certain unsubstituted parent PAH compounds may be present in crude oils; however, crude oils typically contain primarily alkylated PAHs (Zhao et al. 2014).

Crude oil consists of many cyclo-alkane compounds including a variety of polycyclic naphthenes (Zhao et al. 2014). Due to the complex chemical structure of PAH and alkylated PAH compounds they are recalcitrant and often remain present throughout most of the refining processes. Many PAH compounds, particularly alkylated PAHs are more resistant to weathering than their saturated hydrocarbon counterparts (e.g., terpanes and *n*-alkanes). Middle distillate

products, and to a lesser extent, light distillates predominantly contain 2- and 3-ring PAH and alkylated PAHs due to the boiling ranges of these products. In middle distillate products, lower boiling 4-ring PAHs (e.g., fluoranthenes and pyrenes) may also be present. Higher boiling 4-ring PAHs, 5- and 6-ring PAHs are not typically present in middle distillates (Stout and Wang 2016; Wand and Stout 2007).

The aqueous solubility of PAHs decreases approximately logarithmically as molecular mass increases. Two fused aromatic ring (two-ring) PAHs, and to a lesser extent three-ring PAHs, dissolve in water, making them more susceptible to weathering processes than PAHs with four or more aromatic rings. PAH compounds with five or more rings have low solubility in water and low volatility; therefore, in the subsurface these compounds are predominantly observed bound to soil or sediment particles due to adsorption (Jiang et al. 2009).

PAH compounds in crude oils are dominated primarily by the C<sub>1</sub> to C<sub>4</sub> alkylated homologues of the parent PAHs, specifically, chrysene, dibenzothiophene, fluorine, naphthalene, and phenanthrene (Wang et al. 1999). Alkylated PAHs have been shown to be present in higher concentrations in GC/MS analysis of middle distillate samples than parent PAHs. Therefore, alkylated PAHs have extensive and thorough applications in environmental forensic source differentiation and identification as well as product weathering studies (Zhao et al. 2014).

PAHs, such as chrysene and dibenzothiophene, may be removed from middle distillates during distillation. However, alkylated PAH homologues of phenanthrenes and dibenzothiophenes have been reported within fresh diesel fuel samples (Stout et al. 2001). An important feature of the environmental fate of the PAH hydrocarbons is the relative constancy of the C<sub>2</sub>- and C<sub>3</sub>-phenanthrenes and C<sub>2</sub>- and C<sub>3</sub>-dibenzothiophenes over a wide range of concentrations and degrees of weathering (Douglas et al. 1996). Douglas et al. (1996) observed nearly similar rates of depletion of these analytes. Therefore, their ratios (i.e., C<sub>2</sub>-dibenzothiophenes/C<sub>2</sub>-phenanthrenes and C<sub>3</sub>-dibenzothiophenes/C<sub>3</sub>-phenanthrenes) remain relatively constant throughout the increasing extent of weathering. Also, since the concentrations of dibenzothiophenes vary widely in different crude oil sources, the relative concentrations of phenanthrenes and dibenzothiophenes may be useful as source indicators (Stout et al. 2001; Wang et al. 1999; Wang and Stout 2007). Since diesel from different feedstocks will potentially be characteristic of diverse PAH concentrations, the relative distribution patterns of PAH



compounds, particularly chrysene, fluorine and naphthalene compounds, may also be of value for source identification (Wang and Stout, 2007).

PAH homologue patterns are considered valuable classes of hydrocarbons for chemical fingerprinting differentiation and source identification due to the variable thermal stabilities of the various PAH isomers during the formation of crude oil feedstock and distillation processes. A combination of the varied feedstock attributes and distillation processes result in unique PAH isomer distribution patterns in middle distillate products (Stout and Wang 2016).

### **2.7.2 Chemical Distribution Patterns and Diagnostic Ratios**

The extent of weathering processes on a fuel released at the surface will largely be the governing factor in the ability to identify and calculate diagnostic ratios between the resolved chemical compounds present in the chromatogram. Identifying and calculating diagnostic ratios of recalcitrant compounds that have similar environmental behaviors (e.g., pristane/phytane ratios or carbon preference indices among higher-boiling *n*-alkanes) is fundamentally important for middle distillate environmental forensic studies. This is the case both for initial characteristic data interpretation and product characterization. This data also provides some of the first lines of evidence for product differentiation (Stout et al. 2002).

GC-FID analysis allows for quantitation of the individual chemicals that can be chromatographically separated and measured. The absolute concentrations of the individual chemicals can be quantitatively measured through the use of relative concentrations measured using peak areas (Stout and Wang 2016).

The varied distributions of compounds in GC-FID chromatograms from gasoline-impacted samples are not valuable for diagnostic purposes due to a combination of limited variation in refined gasoline products across North America and alteration of the chemical characteristics caused by weathering processes (Mudge 2009). However, the GC/MS TIC provides the chemical components of the analyzed sample which can be used to calculate various diagnostic ratios for gasoline-impacted samples (Onojake et al. 2015). The chemical fingerprint derived from GC/MS TIC represents the relative concentration of individual chemicals present in a sample.

The adverse effects of weathering processes on gasoline released to the subsurface (e.g., gradual release from a UST), can occur rapidly due to the relatively low boiling range of

gasoline and can quickly remove many potentially diagnostic features. However, chemical fingerprinting of the higher boiling range compounds of suspected residual gasoline impacts may still yield useful results. Diagnostic ratios calculated using peak areas of specific compounds of the same molecular weight but with different chemical characteristics (such as volatility, solubility or biodegradability) can provide valuable details to assess variations in chemical compositions in spilled products and reference samples to support product differentiation and source identification.

## **CHAPTER 3 METHODS AND MATERIALS**

In order to fulfill the proposed objective of this study, which was to develop a novel tiered approach to differentiate and identify sources of gasoline and diesel fuel releases at the Study Site, unique sampling and laboratory procedures were developed and employed. The initial step was to complete a critical assessment of all relevant data for the Study Site. Subsequently, relevant contaminated groundwater samples, LNAPL samples, and reference samples were collected from the Study Site. Finally, a modified laboratory analytical strategy was developed and employed to provide sufficient data to satisfy the study objectives.

### **3.1 Environmental Site Assessment Procedures**

Phase I ESA activities were completed as a desktop study with a site visit for visual assessment completed in accordance with the Canadian Standards Association's (CSA) Phase I Environmental Site Assessment Standard Z768-01 (R2012). The Phase I ESA consisted of reviewing publicly available city directories, aerial photographs, geological and topographic maps. A search request for available site information was requested and obtained from the City of North Battleford Fire & Emergency Services. A review of the Government of Saskatchewan Spills Search database was completed. A review of previous environmental reports and existing title searches was completed. A site visit and phone interview with the owner of the Site was conducted to visually assess the Study Site and further interpret the findings of the desktop study results. A detailed review was conducted of Phase II ESA reports completed at the Site in 2007 and 2008 (Stantec 2007; Stantec 2008).

A total of twelve existing monitoring wells at the Study Site were surveyed using a Trimble GeoXT global positioning system (GPS) unit to determine the northings and eastings within the Universal Transverse Mercator (UTM) coordinate system NAD 1983 Zone 13 projection. A vertical survey was completed using a Sokkia B s40 automatic level and metric rod. The top of the east concrete pile of the main entrance sign, located at the northwest portion of the Study Site, was used as a benchmark.

Groundwater monitoring wells at the Site were monitored using a Heron Instruments Inc. oil and water interface meter to measure depths and determine if LNAPL was present. The oil and water interface meter allows for the measurement of the thickness of LNAPL present floating on groundwater within the 50.8 mm (2”) monitoring well column, because LNAPL has a lower density than water.

### **3.2 Sampling Procedures**

Based on the review of historical PHC concentrations in groundwater at certain monitoring well locations across the Study Site, two groundwater samples were suspected gasoline-impacted monitoring wells: RW206 and MW102 (Fig. 4.2). Prior to the groundwater sample collection, stagnant groundwater was purged from the monitoring wells RW206 and MW102 until three well volumes of groundwater had been removed. Groundwater samples were collected on January 31, 2013 once the groundwater had recovered to greater than 90% of the pre-purge static water level. Groundwater samples were collected by using dedicated disposable high density polyethylene (HDPE) bottom-emptying bailers. The bailers were inserted into the water column slowly, attempting minimal disturbance of the water column. The water collected in the bailer was then transferred as slowly as possible into glass laboratory sample containers to limit degassing, volatilization, aeration, and oxidation as much as possible, since these processes could potentially alter the groundwater chemistry. Additionally, a fresh gasoline sample was collected directly from the pump island at the Study Site into glass containers (40 mL vials and 200 mL jars) with no headspace. The fresh gasoline samples was also collected on January 31, 2012.

Monitoring well RW209 (Figure 4.2) was selected as a best candidate at the Study Site to collect a suspect diesel-impacted sample, based on historical LNAPL measurement records. The sample from monitoring well RW209 was collected on November 7, 2012 using the same methodology as the suspect gasoline-impacted samples, attempting minimal disturbance of the substances within the monitoring well column. The sample collected from monitoring well RW209 was largely comprised of LNAPL. A fresh diesel sample was also collected directly from the pump island at the Study Site into glass containers with no headspace.

The samples were transported in a cooler with ice, at 2 to 4 °C, to a laboratory operated by Maxxam Analytics Inc. (Maxxam) in Mississauga, Ontario. The samples were received and logged by the laboratory and stored in a refrigerator at 4 °C until analysis.

### **3.3 Laboratory Procedures**

Laboratory analyses were conducted by Maxxam in Mississauga, Ontario under the direction of Ryan Bernesky.

In order to ensure the comparability of PHC compounds dissolved in groundwater, 2 mL of the fresh gasoline sample was shaken with 41 mL of deionized water in a pre-cleaned 43 mL vial for five minutes and the mixture was allowed to settle for two hours. The fresh gasoline solution and the gasoline-impacted groundwater samples were analyzed for gasoline GC/MS. The fresh diesel and LNAPL samples were analyzed for whole oil GC/MS and alkylated PAHs.

Samples were spiked with recovery surrogates prior to extraction. Recovery surrogates, with physical and chemical properties similar to the PHC target analytes, were used to qualify the efficiency of organic extractions and performance of the laboratory instruments. Volatile organic compounds (VOC) samples were fortified with d<sub>10</sub>-ethylbenzene as a recovery surrogate; while semi-volatile samples were fortified with o-terphenyl as a recovery surrogate. Prior to GC/MS analysis, 500 mL of the aqueous samples were extracted with 5 mL of hexane by tumbling the bottle for 1 hour. An aliquot of 5 mL of the hexane extract was transferred to a pre-cleaned glass tube and concentrated to 1 mL. The fresh diesel and LNAPL samples (100 mg) were dissolved in 10 mL of hexane each and shaken vigorously using a paint shaker. The samples were transferred into clean-up columns filled with 3 g activated silica gel and 1 g of anhydrous sodium sulphate.

A summary of the GC/FID pre-screening analysis, gasoline GC/MS analysis, whole oil GC/MS analysis, and alkylated PAH analysis is provided below.

#### **3.3.1 GC/FID Pre-Screening Analysis**

Samples were pre-screened by GC/FID prior to being subjected to full volatile or semi-volatile analysis by GC/MS. For volatile analysis, pre-screening (C<sub>6</sub> – C<sub>10</sub> hydrocarbons) water samples (10 mL) were analyzed directly without extraction after addition of sodium chloride (1 g) to a 20 mL headspace vial. Product samples were diluted to 1 mg/mL with methanol and an aliquot (0.25 mL) of the methanol extract was mixed with 10 mL of matrix modifying solution (5 g/L of

sodium bisulphate) and 1 g sodium chloride prior to analysis. All samples were fortified with  $d_{10}$ -ethylbenzene as a recovery surrogate prior to extraction. Samples were extracted by a static headspace procedure. Once equilibrium was achieved, a fixed volume of headspace was taken for subsequent determination by gas chromatography / flame ionization detection (GC/FID).

Headspace GC/FID analysis was performed on a Agilent Model 6890 GC equipped with a split/splitless injector (240 °C) used in splitless mode, a DB-1 30m x 0.25mm x 1.0  $\mu$ m film column and a FID detector operated at 250 °C. Helium carrier gas was injected (1 mL) at a flow rate of 0.4 mL/minute (min) for the first 0.5 min, which was increased to 1.5 mL/min for the balance of the run. The FID make-up gas was nitrogen, flowing at 45 mL/min. The column temperature was programmed with an initial temperature set to 40 °C and set to hold for 1 min. The column temperature was then increased from 40 °C to 250 °C at a rate of 30 °C/min, followed by a hold time of 3 min. The signal from the FID detector was used for the determination of PHC Fraction F1 ( $C_{>6}$  to  $C_{10}$ ) by integration of all area counts from the beginning of  $C_6$  peak to the apex of  $C_{10}$  peak. The area counts were quantitated by comparison to the response factor of toluene.

For semi-volatiles pre-screening ( $C_{>10}$  to  $C_{50}$ ) all samples were fortified with o-terphenyl as a recovery surrogate prior to extraction. Water samples (500 mL) were extracted with 5 mL hexane in the supplied bottles by shaking or tumbling for one hour. The recovered hexane layer was dried with sodium sulfate, diluted 1:1 with dichloromethane (DCM), and cleaned up with activated silica gel prior to GC/FID analysis. Product samples were diluted to 1 mg/mL with hexane: DCM (1:1) and cleaned up with activated silica gel prior to GC/FID analysis.

GC/FID analysis was performed on an Agilent Model 6890 GC equipped with a split/splitless injector (350 °C) used in splitless mode, a Restek MXT-1 capillary column (15 m long, 0.25 mm internal diameter (ID), and film thickness 0.1  $\mu$ m) and a FID detector operated at 250 °C. Injection volume was 1 mL. Helium carrier gas was used at 12 psi. FID make-up gas was nitrogen, flowing at 45 mL/min. The initial column temperature was programmed to 55 °C and initial hold time of 3 min. The column temperature was then increased from 55 °C to 240 °C at a rate of 30°C/min, then increased from 240°C to 350 C at a rate of 20 °C/min, with a final hold time of 5 min (i.e., 5 min after  $C_{50}$  elutes). The average response factor of  $C_{10}$ ,  $C_{16}$ , and  $C_{34}$  was

used to calculate the hydrocarbons in each of the ranges PHC Fractions F2 ( $C_{>10}$  to  $C_{16}$ ), F3 ( $C_{>16}$  to  $C_{34}$ ) and F4 ( $C_{>34}$  to  $C_{50}$ ).

### **3.3.2 Gasoline GC/MS Analysis**

Gasoline GC/MS analyses were completed with an Agilent Model 6890 GC equipped with a split/splitless injector used in split mode with a 10:1 to 50:1 split ratio, a Restek Rtx-624 column ( $60\text{ m} \times 0.25\text{ mm I.D. } 1.4\text{ }\mu\text{m}$  film thickness), and an Agilent 5973C mass selective detector (MSD). The oven temperature program started with an initial temperature of  $50\text{ }^\circ\text{C}$  and initial hold time of 3 min. The oven temperature was then increased to  $60\text{ }^\circ\text{C}$  at a rate of  $5\text{ }^\circ\text{C}/\text{min}$ , to  $160\text{ }^\circ\text{C}$  at a rate of  $10\text{ }^\circ\text{C}/\text{min}$ , and then to a maximum temperature of  $220\text{ }^\circ\text{C}$  at a rate of  $4\text{ }^\circ\text{C}/\text{min}$ . The maximum temperature was held for 2 min. Gas flow was set at 1.5 to 2 mL/min. The mass spectrometer was operated in either a full scan (35 to 300 amu) or SIM mode to improve sensitivity. The SIM mode analyses included collection of  $m/z$  ratios of 55, 83, 91, 97, 105, 117, 119, and 128. The chromatography data was collected and processed with Agilent G1701 BA MSD ChemStation with Enviroquant data processing software and EPA/NIST Mass Spectral Library.

In this study, the gasoline GC/MS analysis used a purge-and-trap sample introduction method (USEPA Methods 5030C). Sample introduction was completed using a Tekmar AquaTek 100 autosampler and Tekmar 3100 liquid concentrator system (LCS). 25 mL of the fresh gasoline solution and groundwater extracts was purged by helium with a flow rate of 40 mL/min for 10 min under ambient temperature. The volatiles and purge gas (helium flow rate at 40 mL/min) were then passed through a VOCARB 3000 (Carbopack B/Carboxen 1000 & 1001) sorbent trap, which is designed to absorb a broad range of volatile compounds. The instrumental conditions for the desorb mode are as follows: desorb preheat ( $245\text{ }^\circ\text{C}$ ); desorb temperature ( $250\text{ }^\circ\text{C}$ ); desorb time (1 min); bake time (3 to 7 min); and bake temperature ( $260\text{ }^\circ\text{C}$ ).

### **3.3.3 Whole Oil GC/MS Analysis and Alkylated PAH Analysis**

In this study, the diesel GC/MS analysis used semivolatile organic compounds by GC/MS method (USEPA Methods 8270C). Hexane (12 mL) and DCM in hexane (v/v, 15 mL) were used to elute the saturated and aromatic hydrocarbon fractions of the fresh diesel and LNAPL extracts, respectively. The hexane fraction was used for analysis of aliphatics, *n*-alkanes, and

biomarker compounds including sesquiterpanes, while a DCM/hexane fraction was used for analysis of PAHs. The two fractions were each spiked with internal standard (p-terphenyl-D<sub>14</sub>) and were subsequently analyzed on an Agilent 7890 GC interfaced to an Agilent 5975C MSD with electron impact (70 eV). The Agilent Model 7890 GC was equipped with an Agilent J&W DB-5.625 capillary column (30 m × 0.25 mm I.D. × 0.25 μm film thickness, Agilent Technologies, Santa Clara, CA, USA). Extracts were analyzed by GC/MS in both full scan and SIM mode. Samples were injected in splitless mode with helium as carrier gas flowing at 1.0 mL/min. The GC oven was initially programmed at 50 °C with a 2 min hold time, heated to 310 °C at 5 °C/min, followed by a final hold of 6 min. System control and data acquisition were achieved with the Agilent G1701 BA MSD ChemStation with Enviroquant data processing software and EPA/NIST Mass Spectral Library. The mass range scanned was 35 to 300 amu. The SIM mode was used for quantitative determination of individual compounds in the samples, including *m/z* ratios 85, 113, 123, 134, 179, 191, 193, 207, 217 and 218.

The separation of PAH analytes and their alkylated homologues by GC/MS is based on compound size, boiling point and polarity. The PAH GC/MS analysis was conducted on an Agilent 7890 GC interfaced to an Agilent 5973C MSD with electron impact ionization (70 eV). The Agilent Model 7890 GC was equipped with an Agilent J&W, DB-5MS, 30m x 0.25mm, 0.25 μm, column). Samples were injected in splitless mode (295 °C, 1 μL) with helium as carrier gas flowing at 1.5 mL/min. The GC oven was initially programmed at 45 °C with a 5 min hold time, then heated to 100 °C at 5 °C/min, then heated to 320 °C at 5 °C/min. Target unsubstituted PAHs were quantitated against the average response factor of multipoint calibration curves of these PAHs using the internal standard method. The concentrations of alkylated PAH homologous series were calculated in a similar manner against standards representative of each homologous series.

