MOLECULAR CHARACTERIZATION AND CARBON ISOTOPE RATIO ANALYSIS OF MARINE HYDROCARBONS IN SEDIMENTS FROM TRINITY BAY, NEWFOUNDLAND

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Molecular Characterization and Carbon Isotope Ratio Analysis of Marine Hydrocarbons in Sediments from Trinity Bay, Newfoundland

by

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Abstract

To better understand the cycling of carbon in a cold ocean coastal environment, molecular distributions and stable carbon isotopic compositions of various aliphatic and polycyclic aromatic hydrocarbons (PAH) have been determined for marine sediments of Trinity Bay, Newfoundland. Sediments were collected in the form of grab and core samples from the Northwest and Southwest Arms, extending into Trinity Bay. High levels of sulfur in the sediments required an exhaustive procedure for the complete removal sulfur interferences in chromatography. Separation of aliphatic hydrocarbons from PAH was accomplished through alumina/silica column chromatography. The combination of molecular characterization by gas chromatography/mass spectrometry (GC/MS) and isotopic "fingerprinting" through gas chromatography/combustion/isotope ratio mass spectrometry (GC/C/IRMS) enabled the distinction between marine, terrestrial, and anthropogenic sources of some of the hydrocarbons.

Aliphatic hydrocarbon results indicate large biogenic influences from marine sources, with particular evidence being the abundance of C_{25} highly branched isoprenoid alkenes. It is believed that these compounds are produced by certain diatoms immediately preceding the spring diatom bloom. The molecular distributions and carbon isotopic compositions of *n*-alkanes can be attributed to contributions from marine and terrestrial sources with slight mixing of anthropogenic petroleum sources.

The concentration levels of PAH in most sediment samples are extremely low, revealing that the marine environment in this area is relatively pristine. The distribution patterns and isotopic results of PAH present indicate source inputs from combustion, most likely due to wood-burning, with minor contributions from petroleum sources.

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Special thanks must be extended to my parents, Basil and Cathy, my sister, Leta, and my brother, Trevor. Without their personal support and genuine belief in my ability to succeed, I could not have even attempted such a research project. Final thanks to my husband, Murray, a former graduate student with the Department of Chemistry; recently completing his own thesis has proven to be an excellent motivating factor for me. Without his patience, understanding, and love, completing this project would have been all the more difficult.

Dedication

This thesis is dedicated to the many undergraduate students I had the pleasure of helping in tutorial sessions and laboratory periods during my two years at Memorial University. Whether we were working through a complicated calculation or improving a laboratory technique, these students made me feel appreciated, as though what I did made a difference in their lives. They helped me to realize that what I enjoyed most about chemistry was being able to share with others the knowledge I have gained.

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1.0 Introduction

1.1 General Introduction:

Many communities along the coast of Newfoundland have recently found their survival threatened with the depletion of the groundfish stocks. Concerns have been raised about the impact of human practices and the use of environmental resources on cold ocean ecosystems. In response to this current issue, the multi-disciplinary Eco-Research Project was initiated to determine how cold coastal communities have survived in the past, what has threatened their existence, and what future changes should be made to ensure their sustainability. Considering the many possible factors affecting sustainability, the Eco-Research Project "Sustainability in a Cold Ocean Coastal Environment" developed to encompass environmental science, social science, education, health, and history. The study area extended from the Bonavista headland down the eastern coast to the isthmus of Avalon in Newfoundland (Figure 1), a typical northern maritime ecosystem. The findings of the Eco-Research Project and this particular research study can generally be applied to similar cold coastal ecosystems along the North Atlantic from eastern Canada through Greenland, Iceland, the Faroes, Scotland, and northern Scandinavia.

Both natural changes and anthropogenic influences can profoundly alter the marine ecosystem, modifying the cycling of organic matter and other essential nutrients. To assess the past and present health of the ecosystem in the Trinity Bay area, organic

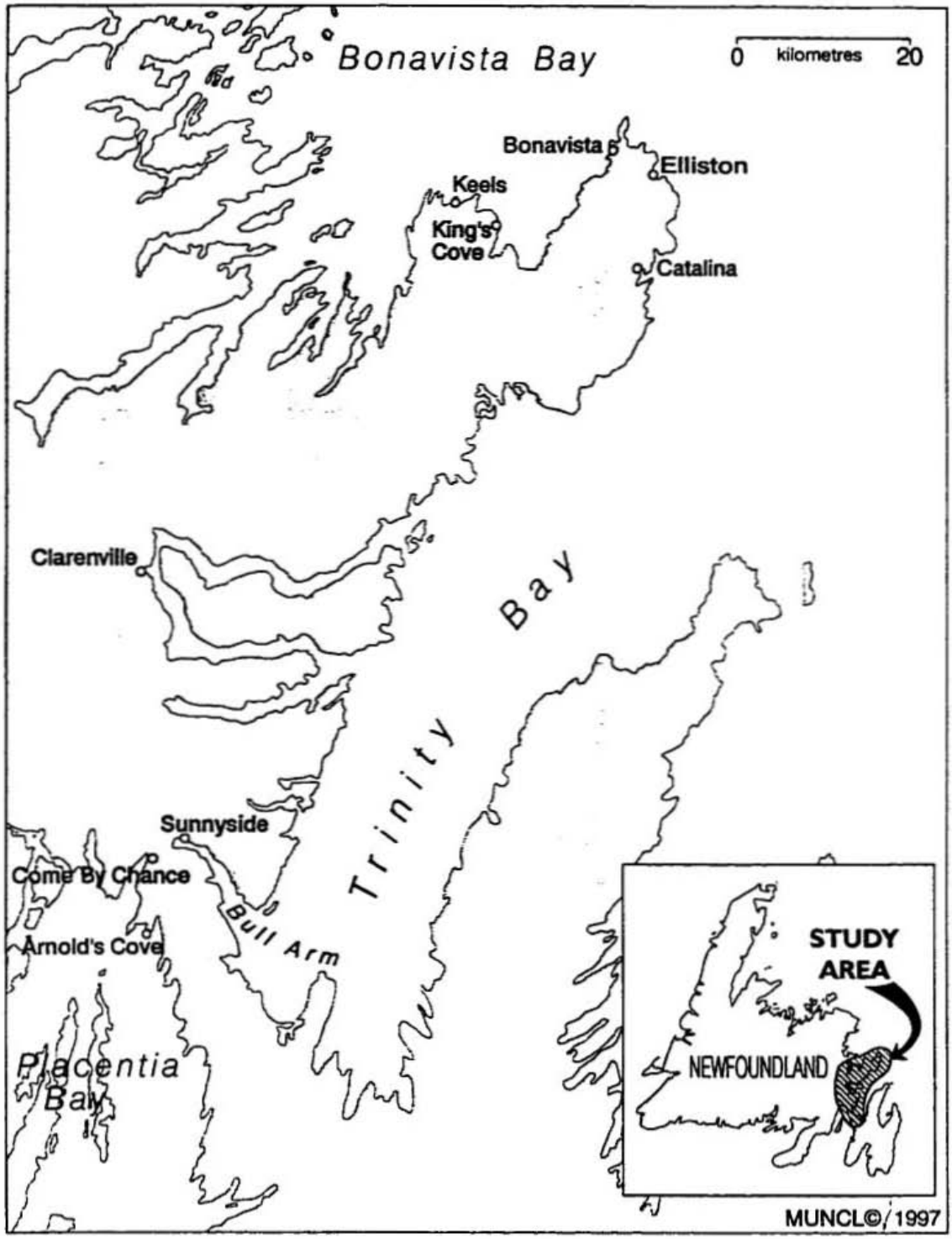


Figure 1: Eco-Research Program Study Area

material (fatty acids, hydrocarbons, lignin, lipids) was chosen for detailed studies by the Marine Group, a subproject of the Eco-Research Project. The cycling of organic matter could be better understood by characterizing the various sources, pathways, and sinks of organic carbon in the environment. While hydrocarbons represent only a small fraction of the organic matter present in the marine environment, they have proven to be a class of compounds easily analyzed. Hydrocarbons act as suitable biogeochemical markers for distinguishing different source inputs in marine sediments (Blumer *et al*, 1971; Saliot, 1981; Bouloubassi and Saliot, 1991). As a result, hydrocarbons have often been selected as the class of compounds to monitor when investigating the cycling of organic matter in the marine environment (Barrick *et al*, 1980; Gearing *et al*, 1976; Farrington and Tripp, 1977; Thompson and Eglinton, 1979; Colombo et al, 1989; Bouloubassi and Saliot, 1993). By adopting the multivariate approach of studying many different classes of hydrocarbons, stronger conclusions can be drawn and a more integrated picture of hydrocarbon cycling can be presented (Lipiatou and Saliot, 1991a; Yunker *et al*, 1995).

Certain hydrocarbons are recognized as hazardous environmental compounds. Polycyclic aromatic hydrocarbons, commonly referred to as PAH, have been classified as "priority pollutants" because of their carcinogenic and mutagenic characteristics (Freudenthal and Jones, 1976; Jones and Leber, 1978). The health risk associated with PAH justifies inclusion of these compounds in a general study of hydrocarbons in surface sediment environments.

In order to assess the various inputs of hydrocarbons into the marine environment, the possible pathways and sinks must be considered. Natural and anthropogenic compounds are introduced into the marine environment through several different mechanisms: the natural activity of marine organisms, river input, atmospheric deposition, petroleum discharge, and seeps from undersea crude oil reservoirs. Coastal sediments act as ultimate reservoirs for these compounds if they are able to survive transport through the water column. When characterizing the hydrocarbons present in the marine environment, coastal sediments are therefore generally favoured as the matrix for analysis.

1.2 Background:

Before continuing with a detailed discussion of this particular research project, it is necessary to introduce the basic concepts and underlying principles of the work involved. The following sections provide a general introduction to the terminology used and a brief discussion of the formation of hydrocarbons, characteristic molecular distributions, and stable carbon isotopic analysis.

1.2.1 Hydrocarbon Terminology:

By definition, hydrocarbons are compounds which are composed solely of carbon and hydrogen atoms. Because there are many compounds which fit into this broad category, hydrocarbons are further classified according to common structural characteristics. This research project involved the analysis of two distinct classes of hydrocarbons: aliphatic

and polycyclic aromatic.

The aliphatic hydrocarbons are those which do not contain any aromatic rings. These compounds may be linear, branched, or cyclic in structure, and may be saturated or unsaturated. Alkanes are those which contain no double bonds, alkenes are those which contain one or more double bonds, and isoprenoids are those which contain a specific regularly-branched structure. Some specific aliphatic hydrocarbons analyzed in this study are shown in Figure 2.

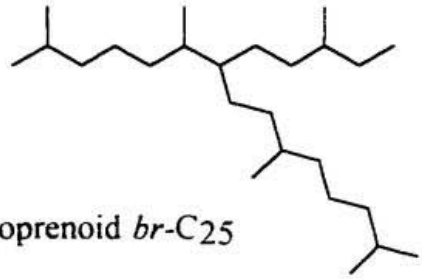
Shorthand notation for the aliphatic hydrocarbons involves describing the general structure as linear, branched, or cyclic, denoted as *n*-, *br*-, or *c*- respectively. This is generally followed by the number of carbon atoms and the number of double bonds present. For example, a straight-chain alkane with 25 carbon atoms and no double bonds would be referred to as *n*-C_{25}. A branched hydrocarbon with 25 carbon atoms and 3 double bonds would be referred to as *br*-$C_{25:3}$.

Polycyclic aromatic hydrocarbons (PAH) are those which contain two or more aromatic rings fused together. Included in this class of compounds are the parental polycyclic aromatic species (containing only the fused rings) as well as the alkylated analogues. Figure 3 shows the structures of some common PAH which were included in this study. Abbreviations are as follows: Naphthalene (Na), Acenaphthylene (Ay), Acenaphthene

n-pentacosane, *n*-C_{25}

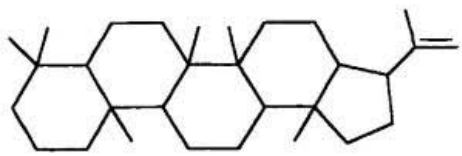
pristane

phytane



highly branched isoprenoid *br*-C_{25}

n-heneicosahexaene, HEH



Diploptene

Figure 2: Aliphatic Hydrocarbons

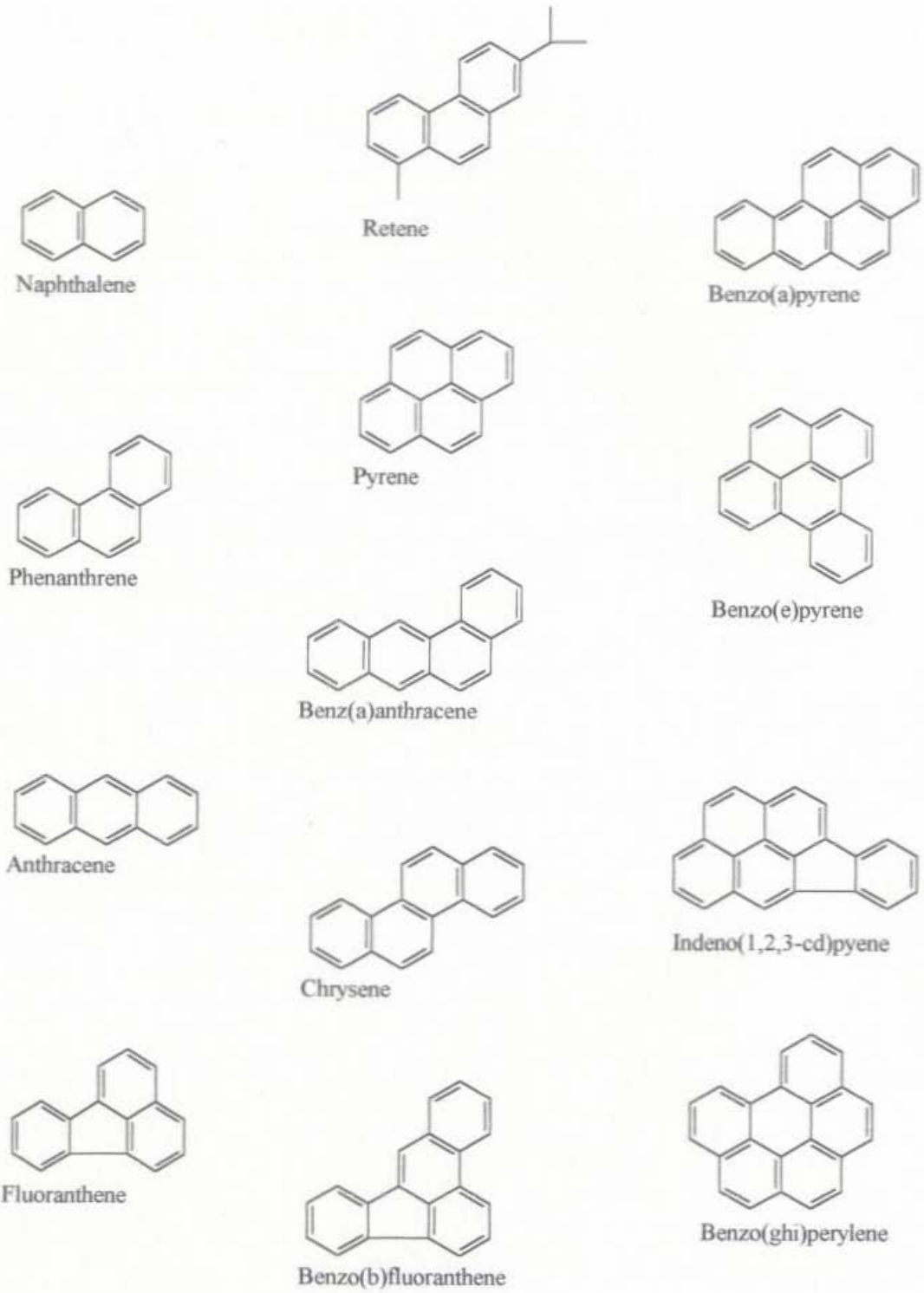


Figure 3: Polycyclic Aromatic Hydrocarbons

(Ae), Fluorene (F), Phenanthrene (Pa), Methylphenanthrene (MPa), Anthracene (A), Fluoranthene (Fl), Pyrene (Py), Benz(a)anthracene (BaA), Chrysene (Chy), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Benzo(e)pyrene (BeP), Indeno(1,2,3-cd)pyrene (Ip), Benzo(ghi)perylene (BPer), Dibenz(a,h)anthracene (DBA), Perylene (Per), and Retene (Ret).

1.2.2 Formation of Hydrocarbons:

Hydrocarbons in the marine environment are generally formed through the modification other related pre-existing structures. These modifications occur through common reactions such as reduction, decarboxylation, or aromatization (Saliot, 1981).

As discussed by Eglinton (1969), long chain fatty acids are synthesized from basic C_2 acetate units by living organisms. Decarboxylation (loss of CO_2) of fatty acids results in the formation of *n*-alkanes and alkenes. Since the even-numbered fatty acid precursors are naturally more abundant, it is not surprising that most naturally occurring *n*-alkanes are odd-numbered. Branching at various positions along the straight chain can occur by methylation of a double bond or the inclusion of a C_3 unit during chain elongation.

Isoprenoid hydrocarbons are considered to be biosynthesized by the polymerization of C_5 isoprene units; these C_5 units originate from the C_6 mevalonic acid, which in turn is also formed from the basic acetate unit in living organisms. Further cyclization of these

isoprenoid hydrocarbons results in the formation of cyclic terpenoid species (Nevenzel, 1989). These types of hydrocarbons can be found in many species of bacteria, diatoms, phytoplankton, zooplankton, fish, and mammals (Nevenzel, 1989).

Petroleum compounds are formed during the diagenesis and catagenesis of non-living organic material buried over millions of years. Affected first by bacteria, then by temperature and pressure, these organic structures undergo many chemical rearrangements to produce the n-alkanes, pristane, phytane, cyclic terpenoids, PAH, and other compounds commonly found in petroleum. These compounds enter the marine environment through petroleum oil spills and seeps from undersea oil reserves.

PAH are generally produced during incomplete combustion of organic-rich materials or fossil fuels. These compounds are introduced into the marine environment through atmospheric deposition. As mentioned previously, PAH may enter the marine environment through the local use of petroleum products. Naturally-derived PAH can be produced by the diagenesis of higher plant resins (Yunker and Macdonald, 1995).

1.2.3 Characteristic Molecular Distributions:

The presence of specific compounds and particular molecular distribution patterns are employed in source identification of hydrocarbons. The following discussion concerns the characteristic distributions of aliphatic hydrocarbons in the marine environment and

their respective sources; a summary of the information can be found in Table 1.

The presence of specific aliphatic hydrocarbons can be used to indicate possible carbon sources. The highly unsaturated 3,6,9,12,15,18-heneicosahexaene (HEH) can be used to indicate marine influences because it is produced by several species of marine phytoplankton (Blumer *et al*, 1970; Blumer *et al*, 1971). Pristane and phytane are produced during the diagenesis of organic material and are commonly used as biomarkers of petroleum contamination. Pristane is also thought to be derived from the phytol side chain of a chlorophyll molecule, as would be present in marine phytoplankton (Blumer *et al*, 1971); pristane may also be used to indicate natural marine influences. Diterpenoid hydrocarbons are considered markers of terrestrial plants, whereas steroid and triterpenoid skeletal structures are thought to be indicators of petroleum inputs (Barrick and Hedges, 1981). In particular, the pentacyclic triterpenoids of the hopane series, such as diploptene, have proven to be important markers for crude oil pollution (Dastillung and Albrecht, 1976; Bieger *et al*, 1996). Highly branched alkanes and alkenes found in marine sediments are thought to originate from natural marine sources, specifically algae or bacteria (Gearing *et al*, 1976; Rowland and Robson, 1990; Bieger, 1994). Recent work has involved the identification of *br*-C_{25} and *br*-C_{30} in cultured diatoms (Volkman *et al*, 1994); the major source of these hydrocarbons in marine sediments and waters is thought to be certain species of diatoms.

Compound	Sources
HEH	marine (phytoplankton)
pristane / phytane	petroleum or marine
diterpenoids	terrestrial plants
steroids / triterpenoids	petroleum
highly-branched alkanes / alkenes	marine (algae or bacteria)
n-C15 and n-C17	dominance indicates marine influences
odd / even n-alkanes	no marked preference indicates petroleum; dominance of odd high MW n-alkanes indicates terrestrial plants
CPI	<2 indicates aquatic plants, bacteria, or petroleum; 4-10 indicates terrestrial plants
UCM	petroleum

Table 1: Characteristic Molecular Distributions of Aliphatic Hydrocarbons

Particular molecular distribution patterns can be used in conjunction with the above criteria to provide further evidence for identifying sources of hydrocarbons. The predominance of odd-chain length high molecular weight *n*-alkanes is generally thought to indicate significant terrestrial influences from higher plant waxes (Blumer *et al*, 1971; Gearing *et al*, 1976; Farrington and Tripp, 1977). In contrast, the relative abundance of *n*-C_{15} and *n*-C_{17} and the lack of an odd/even preference in the *n*-alkanes have been attributed to planktonic and other aquatic contributions (Bouloubassi and Saliot, 1993). Petroleum hydrocarbons show equal or nearly equal abundances of odd- and even-chain *n*-alkanes (Farrington and Tripp, 1977). A carbon preference index (CPI) incorporating the above characteristic distributions can be used to help determine the source of hydrocarbons; the CPI is a ratio obtained by dividing the sum of abundances of total odd-chain *n*-alkanes by total even-chain *n*-alkanes over a specific range of hydrocarbons (Bray and Evans, 1961; Cooper and Bray, 1963). In general, a CPI value of 4 to 10 indicates the influence of terrestrial plants, while a CPI of less than 2 implies input from aquatic plants, bacteria, or petroleum (Barrick *et al*, 1980). Other studies have employed similar ratios to characterize hydrocarbon sources in the marine environment (Colombo *et al*, 1989; Bourbonniere and Meyers, 1996).

An unresolved complex mixture (UCM), appearing as a broad unimodal "bump" in the total ion chromatogram of aliphatic hydrocarbon fraction, is taken as evidence for petroleum contributions (Farrington *et al*, 1977; Gonzales *et al*, 1992). The UCM

consists of many different compounds, formed during the diagenesis and catagenesis of buried organic material. In addition to being resistant to weathering and microbial breakdown, these compounds are extremely difficult to separate and identify individually.

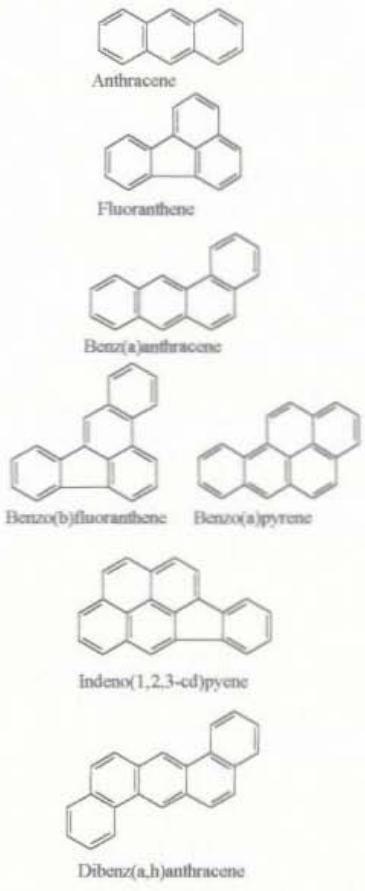
There exists currently a debate over several of these molecular "fingerprints" and their respective sources. It has been proposed that specific aquatic species of macroalgae may also produce a signature similar to the terrestrial plant waxes, such as the predominance of odd-chain high molecular weight *n*-alkanes (Lichtfouse *et al*, 1994). It is also possible, in terms of low levels of n-C_{15} and n-C_{17}, that these aquatic hydrocarbons are selectively remineralized and not well preserved in the sediments (Bouloubassi and Saliot, 1993; Meyers and Eadie, 1993). Consistent concentration profiles of hydrocarbons in sediment cores of increasing depths are usually taken to indicate natural origins. However, it is possible that the anthropogenic compounds are more susceptible to microbial degradation because natural compounds may be "protected" by their associated mineral or organic matrix (Barrick *et al*, 1980). Such a scenario would also lead to apparently consistent concentrations of hydrocarbons, even if anthropogenic influences were present over a long time scale. These problems were described to illustrate how using only one method of source identification can lead to inconclusive findings.