### **3.3.4 Data Interpretation**

Pearson correlation coefficient is a measurement of the linear correlation between two variables. A Pearson correlation coefficient measurement will produce a value between 1 and -1; where 1 is total positive linear correlation, 0 is no linear correlation, and -1 is total negative linear correlation. Pearson correlation coefficients were used to confirm similarities or differences of compound distribution patterns in analytical data.



## **CHAPTER 4 RESULTS AND DISCUSSION**

### **4.1 Introduction**

A tiered environmental forensics strategy has been developed throughout the process of this thesis to effectively differentiate and identify sources of light and middle range distillates, namely gasoline and diesel fuel. The primary components of the tiered strategy can be described as follows:

- Tier 1 - Develop a fundamental understanding of the current and operational history of the Site and surrounding lands, through effective background assessment techniques.
- Tier 2 - Develop a fundamental understanding of the subsurface geology and hydrogeology at the Study Site, through effective site characterization techniques.
- Tier 3 - Determine if laboratory data supports findings, from site background and characterization, suggesting that more than one contaminant source could be present at the Study Site using pre-screening laboratory analytical techniques (i.e., GC/FID analysis).
- Tier 4 – Confirm that more than one distinct contaminant source is present at the Study Site through more robust unique laboratory analytical techniques and data review (i.e., GC/MS full scan and GC/MS selected ion monitoring SIM analysis).
- Tier 5 - Develop a conclusion based on the results which link the technical findings of Tier 3 and Tier 4 back to the practical fundamental findings of Tier 1 and Tier 2. Tier 5 summarizes the lines of evidence differentiating contaminated soils and groundwater and links identified contaminant sources to the evidence.

The Results section has been organized to illustrate the importance of each of the five fundamental tiers of this novel environmental forensics strategy, and show how each component of this strategy is critical for developing a thorough and defensible environmental forensics conclusion.

## **4.2 Tier 1 & Tier 2 - Study Site Background Findings**

### **4.2.1 Site Operational History and Background**

The Study Site was agricultural land until 1959 when it was developed as a retail fuel facility, as determined through a review of aerial photographs and historic land titles. Based on a review of historic land titles and aerial photographs, the Study Site first operated as a retail fuel facility, providing gasoline and/or diesel fuel in 1959. Between 1968 and 1989, the Study Site was a vehicle dealership, during which time it is unknown if the Site included fuel services. In August 1989, the Study Site was purchased by the current landowner and was converted back to a retail fuel facility. The Study Site has consisted of an operational retail fuel facility from 1990 to present day.

A Freedom of Information (FOI) request made to the local Fire and Emergency Services office provided details regarding decommissioning and removal of a UST at the Site in 1989. The UST was constructed of steel with a total volume of 3,780 L (1,000 gallons) and installed possibly in the northeast corner of the current convenience store building (Fig. 1), based on aerial photograph reviews. The response to the FOI request indicated that fuel contaminated soil was observed during UST removal, which was subsequently separated and removed for disposal. The FOI request response document states that a “good, clean excavation site” was left behind (Stantec, 2010). Stating the completeness of an excavation based on a matter of opinion (assumed to have primarily been based on visual and olfactory observations) and not by collecting and analyzing samples appears to have been a common and accepted practice during the 1970s and well into the 1990s, based on the author’s review of FOI request responses for retail fuel facility properties in Western Canada during this time frame. The 2010 FOI request response for the Study Site also indicates that three USTs (two 25,000 L and one 50,000 L), containing gasoline and diesel, respectively, were installed in August 1990.

### **4.3 Surrounding Land Use**

Historical land titles indicate that in 1955, a commercial bulk fuel operator occupied land located immediately south of the current Site boundary. The same bulk fuel operator appears to have procured land comprising the current Site boundaries, through a northern facility expansion in August 1959. A FOI request response provided in January 2013 for the commercial property

located adjacent to the south of the Study Site indicates that a UST was removed in August 1984. However, the location of the UST within the adjacent property, size of the UST, and type of fuel contained within the UST are unknown (Stantec 2013).

A FOI request response obtained in January 2013 for the commercial property located adjacent to the south of the Study Site indicates that a UST was removed in August 1984. However, the location of the UST within the adjacent property, size of the UST, and type of fuel contained within the UST are unknown (Stantec 2013). An additional former retail fuel facility was historically located approximately 80 m south of the Study Site. A second FOI request response provided in January 2013 reported that three fiberglass USTs, ranging in size from 5,000 L to 10,000 L, were removed in 1985. Additionally, known contamination associated with fuel services at this property was reported in the FOI request response; however, the confirmation that the property was remediated was not included.

A separate retail fuel facility was also historically operated at the property located at the northwest corner of the intersection, opposite of the Study Site. The northwest property operated as a retail fuel facility until being abandoned in 2013, as per site observations made by the author. Records of a FOI request response for this property located northwest of the Study Site, were not available to the author for the writing of this thesis. However, an aerial photograph review of this property indicates that it consisted of an operational retail fuel facility prior to approximately 1978 and appears to have consisted of an operational fuel facility until approximately 2013.

It is evident in the 1978 aerial photograph presented in Figure 4.1 that the fuel pump island was present east of the site building. It appears in the 1998 aerial photograph that the fuel pump island is located in a similar, if not same, location twenty years later. A canopy was constructed over the pump island sometime between 1985 and 1998. While completing work on-site in 2013, the author observed several environmental monitoring wells located in the roadways adjacent to the property situated at the northwest intersection property, located approximately 20 m northwest of the Study Site. The presence of monitoring wells on the roadways, south and east of this neighbouring property, suggest that previous environmental assessment found reason to suspect that contamination associated with this property was not delineated on-site and potentially migrated off-site. Off-site assessment would not be required if contamination had

been delineated on-site. The presence of the retail fuel facility located northwest of the Study Site provides a strong case for a potential additional contaminant source, based on the significant timeframe that the Site operated as a retail fuel facility as well as the close proximity to the Study Site.



(a) 1950 aerial photograph



(b) 1960 aerial photograph



(c) 1978 aerial photograph



(d) 1985 aerial photograph



(e) 1998 aerial photograph

**Figure 4.1** - Aerial photographs capturing the Study Site and adjacent south, east and west properties (adapted from Stantec 2013).

Available background information reviewed for the Study Site identified potential contaminant sources both on-site and off-site, beyond the current UST nest.

#### **4.3.1 Summary of Site Characterization**

The review of background information for the Study Site and surrounding properties found at least five potential candidate sources for contamination at the Study Site, which are summarized as follows:

- 1) Study Site: The historic presence of a 1,000 L UST manufactured in 1960 and removed from the Site in 1989. The exact location of this historical UST location was not confirmed.
- 2) Study Site: The three USTs which are currently operational at the Study Site (installed in 1990).
- 3) South Adjacent Property: The property's operational history as a bulk oil and gas plant.
- 4) South Adjacent Property: A UST was removed from the Site in 1984; however, size of the UST, contents, and location within the property boundaries are unknown.

5) Northwest Property: The property located at the northwest corner of the intersection opposite the Study Site operated as a retail fuel facility until being abandoned in 2013.

A significant amount of environmental assessment activities have been completed at the Study Site since 2007. A Phase II ESA completed in 2007 indicated that PHC concentrations in soil and groundwater were greater than applicable guidelines, at the time of assessment, at several locations across the Study Site. The Phase II ESA did not delineate PHC at the Site; however, the report did indicate that PHC impacts may have migrated east and west of the Study Site boundaries (Stantec 2007). To the author's knowledge, a Phase I ESA was not completed for the Study Site prior to completing the 2007 Phase II ESA. The Stantec 2007 Phase II ESA was the first known environmental investigation conducted at the Study Site.

The Phase II ESA found the shallow soil units to generally consist of fill material to a depth of approximately 0.75 meters below ground level (mBGL), followed by glacial till soil to a depth of 6.0 mBGL, with sandy loam and clay loam inclusions throughout (Stantec 2007). The subsurface soil conditions appear to be quite heterogeneous across the Study Site. Shallow groundwater appears to flow in the direction of south/southwest based on historical groundwater monitoring results and lateral and vertical survey data. Subsequent environmental activities included installing recovery wells to facilitate potential remediation activities in 2008 (Stantec 2008). The Study Site is presented in Figure 4.2, showing on-site infrastructure, surrounding land use, and monitoring well and recovery well locations. Contaminant plumes are illustrated on the Study Site Plan; the suspected gasoline and diesel plume extents are depicted with a yellow and red hatched line for the gasoline and diesel plumes, respectively.

Both residential and commercial land use regulatory guidelines apply to the Study Site, as illustrated by 30 m buffer line presented on the Study Site Plan (Figure 4.2), which represents the 30 m setback from the surrounding residential properties.



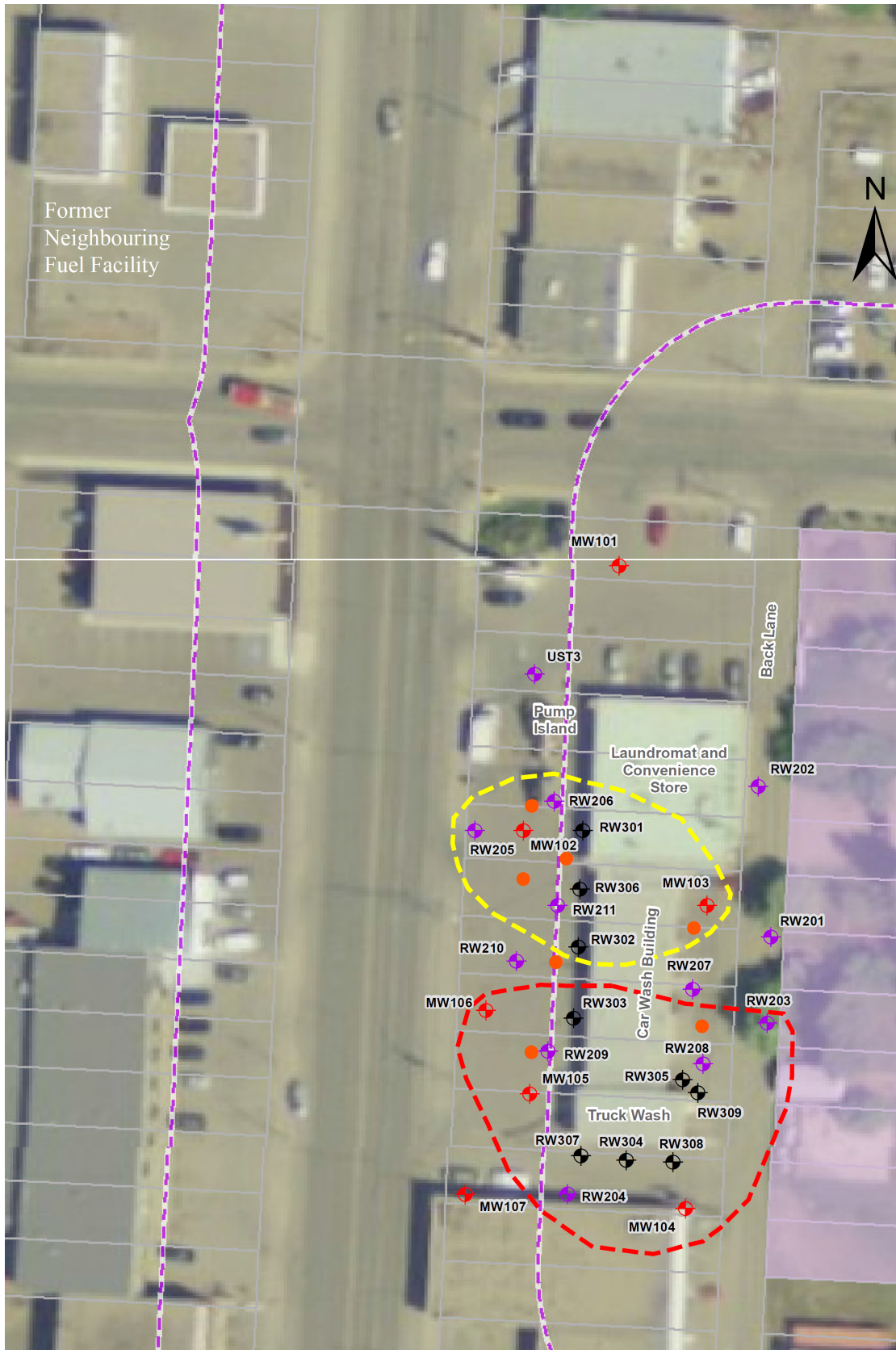


Figure 4.2 - Study Site Plan (adapted from Stantec 2013)

#### 4.4 Tier 3 - GC/FID Pre-Screening

Laboratory analytical results from a groundwater sampling event conducted at the Study Site in September 2009 suggested the potential for at least two different contaminant sources at the Study Site. This hypothesis is based on laboratory analytical results from the 2009 sampling event which indicated that monitoring/recovery wells MW102, RW205, RW206 and RW211, located within the central portion of the Study Site, exhibited elevated benzene and PHC Fraction F1 (equivalent carbon number range C6 - C10) concentrations. While monitoring wells MW104 and MW106, located within the south portion of the Study Site, exhibited elevated PHC Fraction F2 concentrations and lower benzene concentrations relative to the wells located in the central portion of the Site. Concentrations of BTEX and PHC Fraction F1 (carbon range C6 - C10 minus BTEX) and Fraction F2 (equivalent carbon number range greater than C10 – C16) in milligrams per litre (mg/L) within groundwater at six monitoring/recovery wells sampled in September 2009 are shown in Table 4.1.

**Table 4.1** - Concentrations within groundwater at six monitoring/recovery well locations (compiled from Stantec 2009)

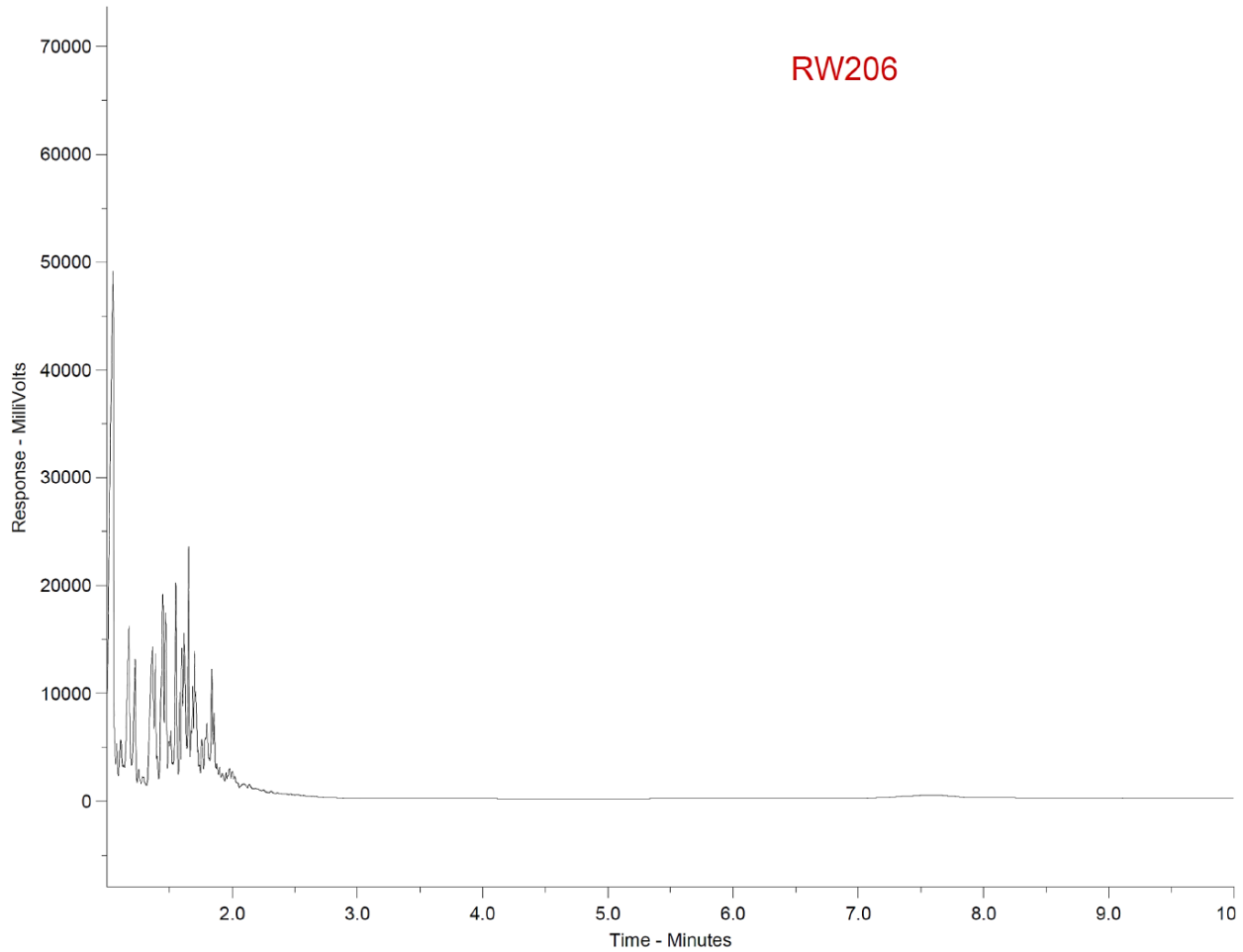
Monitoring/Recovery Well ID		MW 104	MW 106	MW 102	RW 205	RW 206	RW 211
Sample Date		30-Sep-09	30-Sep-09	30-Sep-09	30-Sep-09	30-Sep-09	30-Sep-09
BTEX and PHCs							
Benzene	mg/L	0.006	0.003	35.8	8.17	34.6	10.7
Toluene	mg/L	0.001	< 0.001	1.24	0.084	0.55	0.121
Ethylbenzene	mg/L	0.001	0.002	2.04	0.571	2.56	2.01
Xylenes, Total	mg/L	0.002	0.003	4.78	0.54	4.81	1.51
PHC F1 (C6-C10 range) minus BTEX	mg/L	< 0.20	0.50	< 0.20	4.30	9.17	4.71
PHC F2 (>C10-C16 range)	mg/L	78.6	79.6	2.83	3.33	18.9	2.04

Additional groundwater samples collected in August 2012 further support the hypothesis that two different contaminant plumes were present at the Study Site (Stantec 2013). A layer of LNAPL was observed in recovery wells RW209 and RW307 (located in the south portion of the Study Site) using a disposable HDPE bailer. The groundwater samples from RW209 and RW307