Molecular distributions of PAH are generally used to distinguish between pyrolytic, petroleum, and natural source inputs. The relative amounts of PAH isomers have been used to distinguish specifically between combustion and petroleum sources; this method of source identification is depicted in Table 2 as taken from Yunker and Macdonald (1995). The less-stable/kinetic isomers (A, Fl, BaA, BbF, BaP, In, DBA) appear enhanced when combustion sources of PAH are present; dominance of the more-stable/thermodynamic isomers (Pa, Py, Chy, BeP, BPer) suggests more significant petroleum inputs. Another signature for petroleum sources is the higher amount of alkylated PAH relative to parental PAH (Bouloubassi and Saliot, 1993; Yunker and Macdonald, 1995). Several source-specific markers for natural terrestrial plant inputs and/or wood combustion from coniferous vegetation are Retene, Cadalene, Pimanthrene, and Simonellite (Lipiatou and Saliot, 1991b; Yunker and Macdonald, 1995). Another PAH which may indicate natural or pyrolytic sources is Perylene. In order to identify the major source of PAH as pyrolytic, petrogenic, or natural, all of these variations must be taken into account.

It is possible that the molecular composition of many of the previously mentioned species may be altered by physical, chemical, or microbial actions in the natural environment. Again, molecular distributions alone may not be completely reliable for source identification. As an additional method, compound-specific isotopic analysis of carbon should not be affected by such transformations and can therefore be used as a

Parental vs Alkylated PAH	Abundance of parental PAH indicates combustion; dominance of alkylated PAH indicates petroleum
Source Specific PAH	Acenaphthene and Acenaphthylene are specific for combustion sources. Retene is specific for plant sources.
PAH Stability	Enhanced less-stable/kinetic isomers indicate combustion sources. Dominance of more-stable/thermodynamic isomers suggests petroleum inputs.

Less-stable/kinetic isomers



More-stable/thermodynamic isomers

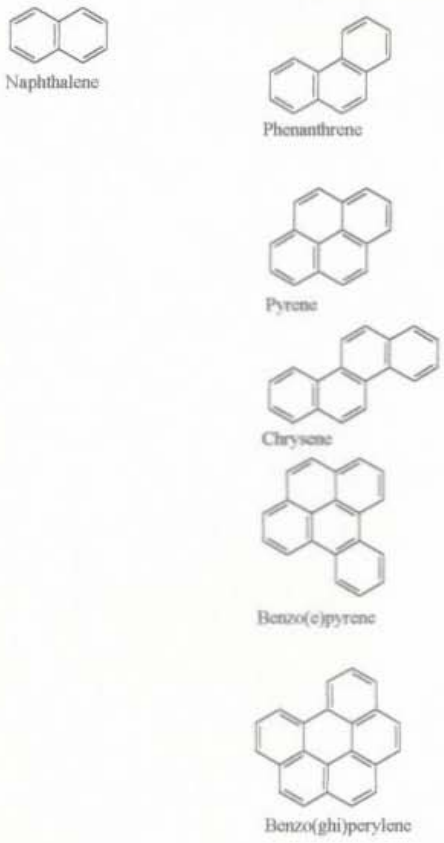


Table 2: Source Identification of PAH

complementary method for determining hydrocarbon inputs (O'Malley *et al*, 1994).

1.2.4 Stable Carbon Isotopic Compositions:

Carbon has two stable isotopes, ^{12}C and ^{13}C in the global abundance of 98.89% and 1.11% respectively. During chemical, physical, biological processes, these relative ratios may be transformed slightly, leading to different isotopic compositions for certain carbon pools. In one such example, ^{12}C is preferred in photosynthesis on land leading to a general depletion of ^{13}C in all terrestrial organic matter. Conversely, the lower vapour pressure of $^{13}CO_2$ results in the dissolved inorganic carbon being enriched in ^{13}C compared to atmospheric CO_2. This results in more enrichment of ^{13}C in marine organic matter relative to terrestrial organic materials. Provided that organic compounds retain the carbon isotopic compositions of their biosynthetic precursors, variations in isotopic compositions may be used to distinguish hydrocarbons of different origin and trace the movement of carbon through organic and inorganic reservoirs (Hayes *et al*, 1989; Murphy and Abrajano, 1994; Dowling *et al*, 1995).

In order to obtain the stable isotopic composition of individual compounds, the components of the sample mixture are separated by GC; the organic carbon of the sample is then quantitatively combusted and converted into carbon dioxide, and the three major isotopic masses of carbon dioxide measured. Results are reported in conventional delta (δ) notation:

$$\delta^{13}C = 1000\,(R_s/R_{std} - 1) \quad (‰)$$

where R represents the ratio $^{13}C/^{12}C$, and s and std refer to the sample and standard respectively. All reported analyses are referred to the internationally accepted standard Pee Dee Belemnite, a calcium carbonate fossil of *Belemnitella americana* from the Cretaceous Pee Dee formation in South Carolina which is assigned a $\delta^{13}C$ value of 0‰.

Stable carbon isotopic compositions have been measured for aliphatic hydrocarbons in marine environments similar to this research study area (Bieger, 1994). To understand the relevance of the following data, a typical $\delta^{13}C$ value of terrestrial plant material is -27‰, and of marine plant material is -21‰ (Pulchan *et al*, 1997). Sediments from Conception Bay, Newfoundland revealed pristane, phytadiene, squalene, and HEH with $\delta^{13}C$ values ranging from -25 to -28‰, n-alkanes ranging from -28.4 to -30.5‰, and a suite of C_{25} HBI considerably isotopically depleted, with $\delta^{13}C$ values ranging from -28.5 to -34.8‰. In addition, the smaller n-alkanes ($<C_{21}$) showed the even-chain species more depleted in ^{13}C relative to the odd-chain homologues, and the reverse trend for the larger n-alkanes ($>C_{27}$). Sedimentary n-alkanes which are predominantly odd, short-chain length, and isotopically heavy (-24 to -27‰) are most likely a result of algal marine production; predominantly odd, long-chain n-alkanes which are isotopically light (-30 to -33‰) are expected to result from terrestrial plant debris (Bieger, 1994). In some other sediments, a systematic depletion of ^{13}C was found in longer fatty acids with similar degrees of unsaturation (Abrajano *et al*, 1994). It is believed that this pattern may also be

observed in the *n*-alkane species as inherited from their precursor fatty acids. However, it is also possible that this decreasing trend is a result of increased terrestrial input.

Stable carbon isotopic compositions have also been characterized for many PAH, with unique signatures for different sources (O'Malley, 1994; O'Malley *et al.* 1994). Figure 4 is taken from O'Malley *et al.* 1994 and outlines isotopic compositions from car soot, crankcase oil, St. John's Harbour sediment, and fireplace soot. Figure 4 shows the PAH isolated from combustion sources are obviously more enriched in ^{13}C than corresponding PAH from petroleum. Isotopic compositions from soot samples (car and fireplace) displayed isotopically heavy 4- and 5-ring PAH with $\delta^{13}C$ values ranging from -24.6 to -26.9‰. Crankcase oil displayed much more depleted $\delta^{13}C$ values for PAH than the corresponding compounds from combustion sources; typical $\delta^{13}C$ values ranged from -26.6 to -28.9‰. In general, the combustion sources showed MPa to be more depleted than Pa, and Fl more depleted than Py. In contrast, petroleum sources showed Pa more depleted than MPa, and Py more depleted than Fl. Sediments taken from St. John's Harbour illustrate the major contribution of PAH is from combustion sources.

Stable carbon isotopic compositions of hydrocarbons provide a method of source identification which is independent of molecular distribution patterns. In order to obtain a clear understanding of hydrocarbon cycling in the marine environment, both methods will be used to identify major source inputs of aliphatic and polycyclic aromatic

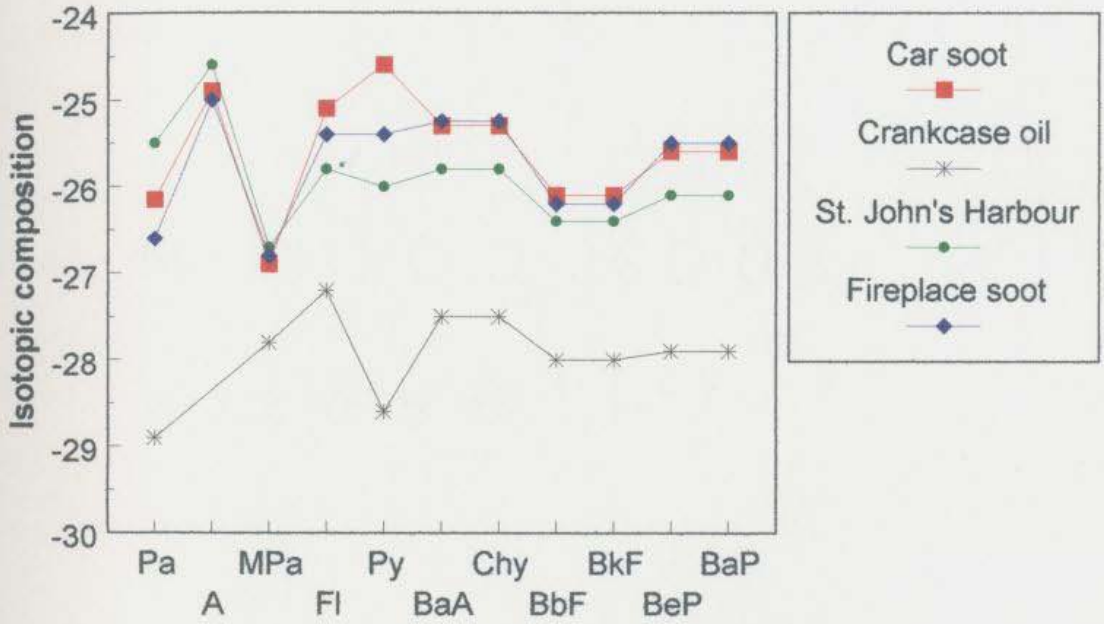


Figure 4: PAH Isotopic Compositions

hydrocarbons.

1.3 Objective of Research:

The purpose of this research was to characterize aliphatic and polycyclic aromatic hydrocarbons in Trinity Bay sediments by their molecular distribution patterns and stable carbon isotopic compositions. These two signature characteristics were used to identify natural and anthropogenic sources of hydrocarbons and allowed distinction between biogenic, petrogenic, and pyrolytic inputs. It was expected that this study would lead to an improved understanding of hydrocarbon cycling, that in turn would aid in assessing past and present health of the marine environment and lead to a better understanding of regional sustainability.

2.0 Experimental

2.1 Sampling:

The study area included Trinity Bay, the Northwest Arm, and the Southwest Arm on the eastern coast of Newfoundland (Figure 5). The environment is characterized by marked seasonal changes in terms of the physical conditions, such as temperature and light, and biological dynamics, such as migration and spawning of marine organisms. The dominant fauna are cod, capelin, seabirds, marine mammals, and salmon. The ecosystem also contains a terrestrial hinterland including boreal forests and coastal barrens with trees, insects, birds, lichen, berries, plants, and game. The human population is spread along the coast, with the central community of this area being Clarenville, a town of 3,000 people, as shown in Figure 1.

Sampling sites were chosen based on their general location, near shore to monitor possible terrestrial inputs and off shore for potential marine influences. Sample sites are numbered as shown in Figure 5. Sediment samples were collected during the spring and summer of 1994 using a 30 cm box corer; in the few locations where coring was impossible, bottom surface sediment grab samples were taken. Sample workup and analyses are outlined in Figure 6.

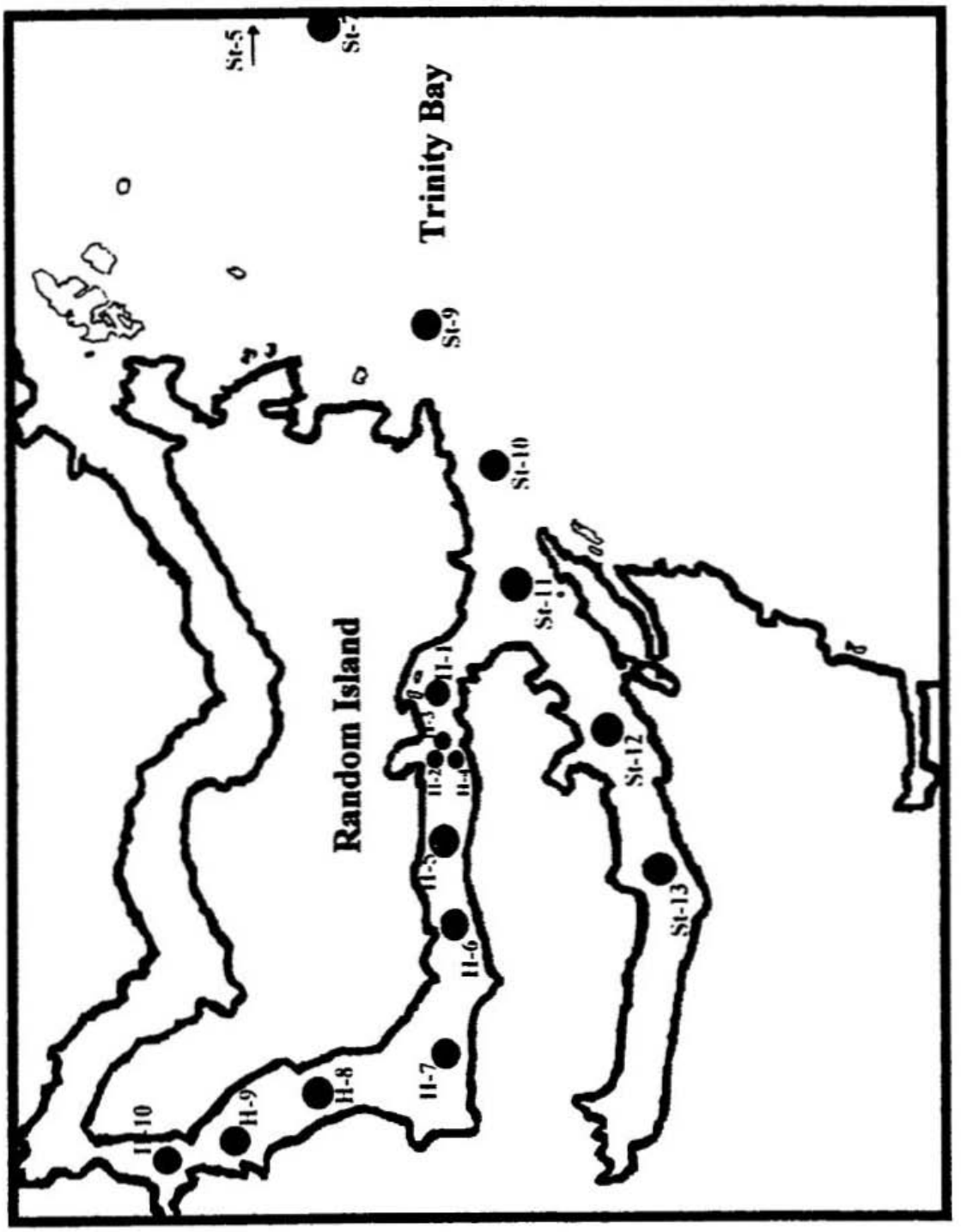


Figure 5: Trinity Bay Study Area

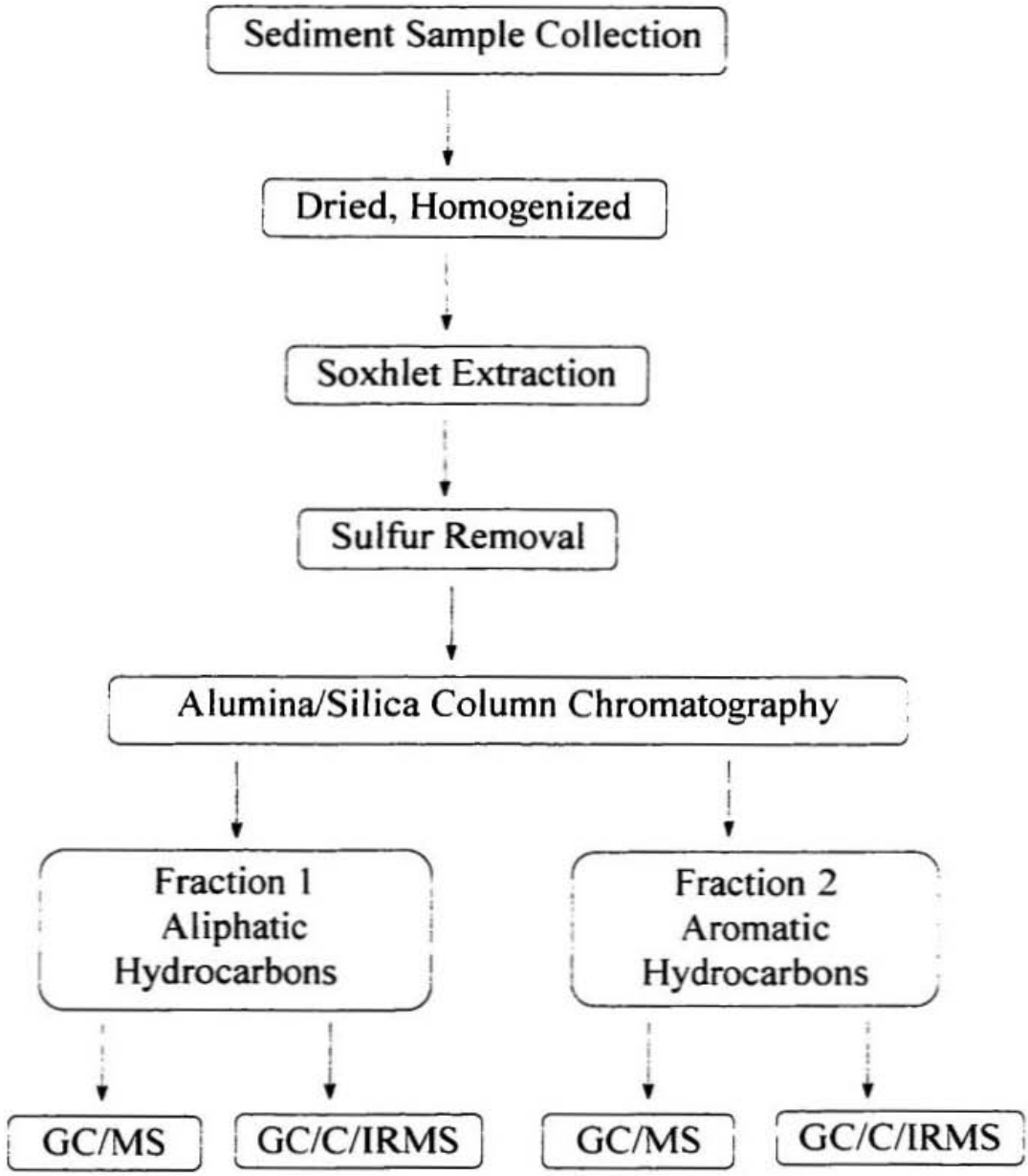


Figure 6: Experimental Procedures

2.2 Sample Preparation:

All collected samples were stored in a freezer at -14 °C until further processing. The outer 1 cm of each core was carefully removed and discarded to lessen the possibility of contamination from the plastic core tubing. Cores were then divided every 2 cm in depth, producing approximately fifteen sections for each core. All sediment cores were separated into these sections so that variations between different depths could be studied and a time-line for the deposition for hydrocarbons be proposed, as certain cores were targeted for ^{210}Pb-dating.

To prepare the sediments for analysis, each sample was placed on a large sheet of cleaned aluminum foil in a dark, 30 °C oven for 24 hours to thaw and dry thoroughly. Any visible pieces of debris (insects, shells, sticks) were removed from the dried sediment just prior to grinding with a mortar and pestle.

2.3 Sediment Extraction:

Soxhlet extraction was employed to remove the hydrocarbons of interest from the sediment matrix. Cellulose thimbles alone were first extracted (in 200 mL 10% methanol in dichloromethane, Optima purity, Fisher Scientific) for 8 hours to remove any possible contaminants which could interfere with the analysis of hydrocarbons. Methanol was added to dichloromethane to produce an azeotropic solvent. Approximately 30 g of sediment from each grab, or 10 g of sediment from each core

section, were weighed out into a clean beaker. To this sub-sample, 10% by mass sodium sulfate was added and mixed thoroughly with the sediment to remove any residual water. Each sediment was then placed in the pre-cleaned cellulose thimble and extracted (in 250 mL 10% methanol in dichloromethane, Optima purity, Fisher Scientific) for 24 hours. Once this procedure was completed, the extract volume was reduced to 50 mL using a rotary-evaporator at room temperature.

2.4 Sulfur Removal:

The sediment extracts appeared to have a relatively high sulfur content, as was evident when the usual method of using 1g copper powder placed on top of an alumina chromatography column (Blumer, 1957) were unsuccessful in removing elemental sulfur from the samples. This abundant level of sulfur was most likely due to the highly anoxic and productive water column and sediment locations. As a result, a more exhaustive method for the removal of elemental sulfur was required, involving activated copper turnings rather than the usual copper powder. Activation was carried out by setting copper turnings (99+% metals basis, Alfa Aesar, Johnson Matthey) in concentrated hydrochloric acid for 10 min, followed by three rinsings with deionized water, two rinsings in methanol, three rinsings in dichloromethane, and final storage under dichloromethane (Optima purity, Fisher Scientific), minimizing contact between the copper turnings and air at all times. Activated copper turnings (1 g) were added to each sediment extract, which was dissolved in 50 mL after volume reduction. The solution

was kept under nitrogen (ultra high purity) and set stirring for 48 hours. After this period, the copper turnings were removed from the flask and thoroughly rinsed with 10% methanol in dichloromethane (Optima purity, Fisher Scientific); these washings were returned to the flask to ensure no loss of hydrocarbons from the solution. The total extract volume was further reduced by rotary-evaporation, transferred to a small sample vial, completely dried under nitrogen (ultra high purity), and weighed. The extract was then redissolved in exactly 4 mL cold hexane (Optima purity, Fisher Scientific) held in an ice bath with the help of ultrasonication, quantitatively divided into four equal parts, and stored at -14 °C. This separation of the extract was performed so that other study groups would also have access to the samples.

2.5 Fractionation of Hydrocarbons:

Column chromatography with alumina overlying silica gel was employed to separate each sediment extract into aliphatic and aromatic hydrocarbon fractions (Gearing *et al*, 1978; Bieger, 1994). Silica and neutral alumina were originally stored in a 100 °C oven. To begin preparation of the columns, 8 g silica and 6 g alumina were placed into separate beakers and each deactivated with 7.5% by mass water. In order to make the silica and alumina easier to load onto the column, dichloromethane (Optima purity, Fisher Scientific) was added to each, creating a slurry. The silica slurry was loaded onto the column first, with the alumina added afterwards, creating a two-layer column. The column was then cleaned with 30 mL dichloromethane followed by 50 mL hexane (each

of Optima purity, Fisher Scientific). A stored subdivided extract, dissolved in 3 mL of hexane, was slowly loaded onto the column. The first fraction, containing the saturated, mono-, di-, and tri-unsaturated hydrocarbons, was collected from the column with 30 mL hexane (Optima purity, Fisher Scientific). The second fraction, containing the more highly unsaturated and polycyclic aromatic hydrocarbons, eluted with 30 mL of a solution of 9:1 hexane:dichloromethane (Optima purity, Fisher Scientific). Using a rotary-evaporator at room temperature, the collected fractions were reduced in volume to a few millilitres. Each fraction was then quantitatively transferred to a small sample vial, dried under nitrogen (ultra high purity), weighed, and stored at -14 °C until further analysis.

Normal phase high performance liquid chromatography (HPLC) was also attempted as an alternative method of separating the extracts into fractions containing saturated and unsaturated hydrocarbons (Marcomini *et al*, 1986). Hexane (Optima purity, Fisher Scientific) was employed as the pumping solvent at a flow rate of 1.0 mL min using the Varian Aerograph HPLC and a 400 µL injection loop. A Prop-Nova-Pak HR Silica Column (6 µm, 3.9 mm by 300 mm), supplied by Waters HPLC Columns, was used for separation. A Perkin Elmer LC-95 UV/Visible Spectrophotometer Detector was used to detect PAH, measuring at 254 nm. A Hewlett Packard HP3395 Integrator was used to produce a hard copy of the chromatogram and perform analysis on chromatographic peaks. The fraction containing the saturated hydrocarbons was expected to elute from

approximately 2 min to 7.5 min, immediately followed by the unsaturated hydrocarbon fraction up to 15 min, as confirmed by aliphatic and PAH standards. Preliminary results showed that this approach to hydrocarbon class fractionation is more rapid and uses less solvent than silica/alumina column chromatography. Unfortunately, pump malfunctioning did not allow for the HPLC method to be used in this study.