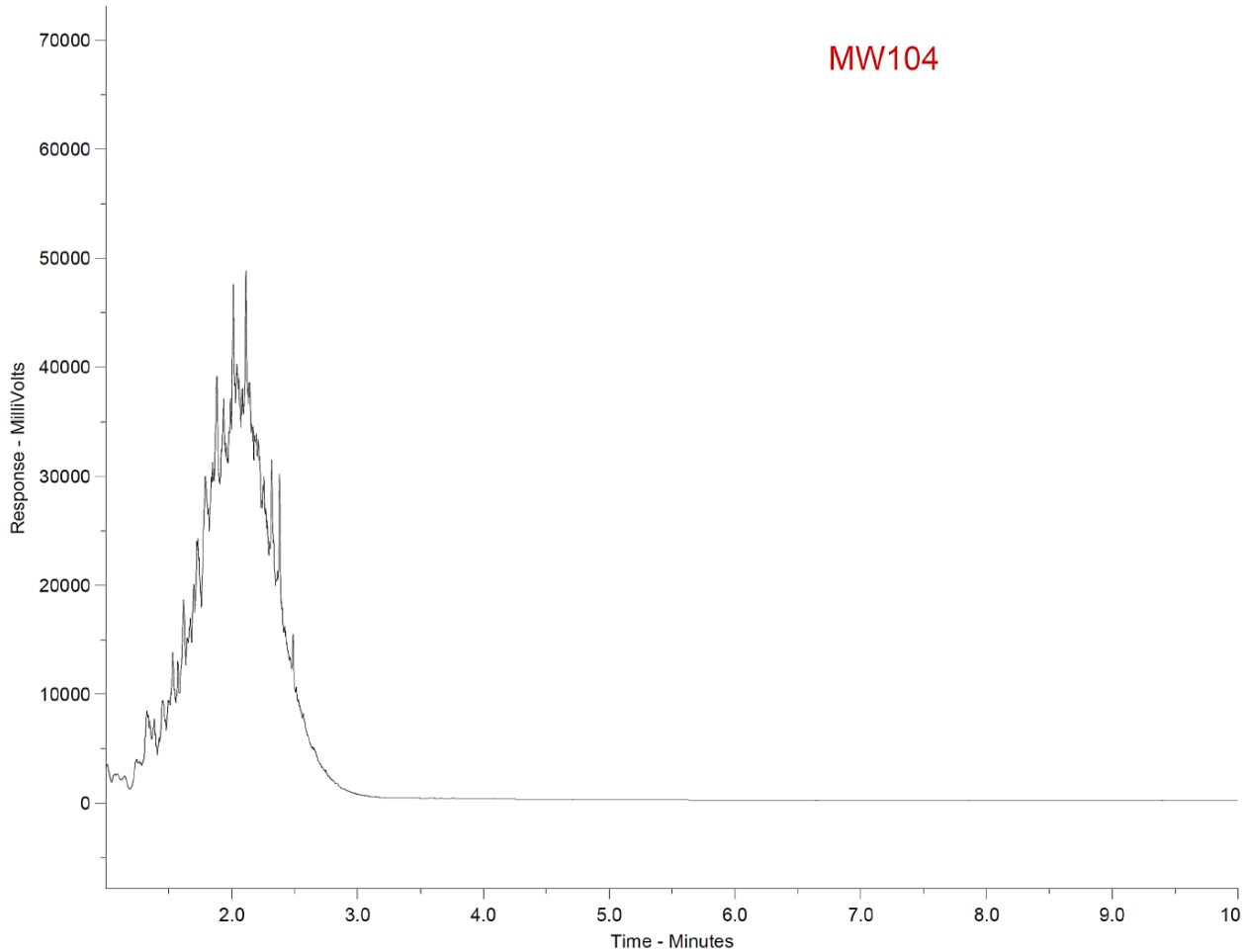


in August 2012 both had relatively elevated concentrations of PHC Fraction F2. This difference in hydrocarbon constituents and concentrations indicates that two different contamination plumes may be present at the Study Site, and therefore, this is supporting evidence for building an environmental forensics case.

The GC/FID chromatograms for groundwater samples from recovery well RW206 and monitoring well MW104 are shown in Figures 4.3 and 4.4, respectively.



**Figure 4.3 - GC/FID chromatogram for RW206 sample.**

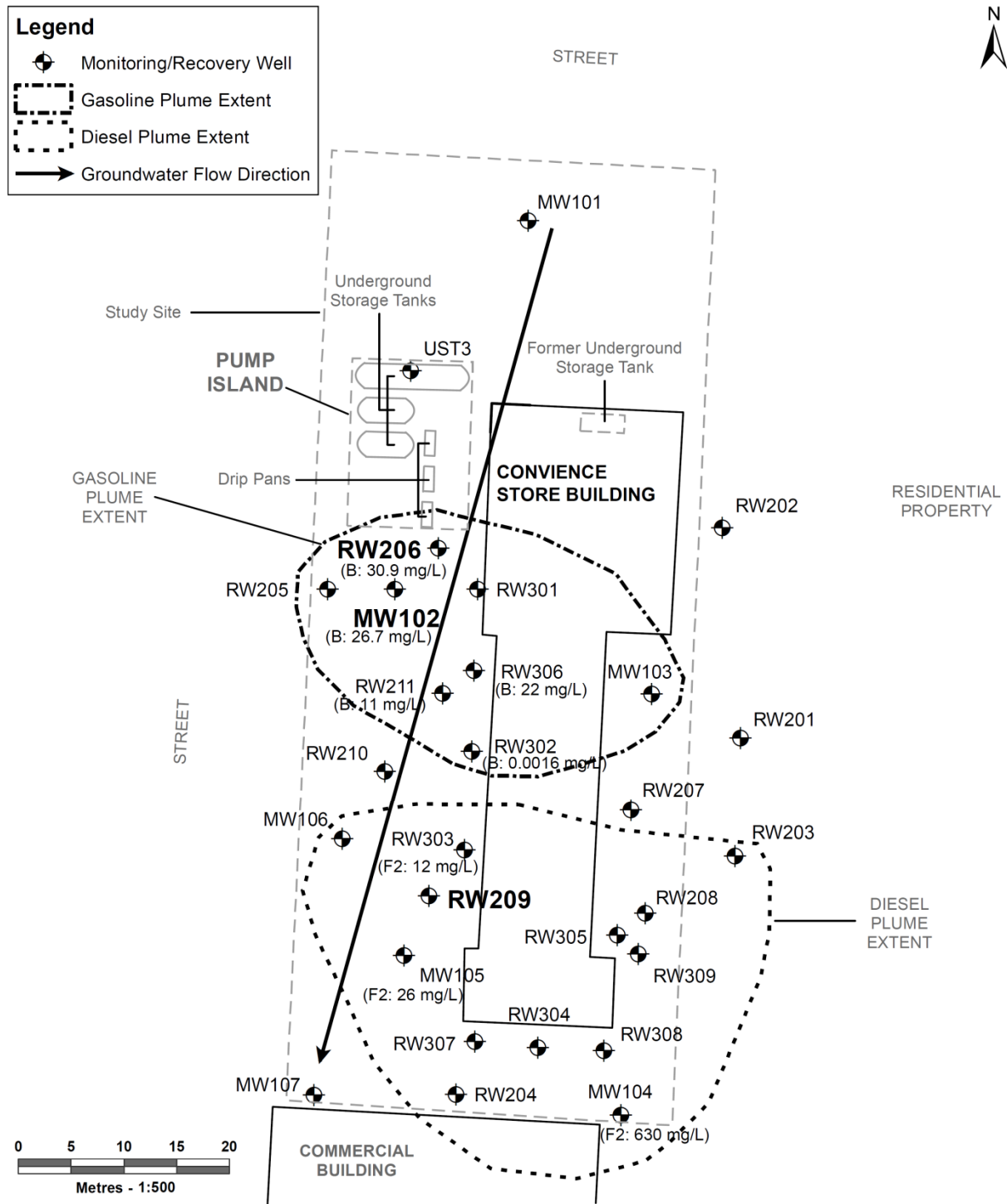


**Figure 4.4 - GC/FID chromatogram for MW104 sample.**

The GC/FID provides a nearly unique response for gasoline and diesel fuel because gasoline is found in the volatile range whereas diesel is found in the extractable range (Farrell-Jones, 2003). GC/FID chromatograms appear to indicate that the Site contains two contaminant plumes, supporting the findings of the laboratory analytical results shown in Table 4.1. The GC/FID chromatograms of RW206 and MW104 groundwater samples indicate that RW206 groundwater was contaminated with gasoline fuel (i.e, chemicals eluding in the volatile range in the compound range less than C<sub>9</sub>), while MW104 groundwater was primarily contaminated with diesel fuel (i.e, chemicals primarily eluding in the compound range between C<sub>10</sub> and C<sub>25</sub>).

The gasoline plume should also have been contaminated by diesel if the current on-site diesel USTs were the source of the diesel contaminants, considering the current UST nest location and

calculated groundwater flow direction. The calculated groundwater flow direction is shown in Figure 4.5 (Stantec 2013).



**Figure 4.5 - Study Site with on-site infrastructures, surrounding land use and groundwater monitoring wells (adapted from Stantec 2013).**

As such, the groundwater monitoring wells within the gasoline plume should have shown significant diesel characteristics in their GC/FID chromatograms. However, the GC/FID chromatogram for RW206 primarily shows a presence of gasoline characteristics. Therefore, the GC/FID pre-screening analysis when combined with the site infrastructure and operation history as well as site hydrogeological information suggest that the diesel plume might not have originated from the current diesel UST.

As discovered during the site background review, the historical presence of an UST in the commercial building property located south of the Study Site could be a potential source candidate for the diesel plume. Concentration of PHC Fraction F2 (equivalent carbon number from C<sub>>10</sub> to C<sub>16</sub>) in groundwater increased from 12 mg/L in RW303 to 26 mg/L in MW205 and to 630 mg/L in MW104, further indicating that the UST at the southern commercial property could be the source for the diesel plume source. PHC Fraction F2 consists of aliphatics and aromatics, primarily within the C<sub>>10</sub> to C<sub>16</sub> carbon range (CCME 2008), and directly correspond to diesel fuel (Gaudet et al. 2000).

The operation of a fuel service station during the period from 1959 to 1968, the removed UST in 1989 and the current gasoline USTs which are located upgradient of the gasoline plume suggest the presence of multiple potential sources for gasoline leakage. Benzene concentration in groundwater decreased from 30.9 mg/L in RW206 to 26.7 mg/L in MW102 to 22 mg/L in RW306 to 11 mg/L in RW211 and to 0.0016 mg/L in RW302. The benzene concentration decreasing trend in the groundwater flow direction indicates the gasoline source could be either the current USTs or the former UST assumed to have been located beneath the footprint of the northwest corner of current site building.

#### **4.4.1 Summary of Findings from Tier 1, Tier 2, and Tier 3**

One contaminant plume, present in the central portion of the Study Site and immediately south of the pump islands, was primarily comprise of light distillate contaminants. The GC/FID chromatograms primarily show a presence of gasoline characteristics; and therefore, are assumed to be associated with gasoline fuel leakage. This approximate contaminant plume extent, based on laboratory analytical results presented in Table 4.1, is illustrated with a red dashed line on Figure 4.2, as well as labeled below in Figure 4.5. The second apparent contaminant plume, indicative of diesel fuel contamination, is situated towards the southeast corner of the Study Site

and is illustrated by a yellow dashed line presented on Figure 4.2, as well as labeled in Figure 4.5 (Stantec 2013).

A thorough comparative analytical review of the laboratory analytical results for samples collected across the Site combined with GC/FID prescreening methods provide a strong line of evidence supporting the hypothesis that separate contaminant sources are present at the Study Site.

#### **4.5 Tier 4 Source Identification and Differentiation using GC/MS**

The objective of Tier 4 is to obtain additional differentiation data and identify the fraction source of both contaminant plumes.

##### **4.5.1 Gasoline Source Identification**

The GC/MS was used to identify the source of the identified PHC impacts in groundwater collected from monitoring wells RW206 and MW102. The MS was operated in either a full scan to obtain total ion chromatograms (TICs) or SIM mode to improve sensitivity on selected compounds. SIM analyses included collection of m/z ratios of 55, 83, 91, 97, 105, 117, 119, and 128. Each of these m/z ratios represents a class of compounds that may be present within the PHC compound mixture that comprises gasoline. Additional details supporting the selection of m/z ratios are provided as follows:

**m/z 55 ratio:** selected to assess the abundance of potential chemicals that may be identified at this ratio within the naphthenes and olefins chemical compound classes (including: 2-methyl-1-butene, trans-2-pentene, cis-2-pentene, cis-2-hexene, cyclopentane, trans-2-hexene, methylcyclohexane, ctc-1,2,4-Trimethylcyclopentane, ctc-1,2,3-Trimethylcyclopentane, 1-octene, trans-2-octene, cis-2-octene, ethylcyclohexane, trans-3-nonene, cis-3-nonene, trans-2-nonene, cis-2-nonene, n-butylcyclopentane, and 1-decene).

**m/z 83 ratio:** selected to assess the abundance of n-alkanes.

**m/z 91 ratio:** selected to assess the abundance of toluene ethylbenzene, m-xylene, p-xylene, o-xylene, and propylbenzene, and n-pentylbenzene.

**m/z 91 ratio:** selected to assess the abundance of 2-methylthiophene, 3-methylthiophene, and 2-ethylthiophene.

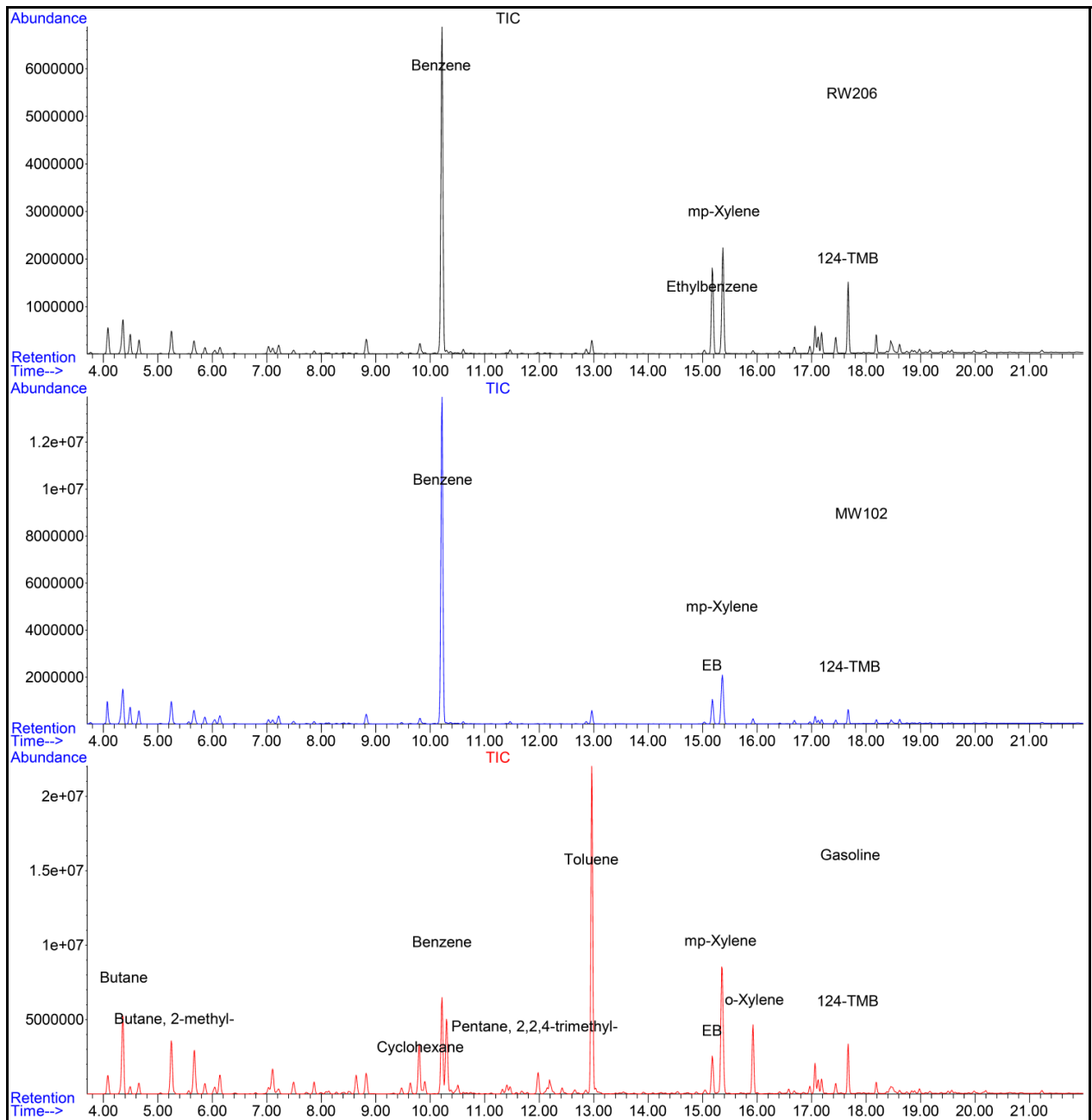
***m/z* 105 ratio:** selected to assess the abundance of C3-alkylbenzene compounds (including: isopropylbenzene, 1-methyl-3-ethylbenzene; 1-methyl-4-ethylbenzene, 1,3,5-trimethylbenzene, 1-methyl-2-ethylbenzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,2-diethylbenzene, 1,3-diethylbenzene, 1,4-diethylbenzene, and 1-methyl-2-n-propylbenzene).

***m/z* 117 ratio:** selected to assess the abundance of indane compounds and their derivatives.

***m/z* 119 ratio:** selected to assess the abundance of C4-alkylbenzene compounds (including: 1,2-dimethyl-4-ethylbenzene, 1,3-dimethyl-2-ethylbenzene, 1,2,4,5-, 1,2,3,5, and 1,2,3,4-tetramethylbenzene).

***m/z* 128 ratio:** selected to assess the abundance of naphthalenes (including: C0, C1, C2, C3, and C-4-naphthalenes).

The GC/MS TIC provides a fingerprint of hydrocarbon compounds in the samples. The TICs of the fresh gasoline solution and the RW206 and MW102 groundwater samples are presented in Figure 4.6.



**Figure 4.6** - Total ion chromatograms (TIC) of the fresh gasoline solution and the RW206 and MW102 groundwater. EB=ethylbenzene, 124-TMB=1,2,4-trimethylbenzene.