2.6 GC/MS Analysis:

Qualitative and quantitative analyses of hydrocarbons were performed through gas chromatography/mass spectrometry (GC/MS). The instrument employed was a Hewlett Packard 5890GC/5971 MS equipped with a CP-Sil 5CB WCOT fused silica column (with dimensions 25 m x 0.25 mm id, 0.12 μm film thickness) and helium (ultra high purity) as the carrier gas. The GC parameters were set as follows: 6.00 min solvent delay, inlet temperature of 280 °C, initial pressure of 14.9 psi, constant flow of 2.0 mL/min, split flow of 50 mL/min with a split ratio of 25:1, and splitless injection for 3.00 min. The oven temperature was initially held at 60 °C for 1.5 min, ramped at a rate of 5.00 °C/min to a final temperature of 280 °C, and held there for 10.00 min, producing a total run time of 55.50 min. The mass spectral data was obtained with the detector temperature at 190 °C, mass scan of 50-400 amu once every 2.0 sec, and in electron impact mode of 70 eV. Each hydrocarbon fraction was redissolved in 25 μL hexane (Optima purity, Fisher Scientific), with 1 μL injected for analysis into the GC/MS.

Aliphatic hydrocarbons were quantitatively characterized by using an extracted ion chromatogram of mass fragment m/z = 57. The *n*-alkanes fragment to a high degree and are often characterized by the fragment $CH_3CH_2CH_2CH_2$ (mass 57); parent ions of *n*-alkanes are rarely observed in the mass spectrum. Analysis of the polycyclic aromatic hydrocarbon fraction was accomplished by performing an additional GC/MS run in SIM (selected ion monitoring) mode; the mass spectrometer was set to scan only parental PAH ions (m/z 128, 154, 166, 178, 192, 202, 219, 223, 228, 231, 252, 276, 278) with all other GC and MS parameters kept the same as above.

2.7 Quality Control / Quality Assurance:

Standard *n*-alkanes, purchased from Aldrich, were dissolved in hexane (Optima purity, Fisher Scientific) to make solutions of known concentrations and used as external standards. Calibration curves were then constructed for quantitative measurement of alkanes using the GC/MS conditions described previously and the extracted ion chromatogram of m/z = 57; the data used to create these curves is shown in Appendix 16. A mixture of ten standard PAH compounds (purchased from Supelco) was used as an external standard for quantifying PAH in all samples. Calibration curves were also obtained by monitoring the standard mixture at various PAH concentrations in the GC/MS SIM mode mentioned previously; actual data for calibration curves is displayed in Appendix 17.

Deuterated standards (phenanthrene-d_{10}, pyrene-d_{10}, and *n*-tetracosane-d_{50}), purchased from Cambridge Isotope Laboratories, were added to selected sediments prior to Soxhlet extraction to calculate recoveries of alkanes and PAH. Calibration curves were initially obtained for each of these three standards by analyzing in SIM mode, monitoring m/z = 188, 202, 50, and 66, the main fragments of the three deuterated standards. Data used for the calibration curves is found in Appendix 18.

2.8 GC/C/IRMS Analysis:

Compound specific isotopic analysis was performed using the Hewlett Packard 5890 GC coupled via a combustion interface to a VG Optima isotope ratio mass spectrometer present in the Department of Earth Sciences, Memorial University of Newfoundland (Bieger, 1994; O'Malley, 1994). A schematic for this instrument is shown in Figure 7, where VSOS represents the capillary outlet splitter, RG is the reference gas valve, and C.O is the change-over valve.

The GC program was similar to that reported for the molecular characterization work (ie GC/MS), with the conditions as follows: using a DB-5 column (60 m), initial temperature of 35 °C held for 1.5 min, ramped at 20 °C/min to 150 °C and held for 1 min, then ramped at 6 °C/min to 280 °C and held for 30 min, producing a total run time of 59.91 min. Hydrocarbons were dissolved in various amounts of hexane to produce sufficient concentrations for isotopic analysis.

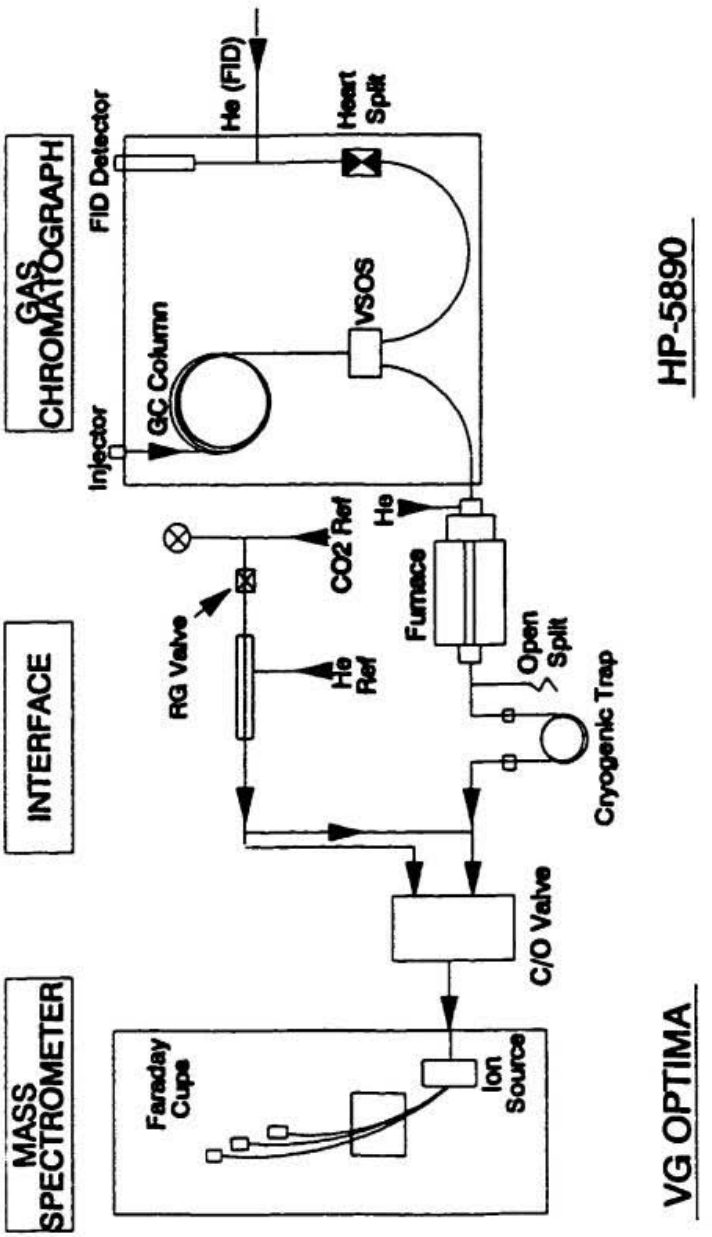


Figure 7: Schematic of the GC/C/IRMS Instrument

3.0 Results

The aliphatic hydrocarbons targeted for detailed analysis included the straight-chain *n*-alkanes, branched alkanes (pristane and phytane), branched alkenes (*br*-$C_{20:1}$ and *br*-$C_{20:1'}$), the suite of C_{25} highly branched isoprenoids, HEH, and diploptene. The parental and alkylated PAH have also been characterized for sediment samples.

The molecular distribution patterns and stable carbon isotopic signatures are reported below for aliphatic hydrocarbons and PAH in marine sediments at the various sampling sites. Results are described for the grab samples (moving from near-shore to off-shore), followed by the top core sections (near-shore through off-shore), and finally the down core sections from sites H9, H1, and St7. Data obtained from the sediment core sections and grab samples have been reported separately because the two forms of samples convey such different information about the sediments. The core sections provide a detailed historical record of the deposition of hydrocarbons in the bottom surface sediments; the grab samples offer a more general description of the organic material present in the sediments, since the various depths have been mixed together during collection of the grab.

3.1 Bottom Surface Sediment Grab Samples:

Sediment grab samples were collected from sites H10, H6, H5, H3, H2, St11, and St5 since it was not possible to recover intact cores from these areas. The concentrations of aliphatic hydrocarbons and PAH in these grab samples are tabulated in Appendices 1 and 2 respectively; in each case the concentrations are reported as nanograms of compound per gram of dry sediment extracted. Stable carbon isotopic analyses of these grab samples are included in Appendix 11 for aliphatic hydrocarbons and Appendix 13 for PAH.

Molecular distribution patterns: Figure 8 illustrates the total ion chromatogram of the aliphatic hydrocarbon fraction found in a sediment sample from site H5. Essential elements of the molecular distributions of aliphatic hydrocarbons are summarized in Table 3. All other grab samples showed similar molecular distributions of aliphatic hydrocarbons. Present in substantial concentrations in all sites were the suite of C_{25} highly branched isoprenoids. These compounds have been reported previously in similar sediment samples from Conception Bay, Newfoundland (Bieger, 1994) and exist as a series of isomers with similar structures differing only by the number and position of the double bonds. In most sediment grab samples, the dominant hydrocarbon was the highly branched isoprenoid *br*-$C_{25:3}$, shown in Figure 8 eluting as the major peak at a time of 25.2 minutes. The one exception was site H10 which was dominated by an unidentified alkene, quite possibly *c*-$C_{25:2}$. Present in much lower concentrations were the *n*-alkanes

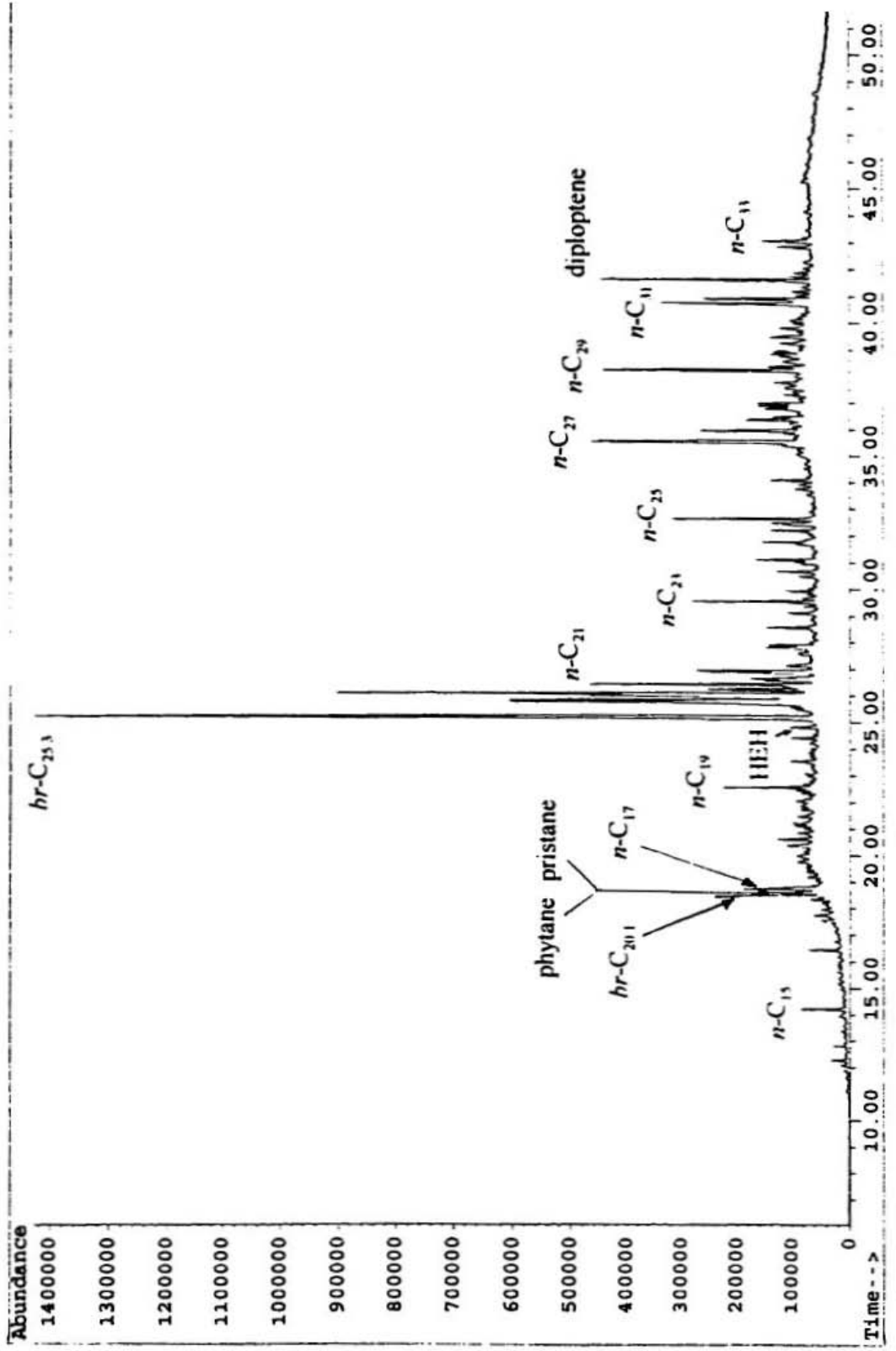


Figure 8: GC/MS Chromatogram of the Aliphatic Hydrocarbon Fraction

Compounds	Relative Abundances
C_{25}HBI	dominant aliphatic hydrocarbons
n-alkanes C_{15}-C_{34}	dominance of odd high molecular weight (maximum at C_{27} or C_{29})
pristane / phytane	low concentrations
diploptene	low concentrations to undetectable
HEH	low concentrations to undetectable
UCM	low (not interfering with analysis)

Table 3: General Trends of Aliphatic Hydrocarbon Molecular Distributions

ranging from n-C_{15} to n-C_{34}. These straight-chain alkanes exhibited a slight predominance of odd high molecular weight species (CPI ranging from 1.3 to 2.9) with a maximum concentration occurring at either n-C_{27} (as in sites H10, H6, H5, H3 and H2) or n-C_{29} (as in sites St11 and St5). This predominance of odd n-alkanes is particularly noticeable in Figure 8 after an elution time of 29.0 minutes. The dominant peaks in this range are C_{23} (29.5 min), C_{25} (32.6 min), C_{27} (35.5 min), C_{29} (38.2 min), and C_{31} (40.7 min). Present in rather high concentrations in sites H10, H6, H5, and St5 was the mono-unsaturated branched alkene br-$C_{20:1}$, shown at an elution time of 18.5 minutes in Figure 8. Pristane and phytane were found in most sediment samples, although present in relatively low concentrations. Diploptene was present in all samples while HEH could be detected in only sites H10, H6, and H5; these two aliphatic hydrocarbons were identified but could not be quantitatively characterized. Figure 8 shows diploptene eluting at 41.5 min, and HEH eluting at 24.8 min as a very small peak immediately preceding br-$C_{25:3}$. A very low UCM was observed in most of the grab samples, but did not interfere with the identification or quantitation of aliphatic hydrocarbons. Total n-alkane and aliphatic hydrocarbon concentrations are much greater at site H6 compared to all other sediment grab samples.

To illustrate the problems associated with extremely high levels of sulfur, Figure 9 shows an early total ion chromatogram of the aliphatic hydrocarbon fraction from sediments of site H10. This chromatogram was collected prior to the exhaustive sulfur removal

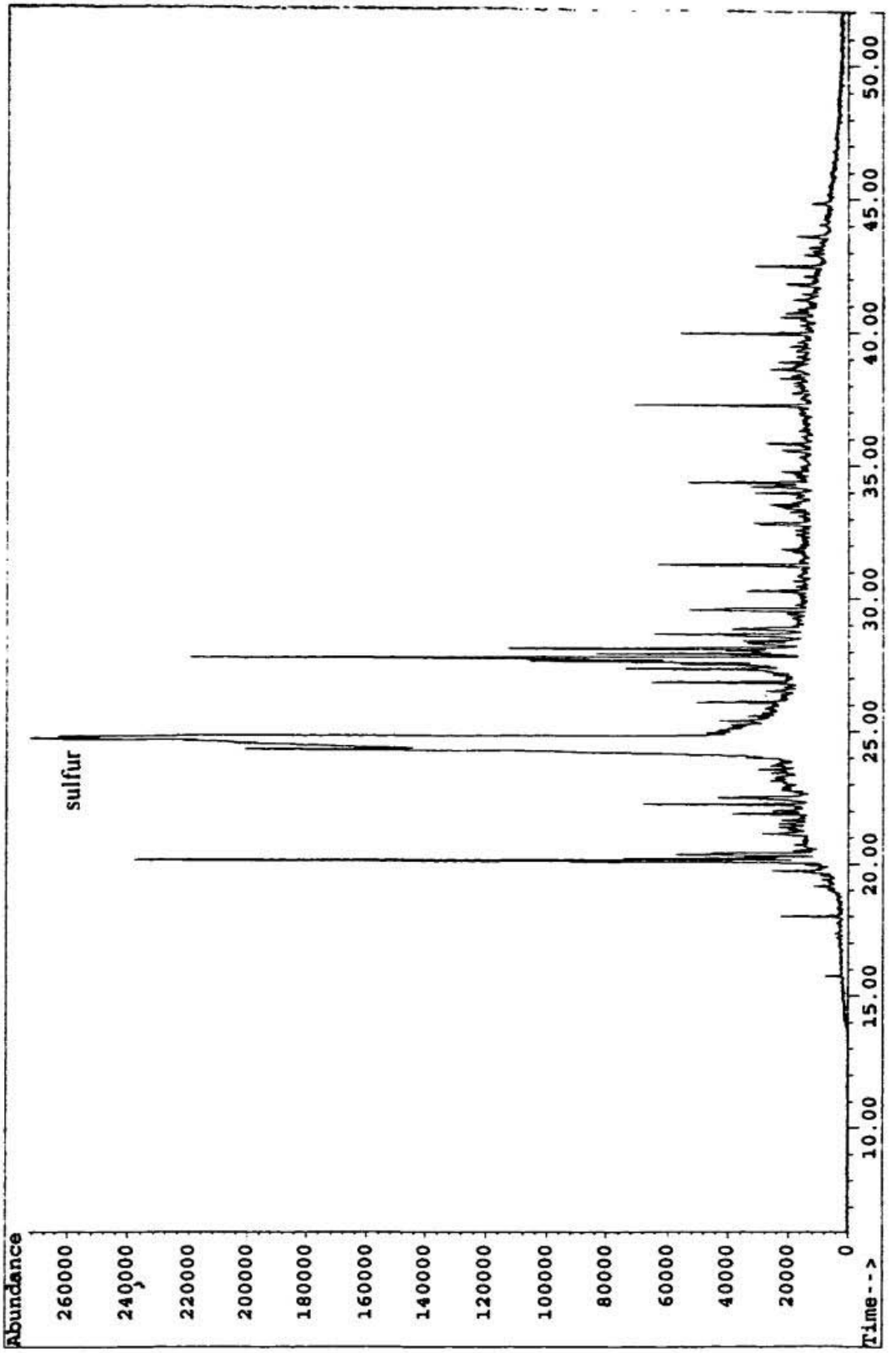


Figure 9: GC/MS Chromatogram of the Aliphatic Hydrocarbon Fraction Prior to Sulfur Removal

procedure later used for all sediment samples analyzed. Sulfur is shown as a broad peak eluting at a time of 24.7 min. Comparing Figures 8 and 9, it is obvious that this sulfur peak is overlying many other aliphatic hydrocarbons, in particular the suite of C_{25} highly branched isoprenoid alkenes.

A typical molecular distribution of PAH is shown in Figure 10, a GC/MS total ion chromatogram from site H3. Essential elements are summarized in Table 4. All grab samples analyzed showed a dominance of the parental PAH species as opposed to the alkylated analogues. Retene was found in all sites (except H5 and St11) shown in Figure 10 as a small peak eluting at 26.6 min. Also clearly shown are the isomers Pa and A (18.5 and 18.7 min), Fl and Py (23.6 and 24.3 min), and BaA and Chy (29.8 and 29.9 min). Present in all grab samples were Pa, Fl, and Py. The higher molecular weight PAH BbF, BkF, BeP, BaP, and Per were found at sites H10, H3, and St5; these compounds appear in Figure 10 as four peaks eluting from 34.2 to 35.5 min. In addition, sediments from H3 were shown to contain the even higher molecular weight In and BPer, found at 39.2 and 39.8 min respectively. In terms of PAH stability, the less-stable kinetic isomers (Fl, BaA, BbF, BkF, BaP, In) appeared more enhanced than the more-stable thermodynamic isomers, with the exception of Pa more abundant than A. Total PAH concentrations in site H1 were substantially greater than those of the other sample locations. It should be noted that possible coelutions exist which have not been identified: other isomers of BF and triphenylene with benzofluoranthenes and chrysene.

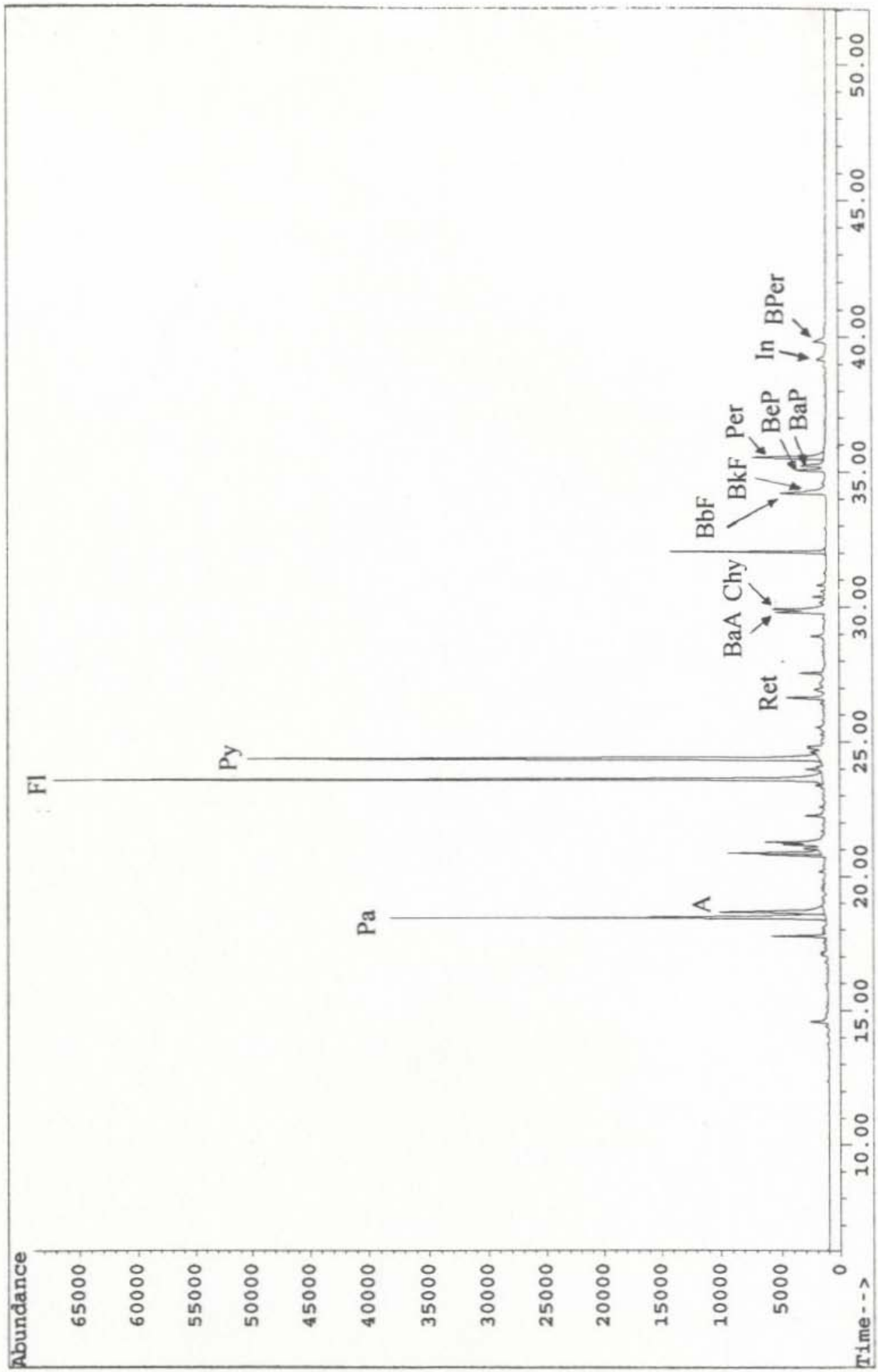


Figure 10: GC/MS Chromatogram of the PAH Fraction

Compounds	Relative Abundances
parental PAH	dominant over alkylated PAH
Pa and A	Pa more abundant
Fl and Py	Fl more abundant
BaA and Chy	BaA more abundant
BbF. BkF. BeP. BaP	low concentrations to undetectable (BbF. BkF. BaP more abundant)
In. BPer	low concentrations to undetectable (In more abundant)
Ret	low concentrations to undetectable
Per	low concentrations to undetectable