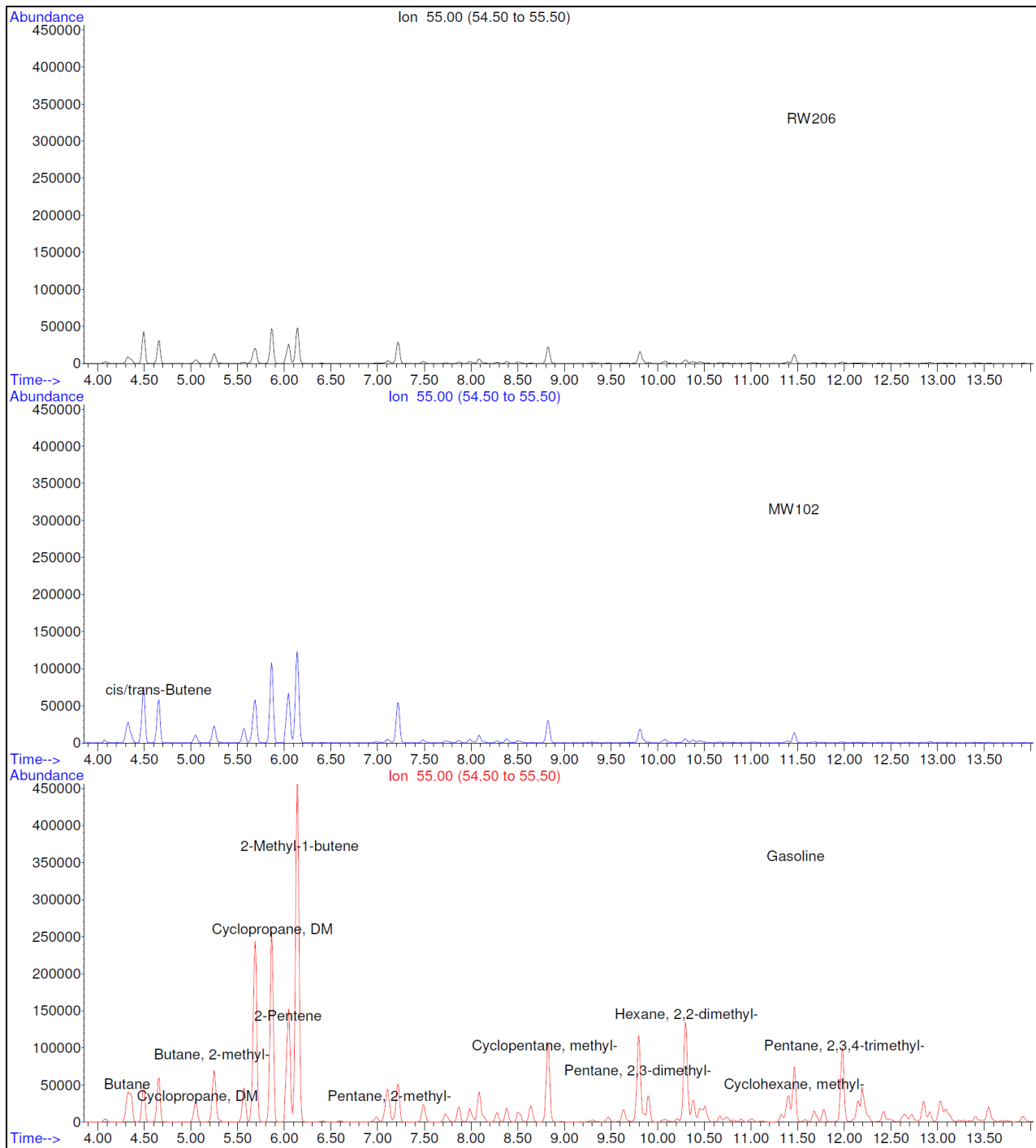
The distribution and positions of dominant peaks of select hydrocarbon compounds; including, butanes, pentanes, BTEX, and 1,2,4-trimethylbenzene (124-TMB), are consistent between the fresh gasoline solution and the groundwater samples collected from monitoring well MW102 and recovery well RW206. The similarity between the samples indicates that contamination of groundwater in RW206 and MW102 resulted from a gasoline source spill or

leakage, confirming the GC/FID classification. The intensities of the dominant peaks especially butanes and toluene in the TICs of the RW206 and MW102 groundwater samples are lower than in the fresh gasoline solution, indicating the hydrocarbon weathering occurred in the RW206 and MW102 groundwater samples. Butane has Henry's law constant values two orders of magnitude greater than benzene and toluene (Sara, 2003). Toluene degrades faster than benzene, ethylbenzene and xylene compounds, while benzene is particularly persistent under anaerobic conditions (Illman and Alvarez 2009).

#### **4.5.1.1 GC/MS Selective Ion Monitoring Analysis**

The RW206 and MW102 fragmentation patterns ( $m/z$  55, 83, 91, 97, 117 and 128) demonstrate that significant weathering has occurred in the product collected at these sample locations as there are significantly fewer peaks and lower abundances chemical compounds identified in the reference sample. Most of  $C_6$  through  $C_8$  hydrocarbons are not present in the chemical compositions of the RW206 and MW102 groundwater samples when they are compared to that of the fresh gasoline solution.

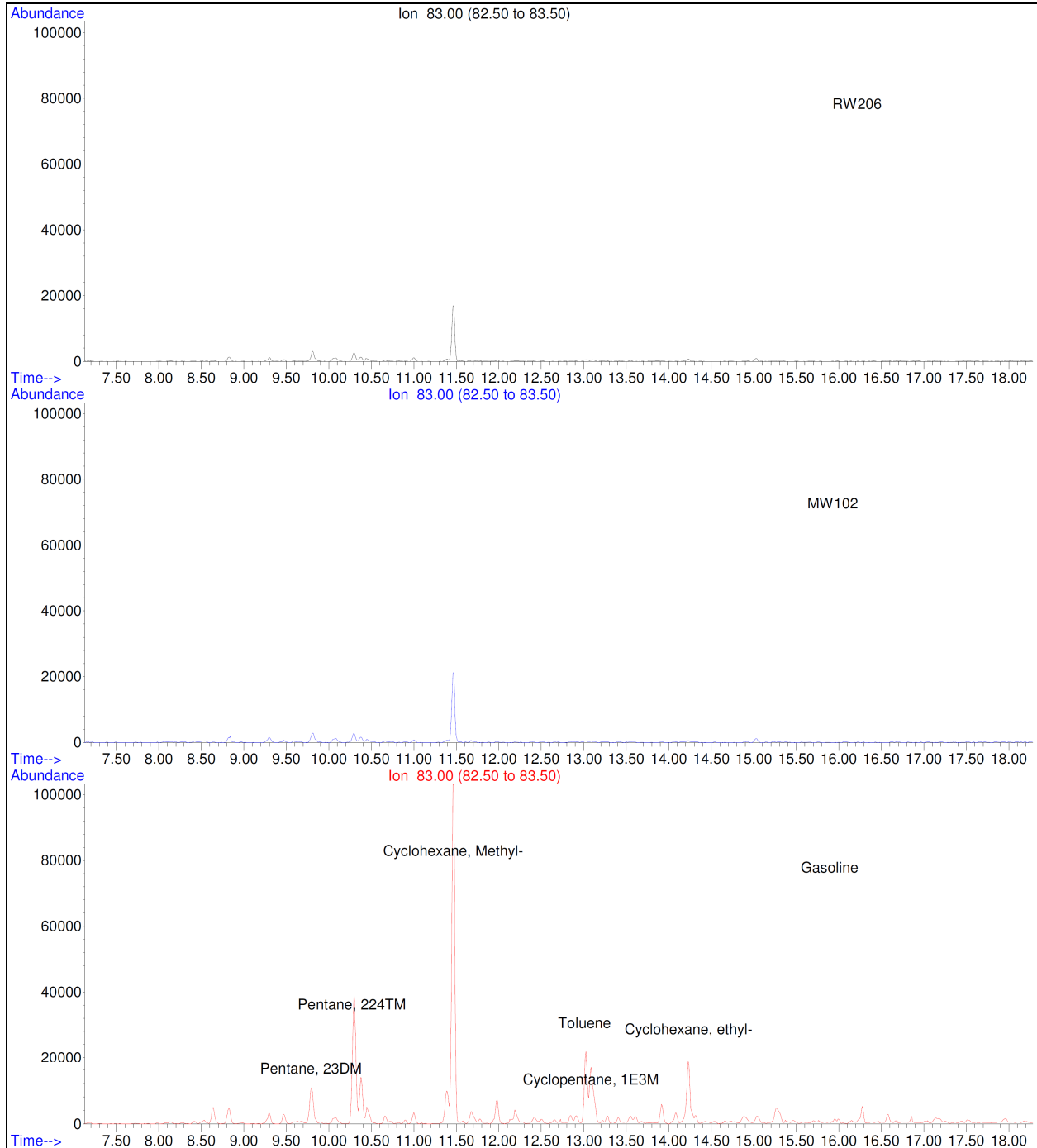




**Figure 4.7 -** Partial m/z 55 chromatograms of the fresh gasoline solution and the RW206 and MW102 groundwater samples.

The partial m/z 55 chromatograms (Figure 4.7) confirm that valuable diagnostic analytes such as cyclopentane and cyclohexane compounds could be present in gasoline following refining processes; however, the chemicals have been substantially removed as a result of weathering in

the subsurface at the Study Site. The m/z 55 chromatogram is suitable for confirming that weathering has occurred within the samples, however, is not suitable for providing valuable diagnostic data.

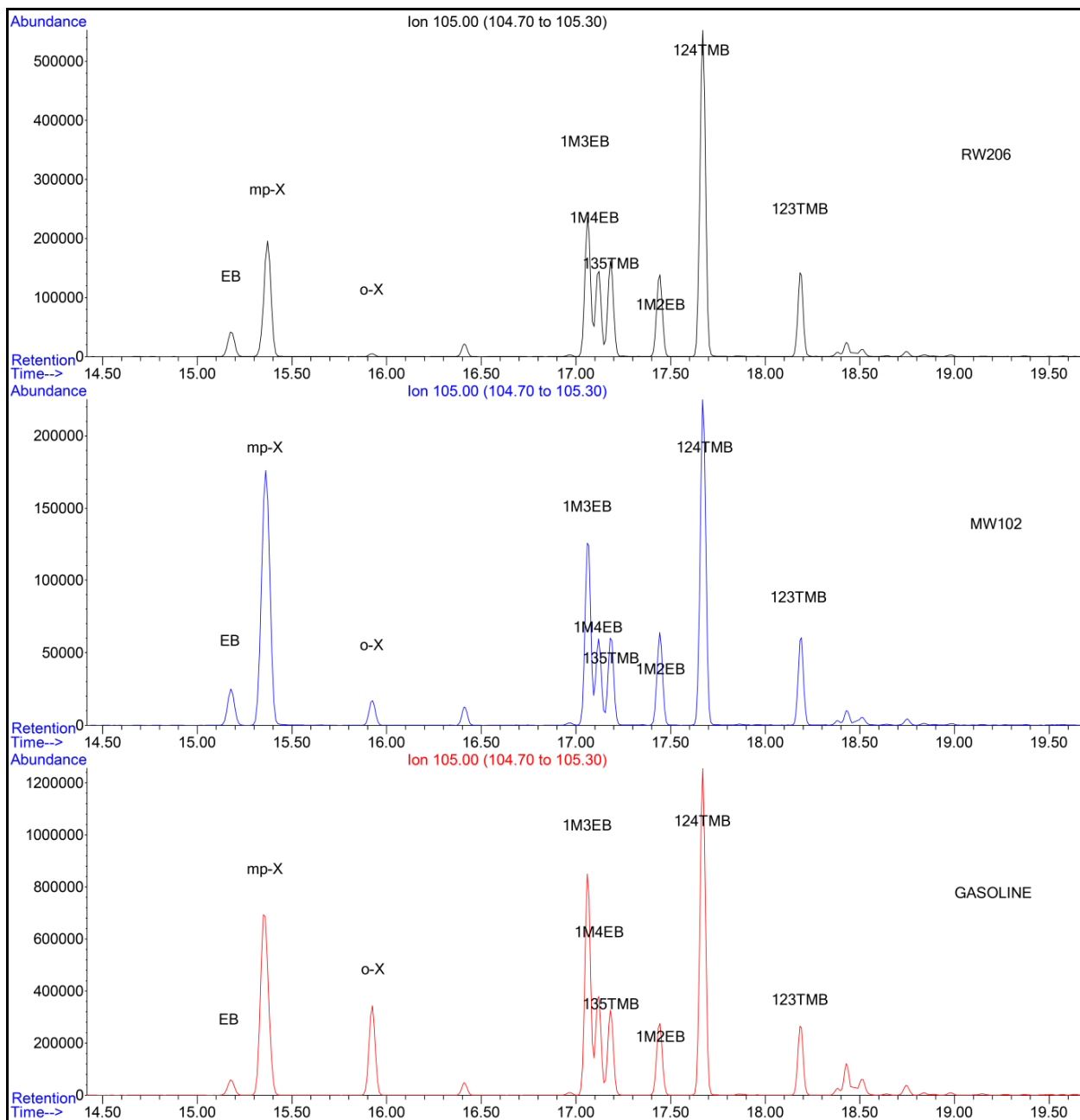


**Figure 4.8** - Partial m/z 83 chromatograms of the fresh gasoline solution and the RW206 and MW102 groundwater samples.

The partial  $m/z$  83 chromatograms (Figure 4.8) show that most *n*-alkanes are depleted as a result of weathering in the subsurface at the Study Site. It is evident that cyclohexane is the most predominant *n*-alkane compound in the gasoline mixture and the last compound to be effectively degraded.

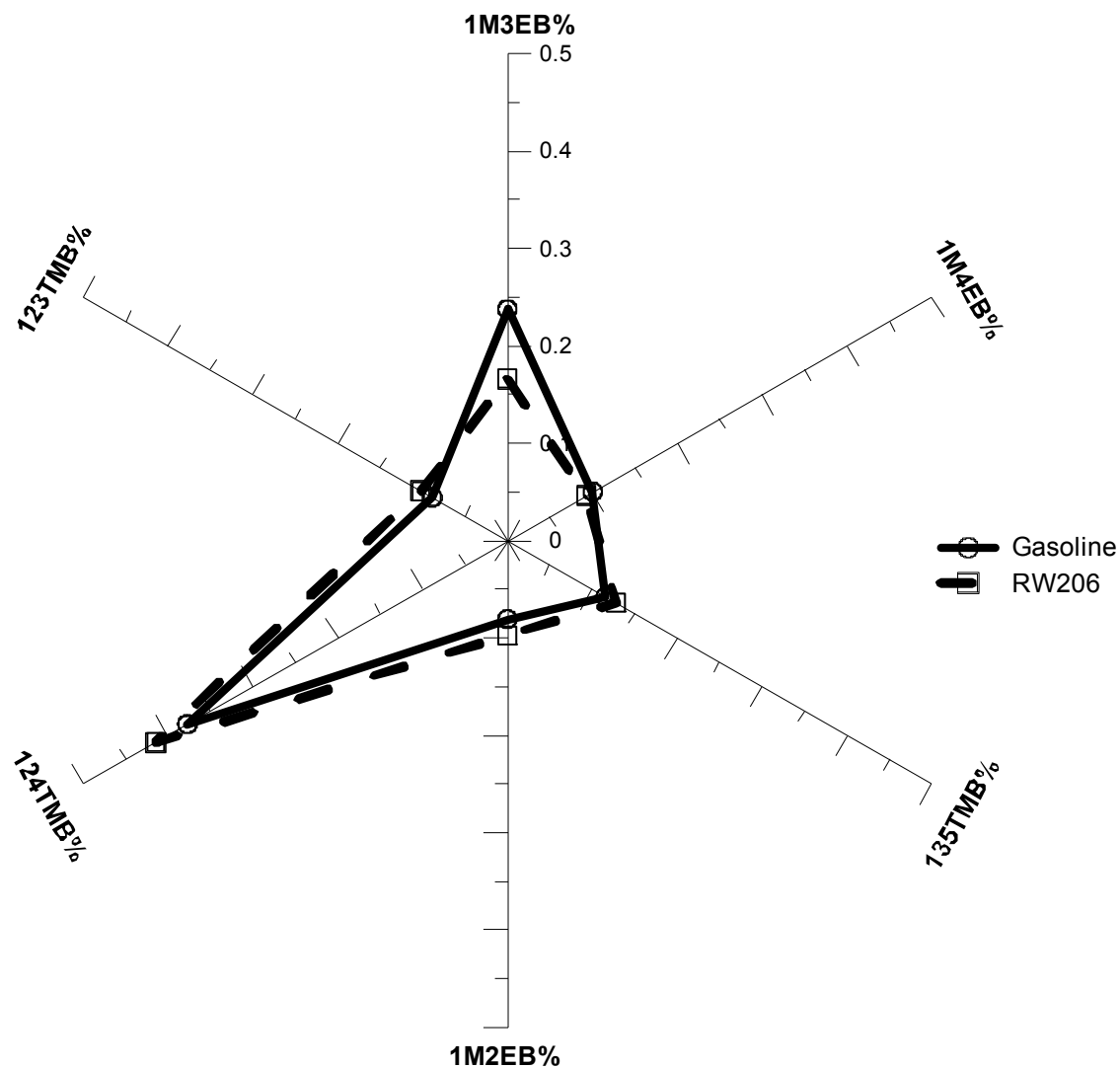
The partial  $m/z$  91 chromatograms indicated that toluene, ethylbenzene, and xylenes compounds have been substantially weathered in the subsurface at the Study Site in comparison to the reference sample (chromatogram figure not shown). The residual concentrations of these compounds do not provide sufficient data for comparison purposes.

Therefore, chemicals present in the C<sub>9</sub> boiling range are essential for product differentiation. Alkylbenzenes, primarily C<sub>3</sub>-alkylbenzenes and C<sub>4</sub>-alkylbenzenes, are among the most stable compounds occurring in gasoline (Wang and Stout 2007). The presence of C<sub>3</sub>-alkylbenzenes and C<sub>4</sub>-alkylbenzenes are represented by  $m/z$  ratios 105 and 119, respectively. A relatively complete composition of C<sub>3</sub>-alkylbenzenes (1-methyl-3-ethyl-benzene (1M3EB); 1-methyl-4-ethyl-benzene (1M4EB); 1,3,5-trimethylbenzene (135-TMB); 1-methyl-2-ethyl-benzene (1M2EB); 124-TMB; and 1,2,3-trimethylbenzene (123-TMB)) was detected in the  $m/z$  105 (C<sub>3</sub>-alkylbenzenes) ion chromatograms of fresh gasoline solution and RW206 and MW102 groundwater samples (Figure 4.9).



**Figure 4.9** - Partial m/z 105 C3-alkylbenzenes chromatograms of the fresh gasoline solution and the RW206 and MW102 groundwater samples.

The relative differences in compound concentrations is reflective of the different blending stock used in the production of parent gasoline. The C<sub>3</sub>-alkylbenzenes distribution, presented as percentages, is shown in Figure 4.10.

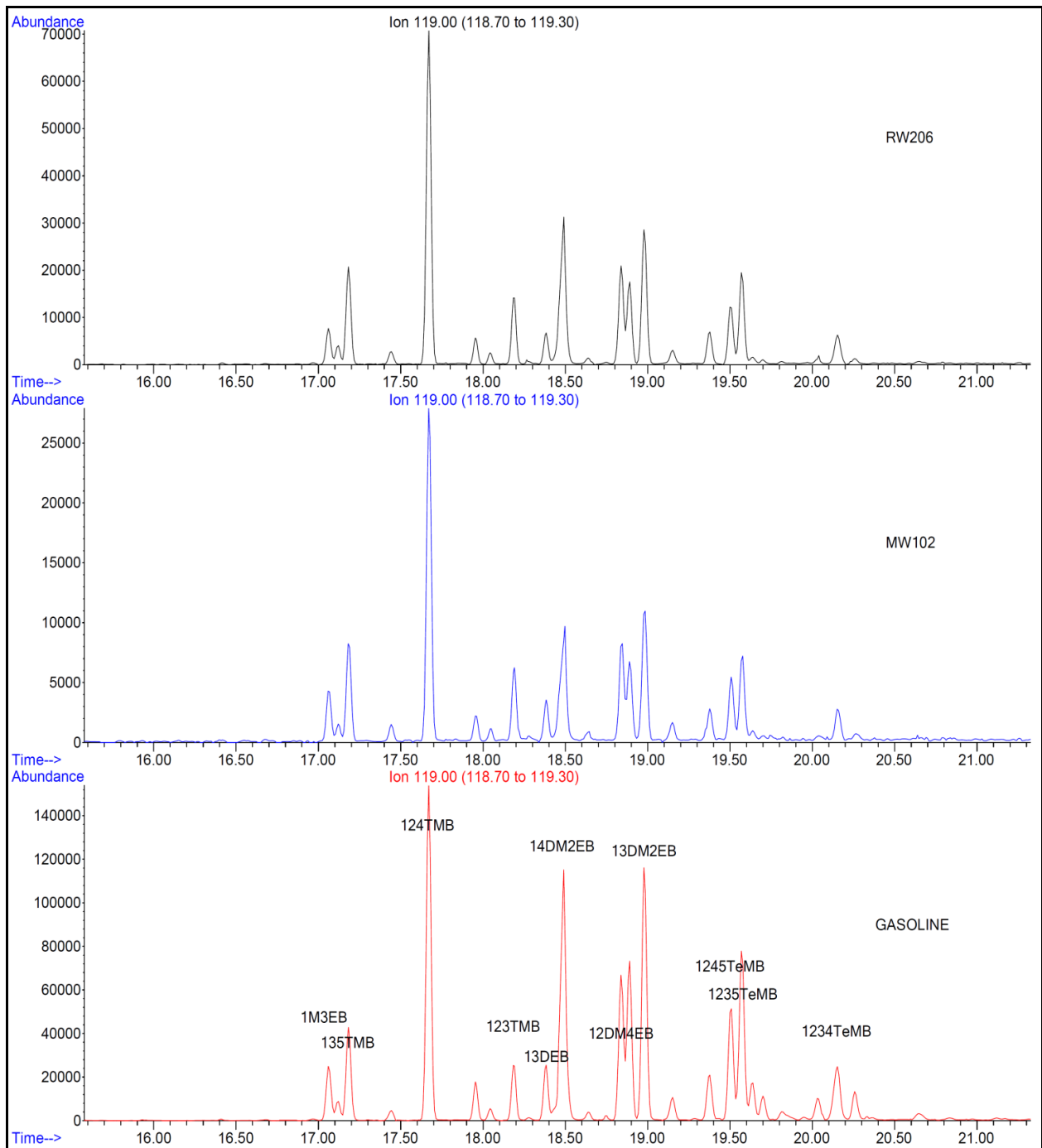


**Figure 4.10** - Distribution of C<sub>3</sub>-alkylbenzenes by using integrated area. E = ethylbenzene, m-p-x and o-x = m,p,o-xylenes, 1M3EB = 1-methyl-3-ethyl-benzene, 1M4EB = 1- methyl-4-ethyl-benzene, 135-TMB = 1,3,5-trimethylbenzene, 1M2EB = 1-methyl-2-ethyl-benzene, 124-TMB = 1,2,4-trimethylbenzene, 123-TMB = 1,2,3-trimethylbenzene.