Table 4: General Trends of PAH Molecular Distributions

Stable carbon isotopic signatures: Although most hydrocarbons could be quantitatively characterized by GC/MS, obtaining stable carbon isotopic values for many compounds was impossible due to their extremely low concentrations, as shown in Appendices 11 and 13. Pristane showed $\delta^{13}C$ values ranging from -20.9 to -26.3‰. The C_{25} highly branched isoprenoids displayed depleted isotopic compositions (-31.2 to -36.4‰). The shorter *n*-alkanes (less than C_{21}) showed the even-chain species to be isotopically more depleted than the odd-chain species. With the longer *n*-alkanes (greater than C_{27}), such a trend was difficult to establish; the even *n*-alkanes could not be isotopically characterized. The longer odd-chain homologues did show more depleted isotopic compositions (-30.2 to -33.7‰). In general, the straight-chain alkanes showed a depletion in isotopic compositions with increasing molecular weight.

Most sediment grab samples displayed isotopically heavy 4- and 5-ring PAH (-23.3 to -26.6‰). The one exception was site H5 where the $\delta^{13}C$ value of A was -29.9‰. In all grab samples, Fl was isotopically more depleted than Py.

3.2 Sediment Core Samples:

Sediment cores were obtained from sites H9, H8, H7, H4, H1, St12, St10, St9, and St7. The top sections (0-2cm depth) of each core have been analyzed with the concentrations of aliphatic hydrocarbons and PAH tabulated in Appendices 3 and 4 respectively. Several sediment cores were more closely examined with sections of increasing depth

along the core analyzed. Concentrations of aliphatic hydrocarbons and PAH are reported in Appendices 5 and 6 for down core H9. Appendices 7 and 8 for down core H1. Appendices 9 and 10 for down core St7. In each case the concentrations are reported as nanograms of compound per gram of dry sediment extracted. Stable carbon isotopic analyses of various core sections are included in Appendix 12 for aliphatic hydrocarbons and Appendix 14 for PAH.

3.2.1 Top Core Sections:

Molecular distribution patterns: The results of molecular characterization for the top core sections are very similar to the previous grab samples, with general trends described in Table 3. The top core sections were dominated by the suite of C_{25} highly branched isoprenoids. The isoprenoid *hr*-$C_{25:3}$ was most abundant in all sediments with the exception of H1, which was dominated by the isomer *hr*-$C_{25:4b}$. The *n*-alkanes in the range of *n*-C_{15} to *n*-C_{34} demonstrated a slight odd predominance (CPI ranging from 1.3 to 4.1) with a maximum *n*-alkane concentration occurring at *n*-C_{27} in all samples. The odd high molecular weight *n*-alkanes were found to have elevated concentrations at site H1. Pristane was present in all samples except St10, with notably high concentrations at site H1. Phytane was found in sites H4, H1, St12, and St10, although its concentrations were relatively low. Diploptene was found in all samples; HEH could not be detected. A low UCM was observed in chromatograms of the top core sections, but did not interfere with analysis of the aliphatic hydrocarbons.

The top core sediments displayed a dominance of parental PAH compared to alkylated PAH. Retene was found at all sites. The higher molecular weight PAH were not abundant in the top core sediment sections, with only BkF and Per at site H9, Per at site St9, and BeP, BaP, and Per at site St7. Substantially higher concentrations of PAH were recorded in the top core sediment from site H1. Of the lower molecular weight PAH, some of the less-stable/kinetic isomers were more enhanced (Fl, BaA, BaP) as were some of the more-stable/thermodynamic isomers (Pa, Chy). Table 4 includes a summary of the general trends found in PAH molecular distributions.

Stable carbon isotopic signatures: Analysis of the aliphatic hydrocarbons in the top core sediment sections showed $\delta^{13}C$ values for pristane in the range of -23.2 to -27.9‰. The HBI *hr*-$C_{25:3}$ displayed isotopic values of -27.7 and -35.8‰; this isoprenoid alkene could only be analyzed at sites St12 and St9. For the straight-chain alkanes, the shorter even homologues ($<C_{21}$) as well as the longer even species ($>C_{27}$) could not be isotopically characterized. As a result, a comparison of odd and even *n*-alkane isotopic compositions could not be made. There was, however, a general decrease in isotopic values with increasing molecular weight.

Top core sections showed that the PAH were more isotopically heavy with $\delta^{13}C$ values ranging from -21.3 to -26.9‰. The one exception was site H4 where Fl was isotopically light (-30.0‰). Sediments from H4 and H1 showed Fl more depleted than Py, whereas

H9 and St12 showed Py more depleted than Fl.

3.2.2 Down Core Sections:

Molecular distribution patterns: Analysis of the deeper sediments from sites H9, H1, and St7 revealed similar distribution patterns to the top core sections. The highly branched isoprenoid alkenes were the most abundant in all sediments; the dominant aliphatic hydrocarbons were *hr*-$C_{20:1}$ or *hr*-$C_{25:3}$ in core sections of site H9, *hr*-$C_{20:1}$, *hr*-$C_{25:4}$, or *n*-C_{27} (20-22 cm depth) in sections from site H1, and *hr*-$C_{25:3}$ in sections from site St7. The *n*-alkanes showed a dominance of the odd high molecular weight species with maximum occurring at *n*-C_{27} or *n*-C_{29}. CPI values ranged from 1.3 to 2.8 and remained quite consistent down each core. Pristane and phytane were present at low concentrations, although slightly greater abundances were observed in the upper sections (0-14 cm depth) of site H1 and middle sections (8-22 cm depth) of site St7. Although a slight UCM was observed, it did not interfere with the characterization of aliphatic hydrocarbons. All core sections displayed a general decrease in total *n*-alkane concentrations downward with a slight increase at the deepest portion of the core. Sediments from sites H9 and H1 showed a similar trend for total aliphatic concentrations.

All down core sediment sections showed the parental PAH more enhanced than the alkylated analogues. Retene was found in all down core sections. Some of the less-stable/kinetic isomers occurred in greater concentrations (Fl, BaA, BbF, BaP) as did

some of the more-stable/thermodynamic isomers (Pa, Chy). Of the higher molecular weight PAH, only BkF and Per were present in H9, and even then only in the top core section (0-2 cm depth). The PAH BbF, BkF, BeP, BaP, and Per were present in H1 only at depths of 4-10 cm. The higher molecular weight BeP, BaP, and Per were present in St7 only in the top core section (0-2 cm depth). Slightly elevated PAH levels occurred from 8-18 cm depth at site H9, from 0-6 cm depth at H1, and from 0-2 cm depth at site St7.

Stable carbon isotopic signatures: Of the down core sediments quantitatively characterized for molecular distribution, only four sections were analyzed isotopically: H9 0-2 cm, H9 24-26 cm, H1 0-2 cm, and H1 28-30 cm. Sediments from H9 showed isotopic compositions slightly enriched for *n*-alkanes and depleted for PAH with increasing depth along the core. Sediments from H1 showed consistent isotopic values regardless of sediment depth.

Sediment sections from site H9 showed a slight change in isotopic values with Fl and Py more depleted at 20-22 cm depth compared to 0-2 cm depth. Sediments from St7 showed Py less depleted at 16-18 cm depth compared to 0-2 cm depth.

^{210}Pb dating of down core sediments: Sediment sections from sites H9, H1, and St7 were analyzed using ^{210}Pb dating techniques (Mycore Laboratories) to determine approximate

ages of the sediment depths and establish a timeline of deposition. Results of the analyses are summarized in Appendix 15. Results from site H9 showed rather high sedimentation rates, with the lower portion of the core (24-26 cm depth) dating back to 1922. The implied sedimentation rate for site H1 was much slower than that of site H9. The sediments from site St7 were extremely disturbed and problematic; tests for ^{210}Pb dating could not be performed on sediment sections from this site.

3.3 Quality of the Analytical Data:

During the course of analysis, recovery experiments were periodically checked with deuterated standards mentioned in Section 2.7. All aliphatic hydrocarbon concentrations reported were corrected using the percent recovery of *n*-tetracosane-d_{50}. All PAH concentrations were corrected with the percent recovery of the deuterated aromatic hydrocarbon standard with the nearest elution time: phenanthrene-d_{10} or pyrene-d_{10}.

A large number of samples were analyzed separately for aliphatic hydrocarbons and PAH; it was felt unreasonable to perform replicate analysis on all sediments from initial Soxhlet extraction to GC analysis. It was decided that only every fourth sediment sample would be analyzed in duplicate. Concentrations of aliphatic hydrocarbons in marine sediments were found to be much higher relative to PAH values, and reproducibility in duplicate analysis was found to be much improved. Individual aliphatic concentrations varied in the range of 10 to 15%. Duplicate values of PAH concentrations ranged from

15 to 20%. Among individual compounds, reproducibility was poorer for lower concentration levels (25 to 40% for 1-10 ng/g range) than for higher concentration levels (10 to 20% for greater than 10 ng/g).

Previous studies using the GC/C/IRMS have shown stable carbon isotopic compositions with a general precision ranging between 0.25 and 0.39‰ and an accuracy ranging between 0.1 and 0.57‰ (O'Malley *et al.*, 1996).

4.0 Discussion

4.1 Source Identification Through Molecular Characterization:

The presence of specific hydrocarbons and characteristic molecular distributions have been employed to distinguish between marine, terrestrial, pyrolytic and petrogenic sources of hydrocarbons. Table 1 outlines the characteristic distributions of aliphatic hydrocarbons and their respective sources; characteristic fingerprints used for source identification of PAH are outlined in Table 2.

The highly unsaturated alkene, HEH, was detected only in sediment grab samples from sites H10, H6, and H5. This particular aliphatic hydrocarbon is produced by several species of marine phytoplankton and is commonly used as a biomarker for marine influences. The absence of HEH in Trinity Bay sediments likely reflects the instability of the compound itself, and not a lack of marine influences on the ecosystem. HEH is a labile compound, quite susceptible to microbial degradation, and is less abundant in surface sediments as compared to upper ocean plankton tows (Bieger, 1994).

Pristane and phytane are also common biomarkers of petroleum source inputs. There is also evidence that pristane may indicate natural marine influences (Blumer *et al*, 1971). Although present in relatively low concentrations, these branched aliphatic hydrocarbons will be used as evidence for petroleum and marine influences in this cold ocean

environment.

Extracted ion chromatograms of fragment ions m/z = 191 and 217amu in GC/MS analysis revealed the only hopane or steroid detected was diploptene. A potential marker of petroleum influences, diploptene was present in all grab samples and top core sediments. The compound could not be quantitatively characterized; the degree of petroleum contamination will be difficult to assess at this point without further supporting evidence from the aromatic hydrocarbons.

The highly branched isoprenoid alkenes, particularly the isomers of *hr*-C_{30} and *hr*-C_{25}, were the most dominant aliphatic hydrocarbons in most sediment samples. These compounds are thought to originate from marine algae or bacteria; similar compounds have been extracted from diatom species (Volkman *et al.*, 1994), however none were found in cultivated diatoms (Bieger, 1994). Although the specific sources of *hr*-C_{30} and *hr*-C_{25} have not yet been determined, the presence of these HBI alkenes will be used to indicate major marine contributions to the Trinity Bay sediments.