With the exception of peak 1M3EB, percentages of peaks (1M4EB, 135-TMB, 1M2EB, 124-TMB, and 123-TMB) of fresh gasoline solution and RW206 groundwater samples are almost the same and also important is that their distribution shapes are similar. The similar distribution of relatively stable C<sub>3</sub>-alkylbenzenes in the fresh gasoline solution and the RW206 sample indicates that the dissolved PHCs in RW206 groundwater may be attributed to contamination from the current on-site gasoline USTs.

The 1M3EB chemical had the shortest retention time among the C<sub>3</sub>-alkylbenzene compounds, as shown on Figure 4.8. A chemical compound that has the shortest retention time usually tends to decrease in peak intensity preferentially by weathering (e.g., evaporation and biodegradation) (Wigger and Torkelson 1997). It was reported that degradations of 1M2EB and 1M4EB were slower than that of 1M3EB (Solano-Serena et al. 1999; Cozzarelli et al. 2010). First order degradation rates of 1M2EB and 1M4EB were lower than 124-TMB and 135-TMB (Cozzarelli et al. 2010). 123-TMB was reported to be less easily consumed than 124-TMB because 124-TMB bears an isolated methyl group on the fourth carbon (Solano-Serena et al., 1999). Therefore, more significant weathering of 1M3EB results in the lower percentage of 1M3EB in both RW206 and MW102 groundwater.

A complete composition of C<sub>4</sub>-alkylbenzenes (peak 1,3,5-trimethylbenzene (135-TMB); peak 124-TMB; peak 132-TMB; peak 1,2,4,5-tetramethylbenzene (1245-TeMB); peak 1235-TeMB; and) was not observed in the m/z 119 (C<sub>4</sub>-alkylbenzenes) ion chromatograms of RW206 and MW102 groundwater samples as compared to the fresh gasoline solution (shown in Figure 4.11). There is more potential for compound co-elution with C<sub>4</sub>-alkylbenzene groups than with than with C<sub>3</sub>-alkylbenzenes; which could explain the incomplete composition observed in the C<sub>4</sub>-alkylbenzene group ion chromatograms (Lentini 2013).



**Figure 4.11** - Partial m/z 119 C4-alkylbenzenes chromatograms of the fresh gasoline solution and the RW206 and MW102 groundwater samples.

#### 4.5.1.2 Diagnostic Ratios from m/z 105 and 119 Chromatograms

Diagnostic ratios were calculated using peak areas of specific compounds with a single chromatogram (i.e., m/z 105 chromatogram (Figure 4.9) and m/z 119 chromatogram (Figure 4.11) that have a comparable aqueous solubility. Different gasoline sources can exhibit different diagnostic ratios, as a result of the variable processes by which gasoline is refined and blended. Similar physicochemical properties of these compounds are expected to exhibit similar behaviors and fates in the environment (Sauer and Costa 2003). Therefore, gasoline supplied from different parent oil sources or manufactured by different refining and blending processes should exhibit different diagnostic ratios (Stout et al. 2010). However, this semi-quantitative method cannot determine the concentrations of individual target compounds or compound groups. Peak areas of specific compounds obtained in the ion m/z 105 and 119 chromatograms are presented in Table A.3 (Appendix A).

Diagnostic ratios calculated by peak areas of specific compounds are presented in Table 4.2, which shows that diagnostic ratios of the analyte pairs (numerator compound and dominator compound) with similar solubility are consistent between the fresh gasoline solution and the RW206 and MW102 groundwater samples.

**Table 4.2** - Diagnostic ratios of paired analytes with similar solubility in fresh gasoline solution and RW206 and MW102 groundwater samples

Diagnostic ratios	Ion m/z	Fresh Gasoline Solution	RW206	MW102
135-TMB/124-TMB	105	0.27	0.30	0.28
123-TMB/124-TMB	105	0.21	0.25	0.26
1M3EB/1M4EB	105	2.26	1.63	2.25
1M2EB/124TMB	105	0.23	0.26	0.28
1M2EB/123-TMB	105	1.10	1.05	1.10
135-TMB/124-TMB	119	0.29	0.30	0.30
123-TMB/124-TMB	119	0.16	0.20	0.22
1245-TMB/1235-TMB	119	0.66	0.66	0.71
1234-TMB/1235-TMB	119	0.41	0.41	0.38
1234-TMB/1245-TMB	119	0.61	0.62	0.54

Pearson correlation coefficients between the diagnostic ratios of RW206 and MW102 groundwater and that of fresh gasoline solution are calculated to be 0.989 and 0.998,



respectively. This similarity further confirms that dissolved PHCs in RW206 and MW102 groundwater likely originated from the leakage of the existing gasoline UST.

#### **4.5.1.3 Analysis of Gasoline Additives**

A review of historical groundwater analytical data at the Study Site indicates that dissolved lead has not been identified in groundwater samples collected to date, which suggests that the gasoline leakage into groundwater could potentially have occurred after the early to mid-1990s. As the historical UST located at the Study Site was installed in 1960 and removed in 1989, these findings provide evidence that suggests the historical 1960 UST may not be the source of the gasoline contaminant plume at the Study Site.

As discussed in detail in Section 2.5.1, oxygenates are blended with gasoline for the purpose of increasing the oxygen content and reducing carbon monoxide emissions. Common oxygenates such as ethanol, MTBE, tertiary-butyl alcohol (TBA), tertiary-amyl-methyl-ether (TAME), ethyl-tertiary-butyl-ether (ETBE), and di-isopropyl ether (DIPE) were not detected in the gasoline solution and the RW206 and MW102 groundwater samples. The non-detectable oxygenates suggest a potential recent gasoline leakage, since the use of oxygenates began to be phased out throughout the 1990s and banned in approximately 1999. Due the regulatory phasing out process of oxygenates (i.e., several years) in addition to the relatively quick weathering characteristics of several oxygenate compounds in the subsurface, oxygenates do not provide a strong line of evidence for age dating gasoline releases (Morrison and Murphy 2006). However, this data does still provide evidence that can be used to support the conclusion.

#### **4.5.1.4 Summary of Gasoline Source Identification**

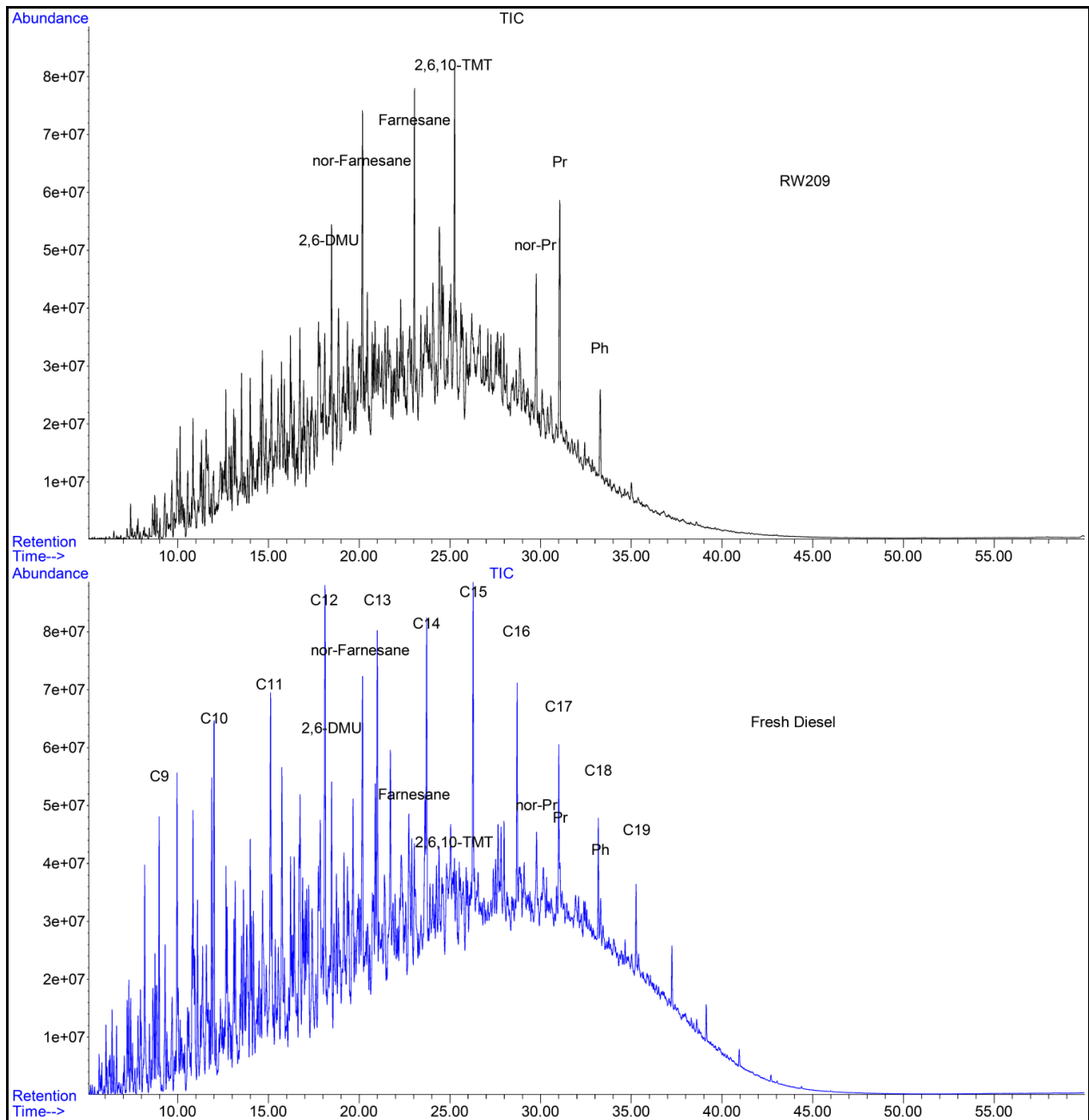
The GC/MS analytical results of the gasoline solution and RW206 and MW102 groundwater samples confirm the gasoline impacts to groundwater. Several lines of evidence including the similar distribution of C<sub>3</sub>-alkylbenzenes, the non-detectable dissolved lead and oxygenates, and the consistent diagnostic ratios of the analyte pairs with similar solubility indicate that the source for the gasoline impacts to groundwater in monitoring wells RW206 and MW102 likely originated from leakage of the USTs that are currently operational at the Study Site.

#### **4.5.2 Diesel Source Identification**

The GC/MS full scan method was used to identify the source of LNAPL collected from monitoring well RW209. The GC/MS full scan method includes evaluation of the total ion chromatogram, and the evaluation of paraffins (alkanes,  $m/z$  85), isoparaffins (isoalkanes,  $m/z$  113), sesquiterpanes ( $m/z$  123, 179, 193, and 207), and the heavy distillate biomarkers terpane ( $m/z$  191) and steelrane ( $m/z$  217 and 218). Each of these represents a class of compounds that may be present in PHCs that are predominantly within the C<sub>8</sub> to C<sub>28</sub> boiling range.

##### **4.5.2.1 GC/MS TIC Analysis and Isoprenoid Diagnostic Ratios**

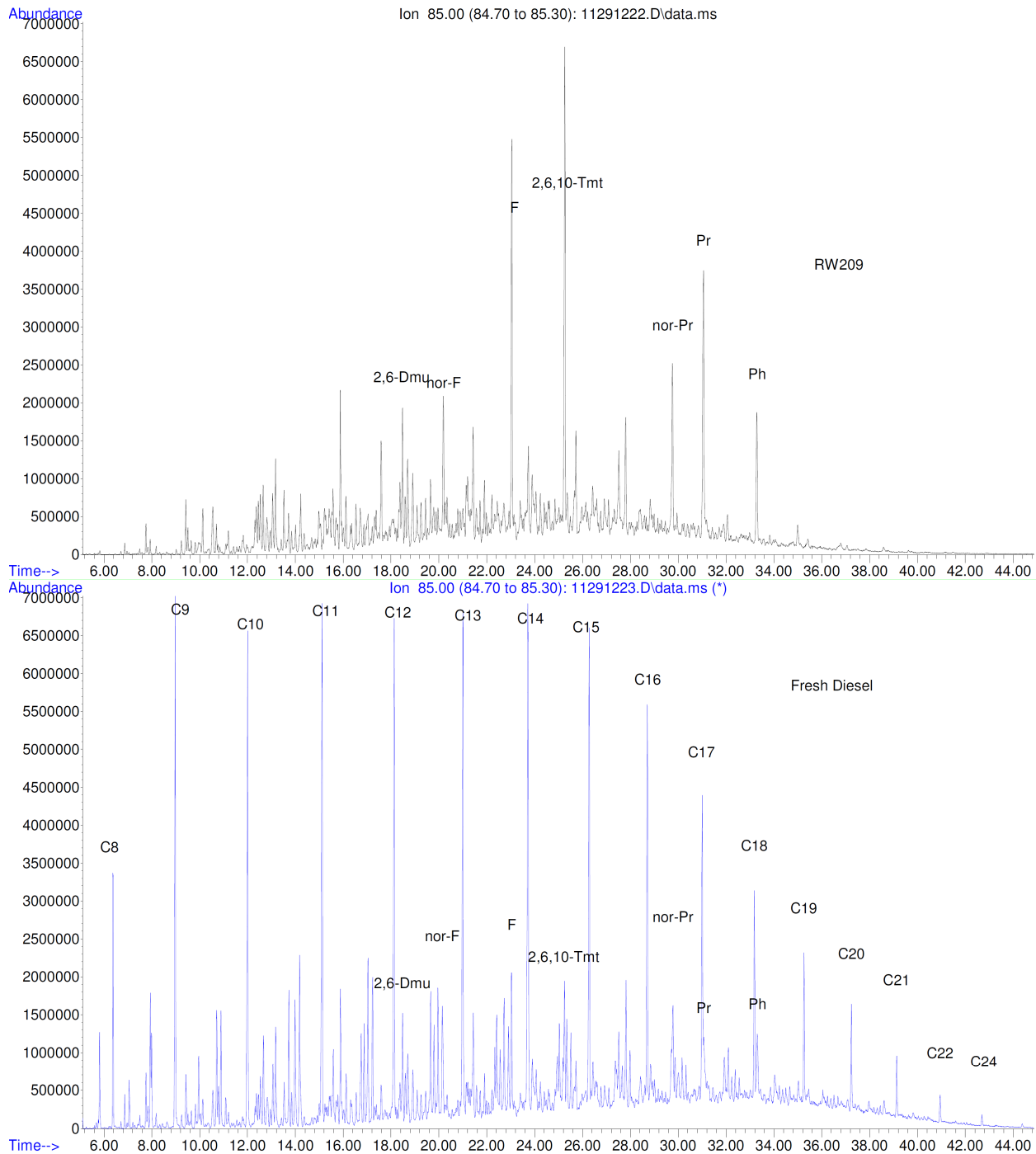
The GC/MS TIC chromatograms of the fresh diesel and the RW209 LNAPL sample are shown in Figure 4.12.



**Figure 4.12** - Total ion chromatograms (TIC) of the fresh diesel and the RW209 LNAPL sample. 2,6-DMU=2,6-dimethylundecane, 2,6,10-TMT=2,6,10-trimethyltridecane, Pr=pristane, Ph=phytane.

A central UCM hump evident in the two chromatograms presented in Figure 4.11, a major characteristic of diesel (Kaplan et al., 1996), indicates that the RW209 LNAPL originated from a diesel fuel spill or leak, confirming the GC/FID classification. The location of the central UCM hump in the fresh diesel solution is slightly different from RW209 LNAPL. The fresh diesel TIC

shows a major distribution of peaks in the carbon range C9 to C17 with small peaks around the carbon range C18 to C23 (retention time of 33 min to 45 min). The major distribution is dominated by norfarnesane and normal alkanes (*n*-alkanes, nC7 to nC11), which are major constituents in diesel. The RW209 LNAPL TIC is dominated by norfarnesane, farnesane, 2,6,10-trimethyltridecane (2,6,10-TMT), norpristane and pristane. The absence of *n*-alkanes in the RW209 TIC (Figure 5.7) is also supported by RW209 LNAPL m/z 85 chromatogram. The partial m/z 85 paraffins (alkanes) chromatograms of fresh diesel and RW209 LNAPL samples are shown on Figure 4.13.



**Figure 4.13** - Partial  $m/z$  85  $n$ -alkanes chromatograms of fresh diesel and RW209 LNAPL. nor-F = norfarnesane, F = farnesane, nor-Pr = norpristane.

The absence of  $n$ -alkanes in the RW209 TIC is again further supported by reported zero diagnostic ratios (C17/pristane, C17/norpristane, C17/farnesane, C17/2,6,10-TMT, C18/norpristane, and C18/phytane). The absence of  $n$ -alkanes occurs because  $n$ -alkanes are relatively

quickly removed, in comparison with other compounds, during weathering (Kaplan et al. 1997; Alimi et al. 2003). The isoprenoid diagnostic ratios obtained from the ion  $m/z$  85 chromatogram are used to determine the biodegradation extent. The isoprenoid diagnostic ratios are presented in Table 4.3.

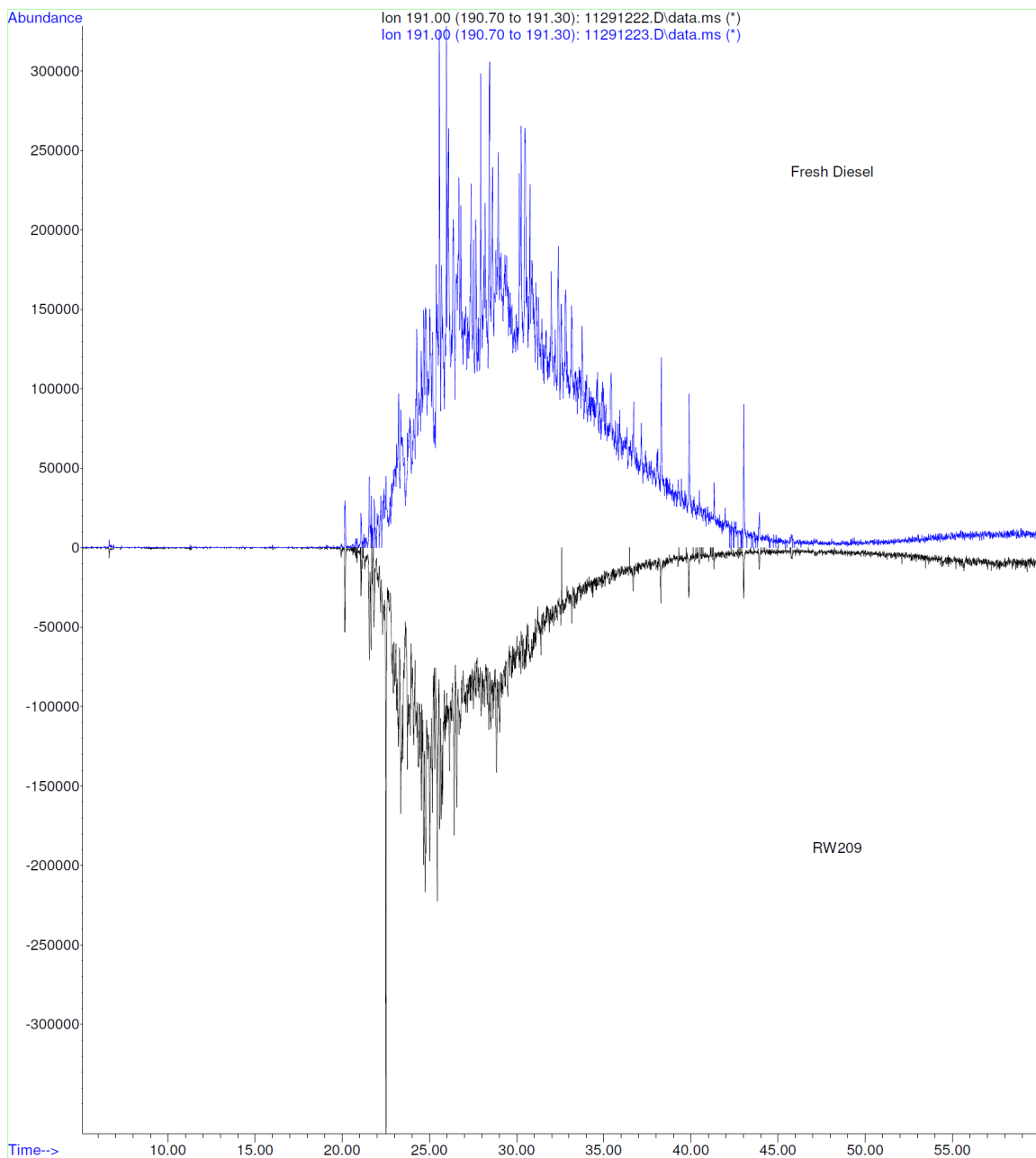
**Table 4.3** - Diagnostic ratios of isoprenoids obtained from the  $m/z$  85 chromatograms

<b>Compound Ratio Identity</b>	<b>RW209</b>	<b>Fresh Diesel</b>
C17/Pristane	0.00	2.63
C17/Norpristane	0.00	1.57
C18/Norpristane	0.00	1.04
C18/Phytane	0.00	2.33
C17/2,6,10-TMT	0.00	2.05
Pristane/Norpristane	1.64	0.60
Pristane/Phytane	2.38	1.34
Pristane/2,6,10-TMT	0.71	0.78
Norpristane/Phytane	1.46	2.24
Norpristane/2,6,10-TMT	0.43	1.30
C17/Farnesane	0.00	2.22
Pristane/Farnesane	0.94	0.85
Norpristane/Farnesane	0.57	1.41

Note: 2,6,10-TMT = 2,6,10-trimethyltridecane

Norpristane is considered to be the isoprenoid chemical compound identified within RW209 LNAPL that is most susceptible to biodegradation and is therefore assumed to biodegrade first (Wang and Stout 2007). The norpristane/farnesane ratio of RW209 LNAPL (0.57) is lower than the fresh diesel (1.41) and the pristane/norpristane ratio of RW209 LNAPL (1.64) is higher than the fresh diesel (0.60), indicating that biodegradation has been occurring within RW209 (Mcintyre et al. 2007). Similar results can be obtained from norpristane/phytane and norpristane/2,6,10-TMT. Farnesane is less resistant to weathering than pristane; therefore, the pristane/farnesane ratio of RW209 LNAPL (0.94) is slightly higher than the fresh diesel (0.85), further indicating that biodegradation processes have occurred. Pristane is highest in relative abundance and phytane is biodegraded more rapidly than pristine (Wang et al. 2006). Therefore, the pristane/phytane ratio RW209 LNAPL (2.38) is higher than the fresh diesel solution (1.34), which further confirms that LNAPL collected in RW209 has been weathered.

Heavy distillate biomarkers terpanes and steranes are typically not present in the middle range distillates, such as diesel fuel, largely due to the higher-molecular-weight tetracyclic steranes and pentacyclic triterpanes being removed during the refining processes. Terpanes and steranes were absent within both the fresh diesel and the RW209 LNAPL, which is consistent with the diesel fuel type. The partial m/z 191 terpane chromatograms of fresh diesel and RW209 LNAPL samples are shown on Figure 4.14.

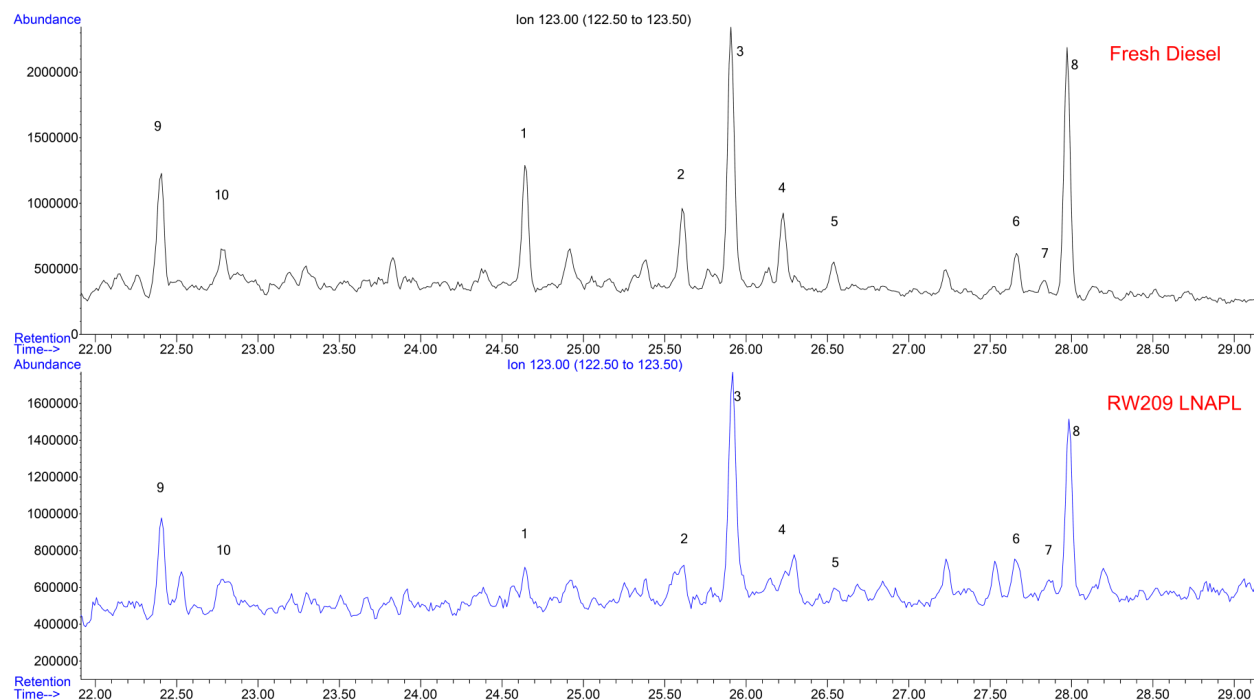


**Figure 4.14** - Partial m/z 191 terpane chromatogram of fresh diesel and RW209 LNAPL.

#### 4.5.2.2 GC/MS Sesquiterpanes Analysis

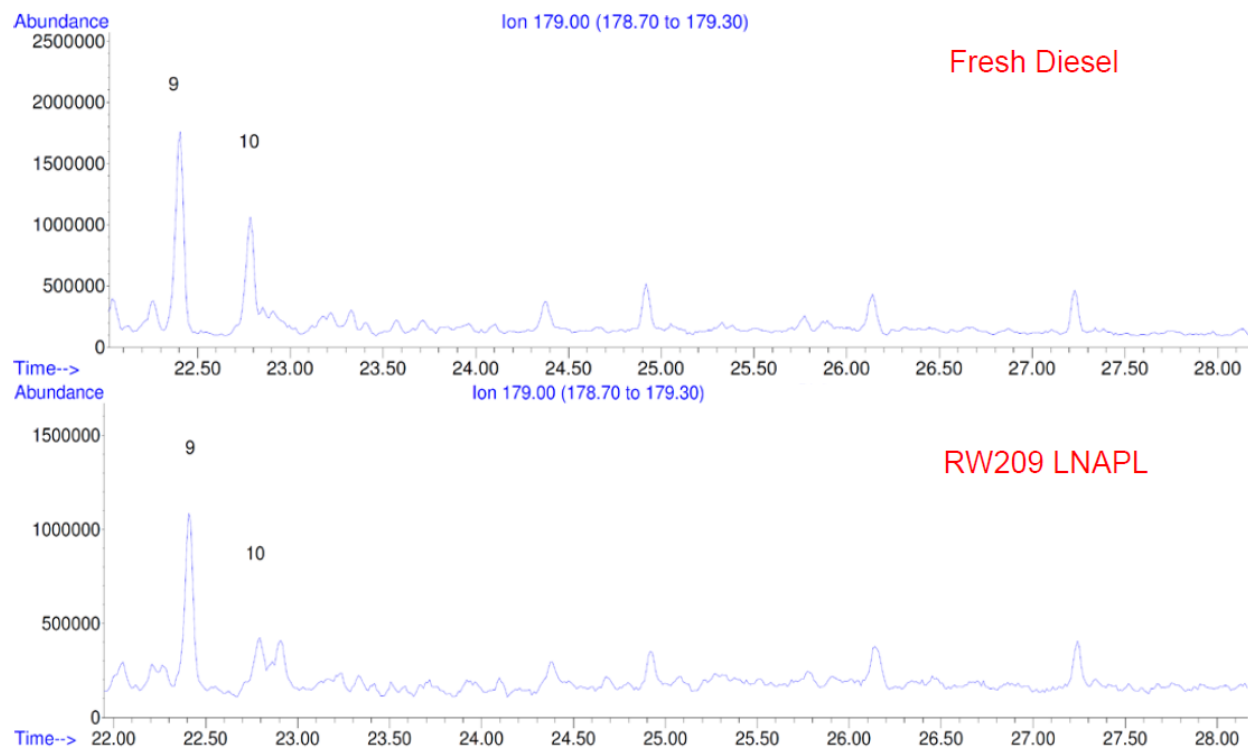
Mudge (2009) describes sesquiterpanes as biomarkers which are typically quite abundant in middle range distillates. Sesquiterpanes are smaller bicyclic biomarkers with a drimane skeleton that occur within the C<sub>13</sub> to C<sub>16</sub> boiling range (Wang et al. 2005; Yang et al. 2012). Therefore, drimane-based bicyclic sesquiterpanes appear to be suitable biomarkers for chemical fingerprinting of middle range distillates (Stout et al. 2005). Wang and Stout (2007) further suggests that sesquiterpanes may provide useful information for source identification of middle-range distillates when other typical hydrocarbon fingerprinting groups, such as high-boiling hopanes and steranes, are absent. The drimane-based sesquiterpanes can provide diagnostic information about the parent crude oil feedstock used in the production of distillate fuels because these compounds exhibit distinguishable distributions in refined middle distillate products. Further, drimane-based sesquiterpanes have been observed to be relatively resistant to environmental weathering compared to other hydrocarbons in middle distillate products (Stout et al., 2005). Differences in the relative distribution patterns of sesquiterpanes are often quite apparent between different middle range distillates (e.g., diesel fuel) (Wang et al. 2005). The partial m/z 123 sesquiterpanes chromatograms of fresh diesel and RW209 LNAPL samples are shown on Figure 4.15.





**Figure 4.15** - Partial m/z 123 sesquiterpanes chromatograms of the fresh diesel and the RW209 LNAPL sample.

A total of ten sesquiterpane compounds were observed within the m/z 123 sesquiterpane chromatogram, as shown in Figure 5.11. The m/z 123 sesquiterpane chromatograms of both the fresh diesel and RW209 LNAPL samples are evidently dominated by 8 $\beta$ (H)-drimane and 8 $\beta$ (H)-homodrimane (compound peaks 3 and 8, respectively), which is common in most diesel fuels (Wang and Stout, 2007). Peaks 9 and 10, 1 to 4, and 5 to 8 are denoted as C14 (C<sub>14</sub>H<sub>26</sub>), C15 (C<sub>15</sub>H<sub>28</sub>), C16 (C<sub>16</sub>H<sub>30</sub>) sesquiterpanes, respectively. Peaks 9 and 10 are verified by the m/z 179 chromatogram (Figure 4.16).



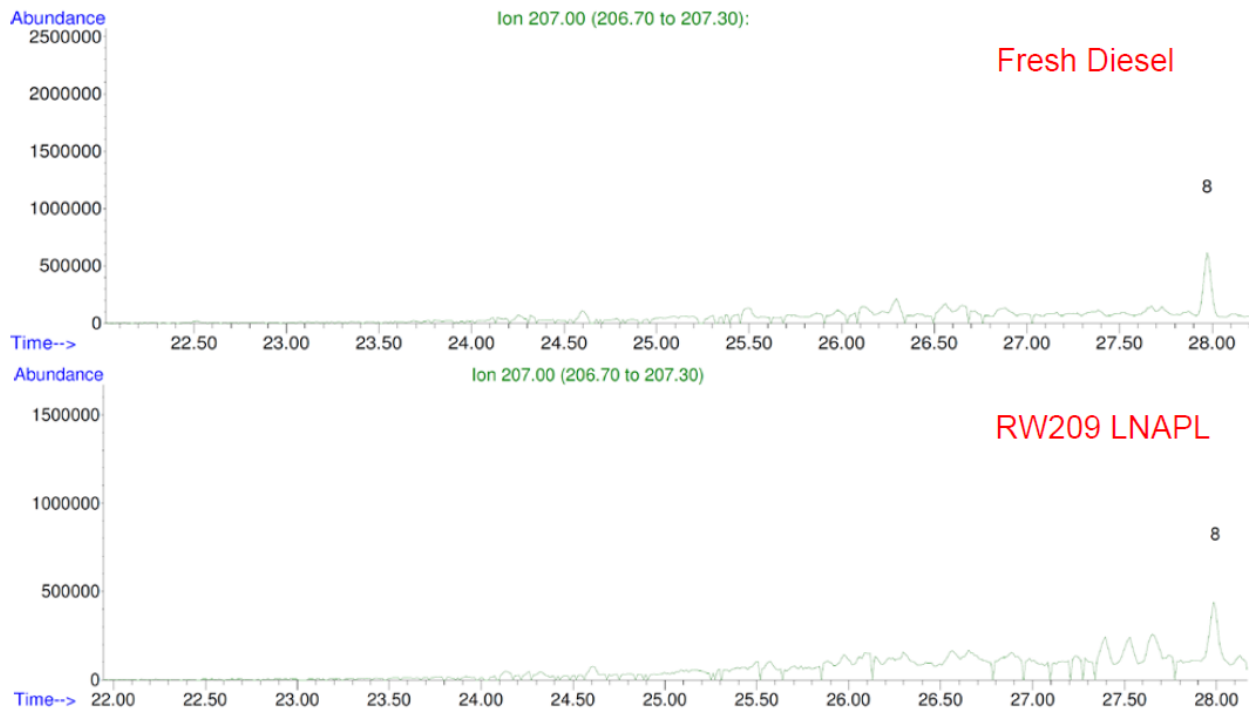
**Figure 4.16** - Partial m/z 179 sesquiterpanes chromatograms of the fresh diesel and the RW209 LNAPL sample.

Peaks 1 to 7 are confirmed by the m/z 193 chromatogram shown in Figure 4.17.



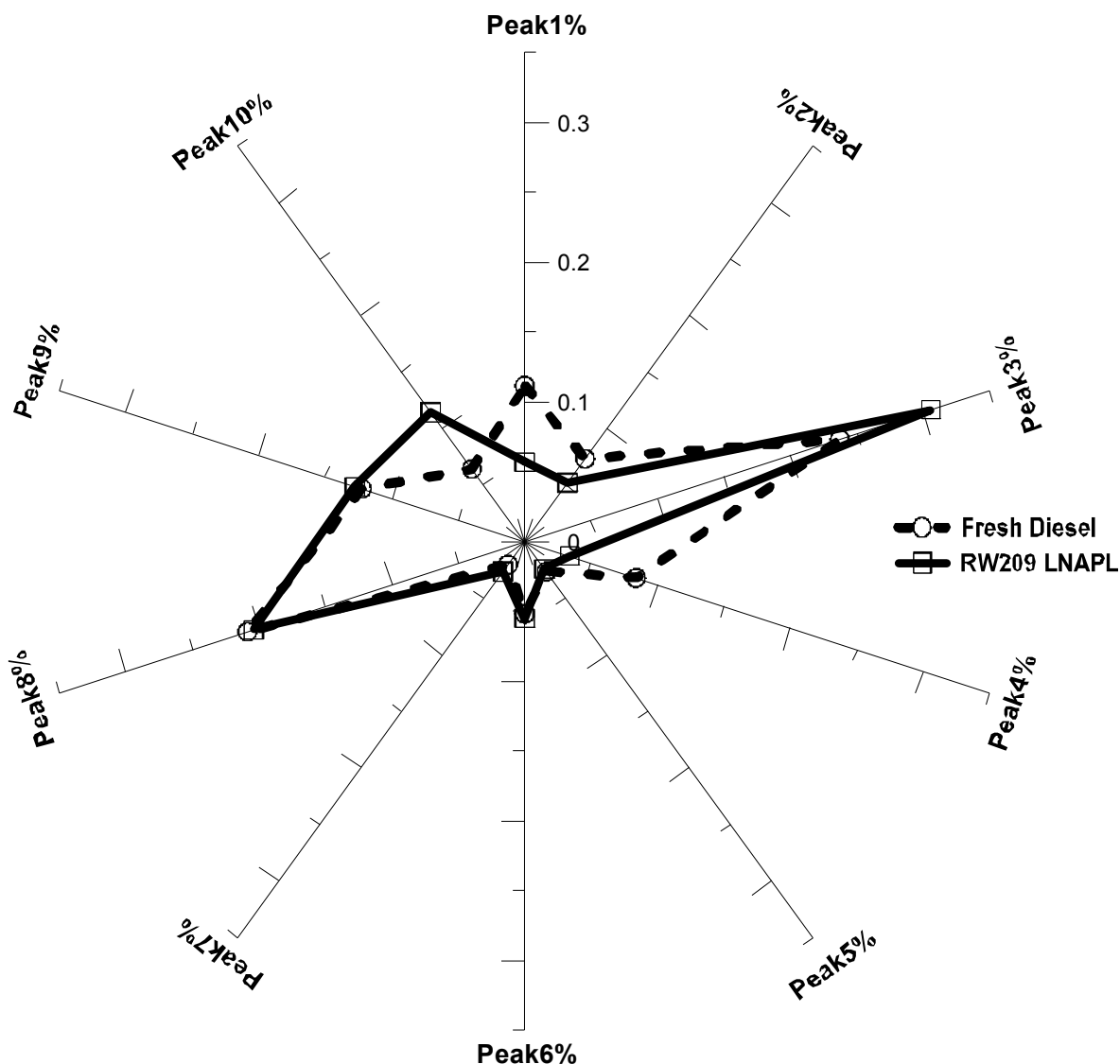
**Figure 4.17** - Partial m/z 193 sesquiterpanes chromatograms of the fresh diesel and the RW209 LNAPL sample.

Peak 8 is confirmed by the m/z 207 chromatogram shown in Figure 4.18.



**Figure 4.18** - Partial m/z 207 sesquiterpanes chromatograms of the fresh diesel and the RW209 LNAPL sample.

The relative distributions sesquiterpanes within fresh diesel and RW209 LNAPL samples are graphically presented in Figure 4.19.



**Figure 4.19** - Distribution of sesquiterpanes within fresh diesel and RW209 LNAPL samples.

The sesquiterpanes relative percentages are calculated using individual peak area, obtained from the m/z 123 sesquiterpanes chromatograms for both fresh diesel and RW209 LNAPL (Figure 5.10), divided by the sum of 10 peak areas. Figure 4.15 and Figure 4.19 show distinct sesquiterpane distribution patterns between the two samples. In Figure 4.18, the black dash line depicts fresh diesel and the black solid line depicts the RW209 LNAPL). Peaks 1, 2, and 4 ( $C_{15}H_{28}$ ) in the RW209 LNAPL distribution are more pronounced than those in the fresh diesel

distribution, while peaks 3 ( $C_{15}H_{28}$ ) and 10 ( $C_{14}H_{26}$ ) in the RW209 LNAPL are notably lower than for the fresh diesel. Relative proportions of  $C_{14}H_{26}$  and  $C_{15}H_{28}$  sesquiterpanes are diagnostic for distillate fuels from different sources (Stout and Wang 2016).  $C_{16}$  sesquiterpanes ( $C_{16}H_{30}$ ) have been observed to be present in similar abundances among diesel fuels, just as the similar percentages of peaks 5 to 8 shown on Figure 4.18 and peak 6/peak 8 ratios shown in Table 4.4. Wang et al. (2011) reported similar  $C_{16}$  group ratios among four spill samples. The relative abundance of  $C_{16}$  sesquiterpanes could be the reason why they are not used to distinguish different distillate fuel sources. The distinct distribution pattern of sesquiterpane isomers indicates that these two samples might have originated from different sources (Wang et al. 2006; Wang and Stout 2007).

Diagnostic ratios of paired sesquiterpane isomers are particularly valuable for source identification of light- and middle-range distillates (Stout et al. 2005; Yang et al. 2009). Table 4.4 summarizes the sesquiterpane diagnostic ratios of the two samples.

**Table 4.4** - Inventory and diagnostic ratios of drimane-based bicyclic sesquiterpane obtained from the m/z 123 chromatogram.

<b>Compound Identity</b>	<b>Peak #</b>	<b>Formula</b>	<b>Confirmation ion</b>
Rearranged C15**	1	C <sub>15</sub> H <sub>28</sub>	193
Rearranged C15**	2	C <sub>15</sub> H <sub>28</sub>	193
8β(H)-Drimane	3	C <sub>15</sub> H <sub>28</sub>	193
Rearranged C15**	4	C <sub>15</sub> H <sub>28</sub>	207
Rearranged C16***	5	C <sub>16</sub> H <sub>30</sub>	207
Rearranged C16***	6	C <sub>16</sub> H <sub>30</sub>	193
Rearranged C16***	7	C <sub>16</sub> H <sub>30</sub>	193
8β(H)-Homodrimane	8	C <sub>16</sub> H <sub>30</sub>	207
Rearranged C14*	9	C <sub>14</sub> H <sub>26</sub>	179
Rearranged C14*	10	C <sub>14</sub> H <sub>26</sub>	179
<b>Diagnostic ratios</b>	<b>RW209</b>	<b>Fresh Diesel</b>	
	<b>C14 Group</b>		
9/10	1.91	1.12	
	<b>C15 Group</b>		
1/3	0.47	0.19	
2/3	0.31	0.17	
4/3	0.35	0.11	
	<b>C16 Group</b>		
6/8	0.25	0.27	
	<b>InterGroup</b>		
9/3	0.52	0.42	
1/8	0.53	0.28	
3/8	1.14	1.50	
9:1:3:8	1.1:1:2.12:1.87	2.24:1:5.35:3.57	

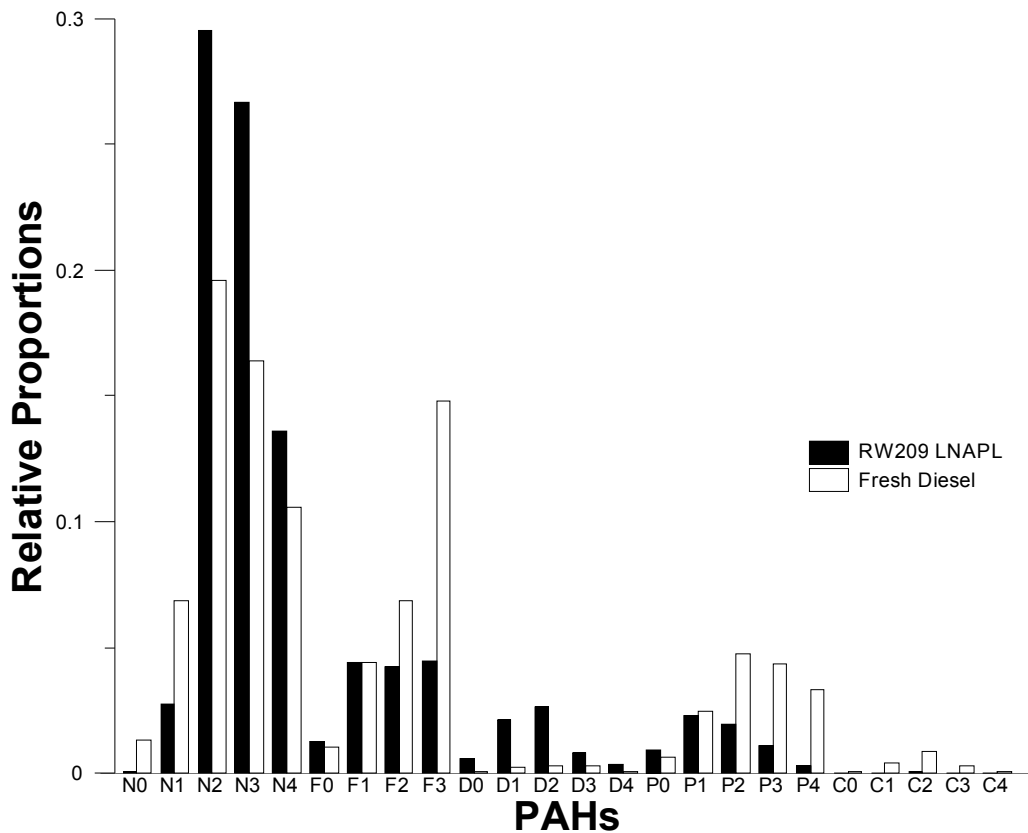
It should be noted that peak numbers are used in Figure 4.19. Tentative identifications for the rearranged sesquiterpanes based upon mass spectral interpretation are reported by Stout et al. (2005).

The C<sub>14</sub> group diagnostic ratio (Peak 9/Peak 10 (9/10)), the C<sub>15</sub> group ratios (1/3, 2/3 and 4/3), and two intergroup ratios (9/3 and 1/8) of the RW209 LNAPL sample are considerably higher than the corresponding ratio values for the fresh diesel. Conversely, the RW209 LNAPL sample has lower ratio of 3/8. In addition, the intergroup ratio (9:1:3:8) is significantly different between these two samples, which indicates that the diesel source for the RW209 LNAPL was produced from a different parent crude oil than the fresh diesel.

### 4.5.2.3 Alkylated Polycyclic Aromatic Hydrocarbons (PAH) Analysis

The diesel source identification by characterization of sesquiterpanes is further validated by quantitative evaluation of alkylated PAH. Approximately 30% to 40% of diesel components (C<sub>8</sub> to C<sub>28</sub> hydrocarbons) are PAHs, which are the most toxic components of PHCs (Carman et al. 2000). Many PAH compounds are more resistant to weathering than their saturated hydrocarbon counterparts (*n*-alkanes and isoprenoids) and volatile alkylbenzene compounds; therefore, PAHs are considered one of the most valuable fingerprinting classes of hydrocarbons for oil source discrimination (Morrison 2000; Wang and Stout 2007).

Crude oil and refined products from different sources can have very different PAH distributions (Chen et al. 2012; Mudge 2009). A bar chart representing the relative distribution of alkylated PAHs for the RW209 LNAPL sample and the fresh diesel is shown in Figure 4.20.



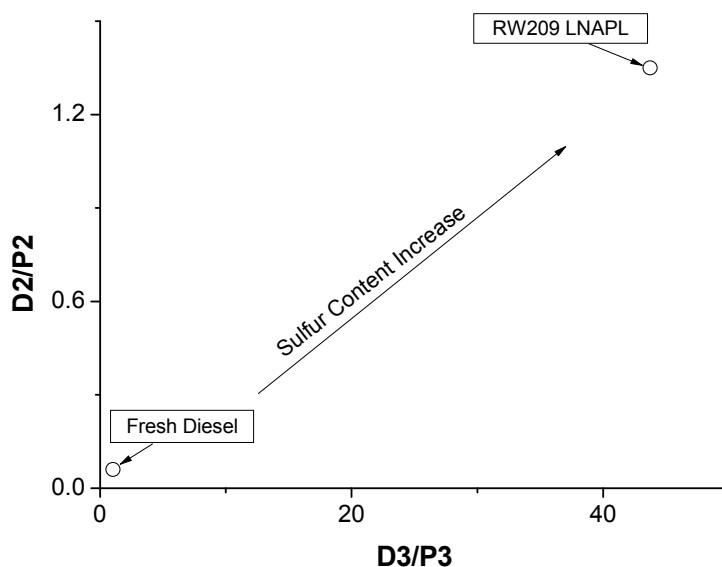
**Figure 4.20** - Normalized bar diagram representing relative distribution of alkylated PAHs for the RW209 LNAPL sample and the fresh diesel. N0=C0-naphthalene, N1 to N4= C1 to C4-naphthalene, F0=C0-fluorene, F1 to F4=C1 to C4-fluorene, D0=C0-dibenzothiophene, D1 to D4=C1 to C4-dibenzothiophene, P0=C0-phenanthrene, P1 to P4= C1 to C4-phenanthrene,



C0=C0-chrysene, C1 to C4=C1 to C4-chrysene. The concentrations of the alkylated PAH constituents are normalized to the percentage of the total PAHs measured.

The concentrations of the alkylated PAH constituents are normalized to the percentages of the total PAHs measured. Three chemicals with the highest percentages in the PAH distribution are (Figure 4.19): C2-naphthalene, C3-naphthalene and C4-naphthalene for the RW209 LNAPL sample and C2-naphthalene, C3-naphthalene and C3-fluorene for the fresh diesel. The normalized distribution of alkylated PAHs for the two samples is significantly different (Figure 5.12), especially percentages of fluorenes (fluorene (F0) to C4-fluorene (F4)), dibenzothiophenes (dibenzothiophene (D0) to C4-dibenzothiophene (D4)), phenanthrenes (phenanthrene (P0) to C4-phenanthrene (P4)), and chrysenes (chrysene (C0) to C4-chrysene (C4)). Chrysenes are the most resistant in the PAH compounds, based on their relative removal rate and biodegradation half-life (Wang and Stout 2007; Morrison 2000). The percentage of chrysenes reported within the RW209 LNAPL sample are substantially lower than the fresh diesel. The different distribution of alkylated PAHs indicates these two samples have different oil sources.

An important feature of the PAHs environmental fate is the similar depletion rates of C2- and C3-phenanthrenes (P2 and P3) and C2- and C3-dibenzothiophenes (D2 and D3) and their relative constancy in concentrations and degrees of weathering (Stout et al., 2001; Wang and Stout, 2007). Therefore, the ratios of D2/P2 and D3/P3 remain relatively stable as weathering proceeds. Dibenzothiophenes are sulphur-containing aromatic compounds, which are formed by the microbial process of sulphate reducing bacteria through incorporating sulphur of sulphate into hydrocarbons. Concentrations of dibenzothiophenes vary widely in different crude sources under different geological and geochemical conditions. The relative amounts of dibenzothiophenes and phenanthrenes; therefore, vary significantly in diesel depending on its parent crude oil source. Source ratios D3/P3 and D2/P2 for the fresh diesel and the RW209 LNAPL sample are plotted and presented on Figure 4.21.



**Figure 4.21** - Plot of source ratios D3/P3 and D2/P2 for the fresh diesel and the RW209 LNAPL sample. D2=C2-dibenzothiophenes, D3=C3-dibenzothiophenes, P2=C2-phenanthrenes, P3=C3-phenanthrenes.

The D2/P2 and D3/P3 ratios of the RW209 LNAPL sample (1.35 and 43.75, respectively) are substantially higher than those of the fresh diesel (0.06 and 1.02, respectively). Figure 5.13 indicates that sulphur content in the RW209 LNAPL sample is higher than that of the fresh diesel. The refining process of hydrodesulphurization can have specific effects on the sulphur-containing aromatic compounds (Kabe et al., 1992; Ishihara et al., 2005). This observation provides an additional line of evidence that the RW209 LNAPL diesel source and the fresh diesel might be produced from different oil sources or were derived from different refining processes.

#### 4.5.2.4 Conclusions from Diesel Source Identification

The GC/MS analytical results demonstrate that the RW209 LPH sample is weathered diesel. However, the distinct distribution and diagnostic ratios of sesquiterpanes and alkylated PAHs confirms that the RW209 LPH sample is a non-match to the fresh diesel and they are originated from a different crude oil source and/or different refining process.

## **CHAPTER 5**

### **SUMMARY AND RECOMMENDATIONS FOR FUTURE WORK**

#### **5.1 Summary**

The tiered strategy developed and presented in this study shows that by applying an integrated environmental forensics approach, through linking unique chemical fingerprinting techniques with detailed site characterization techniques, the outcome and value of the environmental forensics case can be improved. It is advisable that environmental practitioners who would wish to use a similar environmental forensics strategy to thoroughly understand modern and historical refining and blending practices used in the production of light and middle range distillates.

The Study Site background research indicated that the diesel impacts to groundwater may not be caused by the current fuel service station operation. The GC/FID chromatograms of groundwater samples demonstrated that two contaminant plumes, one gasoline and one diesel plume, were separately present at the Study Site.

It was evident that the effects of refinery processes during gasoline production and subsequent weathering of the spilled gasoline rapidly removed many potential diagnostic features. The light distillate components shared a similarity of distribution and locations of dominant peaks such as butanes, pentanes, BTEX, and mesitylene between the samples collected from the gasoline plume and fresh gasoline solution. This suggested that the north contaminated groundwater plume resulted from a gasoline source spill or leakage. Several lines of additional evidence, including the similar distribution of C<sub>3</sub>-alkylbenzenes, non-detectable dissolved lead and oxygenates, and the consistent diagnostic ratios of the analyte pairs with similar solubility, indicate that the source for the gasoline impacts to groundwater at the Study Site likely originates from leakage of the current on-site USTs.

This study found that the distribution of C<sub>3</sub>-alkylbenzenes, obtained by using integrated area, to be of critical importance for chemical fingerprinting light distillates. The following five C<sub>3</sub>-alkylbenzene chemical compounds were found to be key target compounds for differentiating gasoline plumes as well as for identifying gasoline source:

- 1-methyl-3-ethyl-benzene (1M3EB)
- 1-methyl-4-ethyl-benzene (1M4EB)

- 1,3,5-trimethylbenzene (135-TMB)
- 1-methyl-2-ethyl-benzene (1M2EB)
- 1,2,4-trimethylbenzene (124-TMB)
- 1,2,3-trimethylbenzene (123-TMB)

The C<sub>3</sub>-alkylbenzene compound 1M3EB was identified to have the shortest retention time of the five respective compounds identified within the C<sub>3</sub>-alkylbenzene compound group chromatograms. Compounds with shorter retention times typically tend to decrease in peak intensity preferentially by weathering, thus, the 1M3EB compound provided additional data correlating increased evidence of weathering with increasing distance from the source. This provides a further linkage between the gasoline plume and the current on-site USTs. Therefore, this study confirmed that an environmental forensic strategy, specifically targeting the higher boiling fractions (e.g., carbon C<sub>9</sub> range) of residual gasolines can provide valuable data and can be beneficial for applications of chemical fingerprinting light distillates.

A modified GC/MS full scan method was used to identify the source of the contaminated diesel plume at the Site. The GC/MS full scan method included evaluation of the TIC, and the evaluation of paraffins (alkanes, m/z 85), isoparaffins (isoalkanes, m/z 113), sesquiterpanes (m/z 123, 179, 193, and 207), and the heavy distillate biomarkers terpane (m/z 191) and sterane (m/z 217 and 218).

Initial findings from the diesel fuel component of the study identified a UCM hump, evidence that the plume was predominately contaminated by diesel fuel. The location of the central UCM hump in the fresh diesel solution was slightly different than the diesel plume product sample which was evidence that the diesel plume did not originate from the current on-site diesel fuel USTs.

The extent of weathering of chemical compounds was another strong line of evidence for identifying middle distillate source. Isoprenoid diagnostic ratios and relative abundance concentrations were used to determine the extent of weathering in the diesel product sample through knowledge of preferential weathering of the isoprenoid chemical compounds. The weathering study confirmed that the diesel fuel product sample was weathered.

Drimane-based bicyclic sesquiterpane petroleum biomarker compounds were identified and confirmed to be valuable target compounds for chemical fingerprinting of the diesel fuel plume. A total of ten sesquiterpane compounds were observed within the m/z 123 sesquiterpane chromatograms. The sesquiterpanes relative percentages were calculated using individual peak areas, obtained from the m/z 123 sesquiterpanes chromatograms for both the fresh diesel solution and the diesel fuel product sample. Distinct distribution patterns of sesquiterpane isomer compounds indicate that these two samples might have originated from different sources.

Quantitative evaluation of alkylated PAHs was identified as valuable forensic biomarkers, as these chemical compounds can be readily measured using GC/MS through monitoring of characteristic fragment ions. Chrysene compounds have particular importance largely due to their relative removal rate and biodegradation half-life. The percentage of chrysene compounds reported within the diesel fuel product sample were substantially lower than the fresh diesel fuel solution. Dibenzothiophene and phenanthrene compounds were also identified as important alkylated PAH compounds for this study. Concentrations of dibenzothiophenes vary widely between crude sources and at sites with different geological and geochemical conditions. Therefore, the relative amounts of dibenzothiophenes and phenanthrenes vary in middle distillates, largely dependent on the parent crude oil feedstock source. The distinct differences in normalized distribution of these three key alkylated PAHs provided further evidence that confirmed the diesel product sample from the Study Site and the fresh diesel might be produced from different feedstocks or were derived from different refining processes. Since alkylated PAHs are more abundant and persist for a longer time in the environment than the parent PAHs, alkyl homolog concentrations should be combined with their parent concentrations when performing environmental forensic assessments.

It is evident that assessing biomarker compounds, specifically drimane-based bicyclic sesquiterpanes, in conjunction with additional data from analysis of alkylated PAHs, alkanes, and weathering processes can provide sufficient data to defensibly identify middle range distillate sources. This study provided strong evidence that employing a tiered environmental forensics program for differentiation and source identification of light and middle range distillates can be successfully conducted in geographic regions where a more limited number of refineries are operational (e.g., Western Canada).

## 5.2 Recommendations for Future Work

A C<sub>4</sub> alkylbenzene compound group is also expected to be present in almost all fresh light and middle distillates; however, is known to produce more complex patterns than a C<sub>3</sub> alkylbenzene compound group, as there are more ways to build the group. Lentini (2013) reports much more complex C<sub>4</sub> alkylbenzene group patterns are produced in kerosene and diesel fuel chromatograms than gasoline. Although a complete composition of C<sub>4</sub>-alkylbenzenes was not observed in the m/z 119 ion chromatograms in this study, there exists potential to develop more refined analytical procedures to detect the C<sub>4</sub>-alkylbenzene compound group. A refined unique procedure to better identify the composition of C<sub>4</sub>-alkylbenzene compound groups could be of significant benefit to chemical fingerprinting light distillates and is a knowledge gap that requires further study. Additional groups of compounds, dihydroindene and methylindans, that could be extracted using m/z 117 and 131, respectively, are also expected to be present in most fresh light and middle range distillates.

Adamantanes and diamantanes are low boiling diamondoids that elute in the C<sub>10</sub> to C<sub>13</sub> and C<sub>15</sub> to C<sub>17</sub> boiling ranges, respectively. Adamantane and diamondoid compounds were not identified in the samples analyzed in this study; however, there is potential that adamantanes could be present in gasoline impacted samples and both biomarker compounds could be present in middle distillate impacted samples at other sites. Stout and Wang (2016) describe diamondoid as being comprised of complex carbon skeletons that make them recalcitrant to weathering processes. As such, it is not clear why adamantanes or diamantanes were not identified in the analytical data sets from the Study Site. It could be attributed to a lack of these compounds being present in the crude oil feedstock or certain refining processes used for the distillates that impacted the Study Site. However, further analysis of these compounds at other impacted sites would be beneficial to provide more insight to the value of targeting these compounds in future studies.

Additional research on these compounds and compound groups, in respect to the application of environmental forensics of light and middle range distillates could provide additional value for this body of knowledge. The tiered methodology developed in this study could also be expanded and applied to other contaminant studies such as hydraulic fluid contaminated sites; however, the target biomarker analytes would be different.

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**APPENDIX A**  
**REFERENCE TABLES**

**Table A.1** - Inventory of Target Saturated Hydrocarbons (SHC), PAHs, and Biomarkers Commonly Analyzed by GC/FID and GC/MS-SIM in Oil Spill Studies (modified from Wang et al. 1999)

<b>Target SHC and PAH Compounds</b>	<b>Target Ions</b>
<b>SHC - GC/FID</b>	
n-C8 > n-C40, pristane, phytane	n/a
nor-pristane, TPH (C8–C44)	n/a
<b>PAH Groups - GC/FID</b>	
Naphthalene	128
C <sub>1</sub> - naphthalenes	142
C <sub>2</sub> - naphthalenes	156
C <sub>3</sub> - naphthalenes	170
C <sub>4</sub> - naphthalenes	184
Acenaphthylene	152
Acenaphthene	154
Biphenyl	154
Dibenzofuran	168
Fluorene	166
C1-Fluorenes	180
C2-Fluorenes	194
C3-Fluorenes	208
Dibenzothiophene	184
C1-Dibenzothiophenes	198
C2-Dibenzothiophenes	212
C3-Dibenzothiophenes	226
C4-Dibenzothiophenes	240
Anthracene	178
Phenanthrene	178
C1-Phenanthrenes/Anthracenes	192
C2-Phenanthrenes/Anthracenes	206
C3-Phenanthrenes/Anthracenes	220
C4-Phenanthrenes/Anthracenes	234
Fluoranthene	202
Pyrene	202
C1-Fluoranthenes/Pyrenes	216
C2-Fluoranthenes/Pyrenes	230
C3-Fluoranthenes/Pyrenes	244
C4-Fluoranthenes/Pyrenes	258
Naphthobenzothiophenes	234
C1-Naphthobenzothiophenes	248
C2-Naphthobenzothiophenes	262
C3-Naphthobenzothiophenes	276
C4-Naphthobenzothiophenes	290
Benzo[a]anthracene	228



**Table A.1** - Inventory of Target Saturated Hydrocarbons (SHC), PAHs, and Biomarkers Commonly Analyzed by GC/FID and GC/MS-SIM in Oil Spill Studies (modified from Wang et al., 1999)

Chrysene	228
C1-Chrysenes	242
C2-Chrysenes	256
C3-Chrysenes	270
C4-Chrysenes	284
Benzo[b]fluoranthene	252
Benzo[j,k]fluoranthene	252
Benzo[a]fluoranthene	252
Benzo[a]pyrene	252
Benzo[e]pyrene	252
Perylene	252
Indeno[1,2,3-c,d]pyrene	276
Dibenzo[a,h]anthracene	278
Benzo[g,h,i]perylene	276
<b>Single PAHs</b>	
4-Methyldibenzothiophene	198
2/3-Methyldibenzothiophene	198
1-Methyldibenzothiophene	198
3-Methylphenanthrene	192
2/4-Methylphenanthrene	192
2-Methylantracene	192
9-Methylphenanthrene	192
1-Methylphenanthrene	192
Retene	234
Cadalene	198
5-Methylchrysene	242
<b>Sesquiterpanes</b>	123
<b>Alkylcyclohexanes</b>	83
<b>Tricyclic Triterpanes — GC/MS</b>	
C <sub>23</sub> Tricyclic triterpane	191
C <sub>24</sub> Tricyclic triterpane	191
C <sub>25</sub> Tricyclic triterpane	191
C <sub>26</sub> Tricyclic triterpane	191
C <sub>27</sub> Tricyclic triterpane	191
C <sub>28</sub> Tricyclic triterpane	191
C <sub>29</sub> Tricyclic triterpane	191
C <sub>30</sub> Tricyclic triterpane	191
<b>Pentacyclic Triterpanes — GC/MS</b>	
18 $\alpha$ (H)-22,29,30-trisnorhopane ( <b>T<sub>s</sub></b> )	191
18 $\alpha$ (H)-22,29,30-trisnorhopane ( <b>T<sub>m</sub></b> )	191
17 $\alpha$ (H),21 $\beta$ (H)-28,30-bisnorhopane	191

**Table A.1** - Inventory of Target Saturated Hydrocarbons (SHC), PAHs, and Biomarkers Commonly Analyzed by GC/FID and GC/MS-SIM in Oil Spill Studies (modified from Wang et al., 1999)

17 $\alpha$ (H),21 $\beta$ (H)-25-norhopane	191
17 $\alpha$ (H),21 $\beta$ (H)-30-norhopane	191
18 $\alpha$ (H)-30-norneohopane ( <b>C<sub>29</sub>T<sub>s</sub></b> )	191
17 $\beta$ (H),21 $\alpha$ (H)-normoretane	191
18 $\alpha$ (H) and 18 $\beta$ (H) oleanane	191
17 $\alpha$ (H),21 $\beta$ (H)-hopane ( <b>Hop</b> )	191
17 $\beta$ (H),21 $\alpha$ (H)-moretane	191
22S-17 $\alpha$ (H),21 $\beta$ (H)-30-homohopane	191
22R-17 $\alpha$ (H),21 $\beta$ (H)-30-homohopane	191
Gammacerane	191
22S-17 $\alpha$ (H),21 $\beta$ (H)-30-bishomohopane	191
22R-17 $\alpha$ (H),21 $\beta$ (H)-30-bishomohopane	191
22S-17 $\alpha$ (H),21 $\beta$ (H)-30-trishomohopane	191
22R-17 $\alpha$ (H),21 $\beta$ (H)-30-trishomohopane	191
22S-17 $\alpha$ (H),21 $\beta$ (H)-30-tetrakishomohopane	191
22R-17 $\alpha$ (H),21 $\beta$ (H)-30-tetrakishomohopane	191
22S-17 $\alpha$ (H),21 $\beta$ (H)-30-pentakishomohopane	191
22R-17 $\alpha$ (H),21 $\beta$ (H)-30-pentakishomohopane	191
<b>Steranes - GC/MS</b>	
13 $\beta$ ,17 $\alpha$ -diacholestane(20S)	217
13 $\beta$ ,17 $\alpha$ -diacholestane(20R)	217
5 $\alpha$ ,14 $\beta$ ,17 $\beta$ -cholestane(20R)	218
5 $\alpha$ ,14 $\beta$ ,17 $\beta$ -cholestane(20S)	218
5 $\alpha$ ,14 $\alpha$ ,17 $\alpha$ -cholestane(20R)	217
5 $\alpha$ ,14 $\beta$ ,17 $\beta$ ,24-methylcholestane(20R)	218
5 $\alpha$ ,14 $\beta$ ,17 $\beta$ ,24-methylcholestane(20S)	218
5 $\alpha$ ,14 $\alpha$ ,17 $\alpha$ ,24-ethylcholestane(20S)	217
5 $\alpha$ ,14 $\beta$ ,17 $\beta$ ,24-ethylcholestane(20R)	217
5 $\alpha$ ,14 $\beta$ ,17 $\beta$ ,24-ethylcholestane(20S)	218
5 $\alpha$ ,14 $\alpha$ ,17 $\alpha$ ,24-ethylcholestane(20R)	218
5 $\beta$ (H)cholane ( <b>Chol</b> )	217/218
<b>Triaromatic Steroids (TAS) — GC/MS</b>	
C <sub>20</sub> - TAS	231
C <sub>21</sub> - TAS	231
C <sub>26</sub> ,20S - TAS	231
C <sub>26</sub> 20R + C <sub>27</sub> ,20S - TAS	231
C <sub>28</sub> ,20S — TAS	231
C <sub>27</sub> ,20R — TAS	231
C <sub>28</sub> ,20R — TAS	231
<b>Decalins</b>	
Decalin	138

**Table A.1** - Inventory of Target Saturated Hydrocarbons (SHC), PAHs, and Biomarkers Commonly Analyzed by GC/FID and GC/MS-SIM in Oil Spill Studies (modified from Wang et al., 1999)

C1-Decalins	152
C2-Decalins	166
C3-Decalins	180
C4-Decalins	194

**Table A.2** - Gasoline Sample Target Analytes and Associated Mass Spectral Quantification Ions (modified from Uhler et al., 2002)

Peak #	Compound Name	Compound Class	Quantification ion m/z	Confirmation ion m/z
1	Isopentane	I	43	57
2	1-Pentene	O	42	52
3	2-Methyl-1-butene	O	55	42
4	<i>n</i> -C5 (pentane)	P	43	57
5	<i>trans</i> -2-Pentene	O	55	42
6	<i>cis</i> -2-Pentene	O	55	42
7	2,2-Dimethylbutane	I	57	71
8	<i>t</i> -Butanol	OX	59	41
9	Cyclopentane	N	42	55
10	Methyl- <i>tert</i> -butyl ether	OX	73	43
11	2-Methylpentane	I	43	71
12	3-Methylpentane	I	57	56
13	1-Hexene	O	56	41
14	<i>n</i> -C6 (hexane)	P	57	43
15	Di-isopropyl ether	OX	45	87
16	<i>trans</i> -2-Hexene	O	55	84
17	2-Methylpentene-2	O	69	41
18	<i>cis</i> -2-Hexene	O	55	84
19	Ethyl- <i>tert</i> -butyl ether	OX	59	87
20	2,2-Dimethylpentane	I	57	85
21	1,2-Dichloroethane	ADD	62	64
22	Methylcyclopentane	N	56	42
23	2,4-Dimethylpentane	I	43	57
24	Benzene	A	78	-
25	Thiophene	S	84	58
26	Cyclohexane	N	56	84
27	2-Methylhexane	I	43	85
28	2,3-Dimethylpentane	I	56	43
29	<i>Tert</i> -amyl-methyl ether	OX	73	43
30	3-Methylhexane	I	43	57
31	2-Methyl-1-hexene	O	56	41
32	2,2,4-Trimethylpentane	I	57	41
33	<i>trans</i> -3-Heptene	O	41	56
34	<i>n</i> -C7 (heptane)	P	43	57
35	<i>cis</i> -3-Heptene	O	41	56
36	<i>trans</i> -2-Heptene	O	55	56
37	<i>cis</i> -2-Heptene	O	56	41
38	Methylcyclohexane	N	83	55
39	2,4-Dimethylhexane	I	43	57
40	<i>ctc</i> -1,2,4-Trimethylcyclopentane	N	70	55
41	<i>ctc</i> -1,2,3-Trimethylcyclopentane	N	70	55
42	2,3,4-Trimethylpentane	I	43	71
43	Toluene	A	91	92
44	2,3,3-Trimethylpentane	I	43	71
45	2-Methylthiophene	S	97	98
46	2,3-Dimethylhexane	I	43	70

**Table A.2 - Gasoline Sample Target Analytes and Associated Mass Spectral Quantification Ions (modified from Uhler et al., 2002)**

47	3-Methylthiophene	S	97	98
48	2-Methylheptane	I	43	57
49	1,2-Dibromoethane (EDB)	ADD	107	109
50	1-Octene	O	55	41
51	2,2-Dimethylheptane	I	57	56
52	<i>trans</i> -2-Octene	O	55	41
53	Isopropylcyclopentane	N	68	69
54	<i>cis</i> -2-Octene	O	55	41
55	2,2,4-Trimethylhexane	I	57	56
56	2,4-Dimethylheptane	I	43	85
57	1,1,4-Trimethylcyclohexane	N	111	69
58	Ethylcyclohexane	N	83	55
59	2,6-Dimethylheptane	I	43	57
60	<i>n</i> -C8 (octane)	P	43	57
61	Ethylbenzene	A	91	106
62	2-Ethylthiophene	S	97	112
63	<i>ctt</i> -1,2,4-	N	111	69
64	<i>m</i> -Xylene	A	91	106
65	<i>p</i> -Xylene	A	91	106
66	2,3-Dimethylheptane	I	43	41
67	4-Methyloctane	I	43	85
68	2-Methyloctane	I	43	57
69	<i>ctc</i> -1,2,4-	N	69	111
70	1,1,2-Trimethylcyclohexane	N	69	111
71	<i>o</i> -Xylene	A	91	106
72	1-Nonene	O	56	41
73	<i>trans</i> -3-Nonene	O	55	41
74	<i>cis</i> -3-Nonene	O	55	41
75	<i>n</i> -C9 (nonane)	P	43	57
76	<i>trans</i> -2-Nonene	O	55	41
77	Isopropylbenzene	A	105	120
78	<i>cis</i> -2-Nonene	O	55	41
79	Isopropylcyclohexane	N	83	82
80	2,2-Dimethyloctane	I	57	56
81	<i>n</i> -Butylcyclopentane	N	69	55
82	3,3-Dimethyloctane	I	71	43
83	Propylbenzene	A	91	120
84	1-Methyl-3-ethylbenzene	A	105	120
85	1-Methyl-4-ethylbenzene	A	105	120
86	1,3,5-Trimethylbenzene	A	105	120
87	1-Methyl-2-ethylbenzene	A	105	120
88	3-Methylnonane	I	57	71
89	1,2,4-Trimethylbenzene	A	105	120
90	1-Decene	O	41	55
91	<i>sec</i> -Butylbenzene	A	105	134
92	<i>n</i> -C10 (decane)	P	43	57
93	1,2,3-Trimethylbenzene	A	105	120
94	Indane (indan)	A	117	118
95	1,3-Diethylbenzene	A	105	119
96	1,4-Diethylbenzene	A	105	119

**Table A.2 - Gasoline Sample Target Analytes and Associated Mass Spectral Quantification Ions (modified from Uhler et al., 2002)**

97	1,3-Dimethyl-5-ethylbenzene	A	119	134
98	1,2-Diethylbenzene	A	105	119
99	1-Methyl-2- <i>n</i> -propylbenzene	A	105	134
100	1,2-Dimethyl-4-ethylbenzene	A	119	134
101	1,3-Dimethyl-2-ethylbenzene	A	119	134
102	<i>n</i> -C11 (undecane)	P	57	43
103	1,2,4,5-Tetramethylbenzene	A	119	134
104	1,2,3,5-Tetramethylbenzene	A	119	134
105	1,2,3,4-Tetramethylbenzene	A	119	134
106	<i>n</i> -Pentylbenzene	A	91	148
107	MMT	ADD	120	55
108	Benzothiophene	S	134	147
109	<i>n</i> -C12 (dodecane)	P	43	57

Notes:

P - Paraffins

I - Isoparaffins

A - Aromatics

N - Napthenes

O - Olefins

OX - Oxygeneate

ADD - Additive

S - Sulfur-containing

**Table A.3** - Analytical results of specific C3-alkylbenzenes and C4-Alkylbenzenes by Using Ion m/z 105 and 119 Analysis

<b>Compound Name</b>	<b>Ion m/z</b>	<b>Gasoline Peak Area</b>	<b>RW206 Peak Area</b>	<b>MW102 Peak Area</b>
1,3,5-Trimethylbenzene (135TMB)	105	6844417	3405242	1298979
1,2,4-Trimethylbenzene (124TMB)	105	25697086	11398044	4684924
1,2,3-Trimethylbenzene (123TMB)	105	5294849	2825219	1203560
1-Methyl-3-EthylBenzene (1M3EB)	105	17852528	4976210	2736263
1-Methyl-4-EthylBenzene (1M4EB)	105	7884732	3057512	1218179
1-Methyl-2-EthylBenzene (1M2EB)	119	5847641	2955271	1319987
1,3,5-Trimethylbenzene (135TMB)	119	912830	430977	174773
1,2,4-Trimethylbenzene (124TMB)	119	3154539	1435464	578990
1,2,3-Trimethylbenzene (123TMB)	119	504344	282727	128308
1,2,4,5-Tetramethylbenzene (1245TeMB)	119	1146740	255844	110447
1,2,3,5-Tetramethylbenzene (1235TeMB)	119	1725302	389134	155992
1,2,3,4-Tetramethylbenzene (1245TeMB)	119	702787	159649	59816