Molecular distributions of the *n*-alkanes in sediment samples show a slight predominance of the odd-chain high molecular weight analogues, with maximum concentrations occurring at *n*-C_{27} or *n*-C_{29}. A typical *n*-alkane distribution is shown in Figure 11, taken from site H3. This characteristic distribution in itself would seem to indicate significant

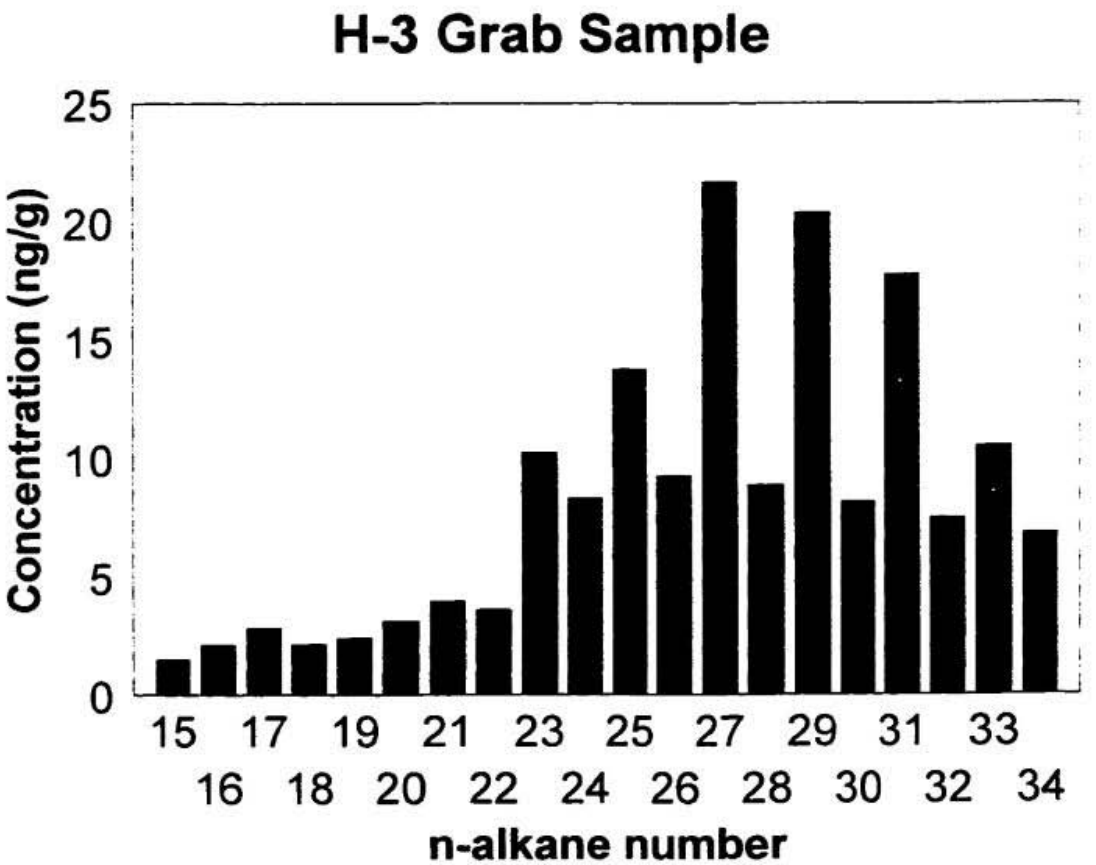


Figure 11: Molecular Distribution of *n*-alkanes from Site H3

terrestrial influences. With overall CPI values ranging from 1.3 to 4.1, terrestrial plants are not the sole source of *n*-alkanes, otherwise CPI values would be much higher. It is more likely that a mixing of aquatic and terrestrial *n*-alkanes has taken place, with possible contributions from petroleum sources as well.

A slight unresolved complex mixture was present in some sediment samples, indicating minor petroleum contributions. Sediments which are highly contaminated with petroleum typically produce a large UCM which covers other aliphatic hydrocarbons in the total ion chromatogram. In sediments samples of this study, the relative size of the UCM was extremely low to negligible, not interfering with any qualitative analysis of other aliphatic hydrocarbons. This suggests that the petroleum influences are slight in the Trinity Bay sediments.

Total aliphatic hydrocarbon concentrations were extremely elevated in sediments from sites H6 and H1. This observation is attributed to an increase in terrestrial contributions from watersheds deposited into the marine ecosystem; site H1 in particular is located near the mouth of Hickman's Harbour, where rivers and streams flow off Random Island and empty into the harbour. It would seem that high sedimentation rates should therefore accompany the elevated aliphatic hydrocarbon concentrations, however results of ^{210}Pb analysis show extremely slow sedimentation rates at site H1. For this reason, it is suspected that the implied sedimentation rate for site H1 is too slow.

The higher amounts of parental PAH relative to alkylated PAH in all sediment samples indicate major influences from pyrolytic sources as opposed to petrogenic sources. Many of the less-stable/kinetic isomers (Fl, BbF, BaP, In, DBA) were enhanced in sediments, further evidence for pyrolytic inputs into the marine environment. In addition, retene was found in almost all sediments, indicating PAH from natural terrestrial plant inputs and/or combustion of wood from coniferous vegetation.

In all sediment samples, the more-stable/thermodynamic phenanthrene appeared more dominant than its isomer anthracene, indicating some slight petroleum contamination in the Trinity Bay sediments. Chrysene was also more enhanced than its isomer benzo(a)anthracene at sites H9 (0-2 cm depth), H4, St12, and St10, indicating further petrogenic influences. Both the Northwest and Southwest Arms house small communities along their coastlines; the slight petroleum contamination observed is likely a result of seepage from outboard motors of the many boats used in the area.

Total PAH concentrations were substantially higher in sediments from site H1, particularly at depths of 0–4 cm. Characteristic molecular distributions of PAH at these sediment sections reveals Pa much more enhanced than A, indicative of stronger petroleum contamination. This is likely due to spillage from smaller boats in the Hickman's Harbour region.

While source identification of PAH points to major pyrolytic sources with some slight petrogenic contributions, it is important to realize that the total PAH concentrations are relatively low in the Trinity Bay sediments. The most elevated levels of PAH occurred at site H1, where total PAH concentrations were found to be 600 ng/g. This concentration is extremely low compared to the more contaminated site of St. John's Harbour, where total PAH concentrations averaged 17000 ng/g (O'Malley, 1994). This suggests that in spite of PAH present in Trinity Bay sediments, the values represent background values and the marine environment in this area is relatively pristine.

4.2 Source Identification Through Isotopic Analysis:

Isotopic analysis of the aliphatic hydrocarbons revealed isotopically enriched values for pristane in all sediment samples suggesting marine origins of these compounds. The suite of C_{25} highly branched isoprenoid alkenes were isotopically light, as was also the case in sediments from Conception Bay (Bieger, 1994). The significantly depleted $\delta^{13}C$ values of the HBI indicate that these compounds originate from a different source than the other aliphatic hydrocarbons analyzed. Varying isotopic compositions for *br*-$C_{25:3}$ were found, ranging from -27.7 to -36.4‰, suggesting more than one possible source for this highly branched isoprenoid alkene. It has been previously suggested that different species of marine diatoms produce these compounds (Bieger, 1994; Rowland *et al*, 1990).

Sediment grab samples and core sections showed the predominant *n*-alkanes as the odd, long-chain analogues displaying isotopically light $\delta^{13}C$ values. This type of distribution is indicative of terrestrial plant sources of the *n*-alkanes (Bieger, 1994). The general decrease in isotopic composition with increasing molecular weight may signify an increase in terrestrial input, or possibly marine influences with the decreasing trend inherited from precursor fatty acids.

Stable carbon isotopic compositions of the aromatic hydrocarbons were isotopically enriched in ^{13}C, suggesting combustion as the dominant source of PAH. Isotopic depletion of Fl relative to Py, which was observed in this case, is regarded as further evidence for a pyrolytic source of PAH. Although many PAH could not be isotopically characterized, stable carbon isotopic compositions of those compounds which could be analyzed does seem to suggest combustion as the dominant source of PAH. Figure 12 shows the isotopic compositions of PAH from site H1 relative to other primary sources (Bieger, 1994); those PAH which have been isotopically characterized overlap the combustion sources of car soot and fireplace soot: Pa (-26.5‰), A (-25.3‰), Fl (-25.0‰), and Py (-24.6‰). Sediments taken from sites H9 and St12 showed Py more isotopically depleted than Fl, suggesting slight contamination from petroleum in these areas.

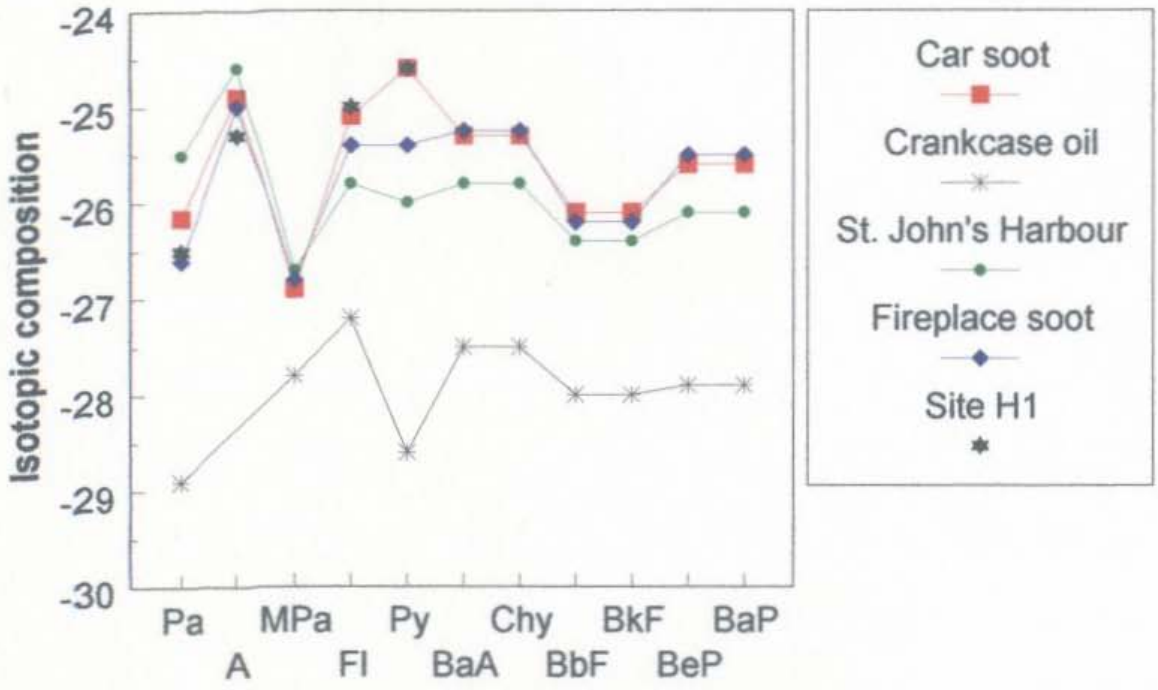


Figure 12: PAH Isotopic Compositions of H1 and Other Primary Sources

4.3 Spatial Variations in Sediments:

Levels of *n*-alkanes and total aliphatic hydrocarbons remain relatively constant throughout the study area with some notable exceptions. Slightly elevated levels of *n*-alkanes were observed at sites H9 (near Clarenville) and H1 (Hickman's Harbour). These increased concentrations are likely a result of terrestrial influences, flowing through water systems and ultimately deposited in these areas. However, if terrestrial input was the sole source of increased aliphatics, the CPI would be expected to be higher (greater than 4) in these areas. The lower CPI value at sites H9 and H1 (1.3) suggests that increased *n*-alkane concentrations may also be due to a higher level of marine productivity in these regions.

Figure 13 shows the spatial variation of total PAH concentrations in top core sediment sections. Levels of PAH in sediment grab samples and core sections are extremely low except at sites H1, St7, and St5, suggesting increased anthropogenic activity near these areas. Concentrations of both kinetic and thermodynamic isomers of PAH are elevated in these three sediments, indicating both pyrolytic and petrogenic sources of hydrocarbons. The slight dominance of Pa over A suggests minor petroleum contamination. The major source of PAH appears to be combustion with Fl more enhanced than Py, BaA more dominant than Chy (at site St7 and St5), and BaP greater than BeP (at site St5). With pyrolytic PAH transported through the atmosphere before being ultimately deposited in the marine sediments, the source of the increased concentrations seen at sites H1, St7,

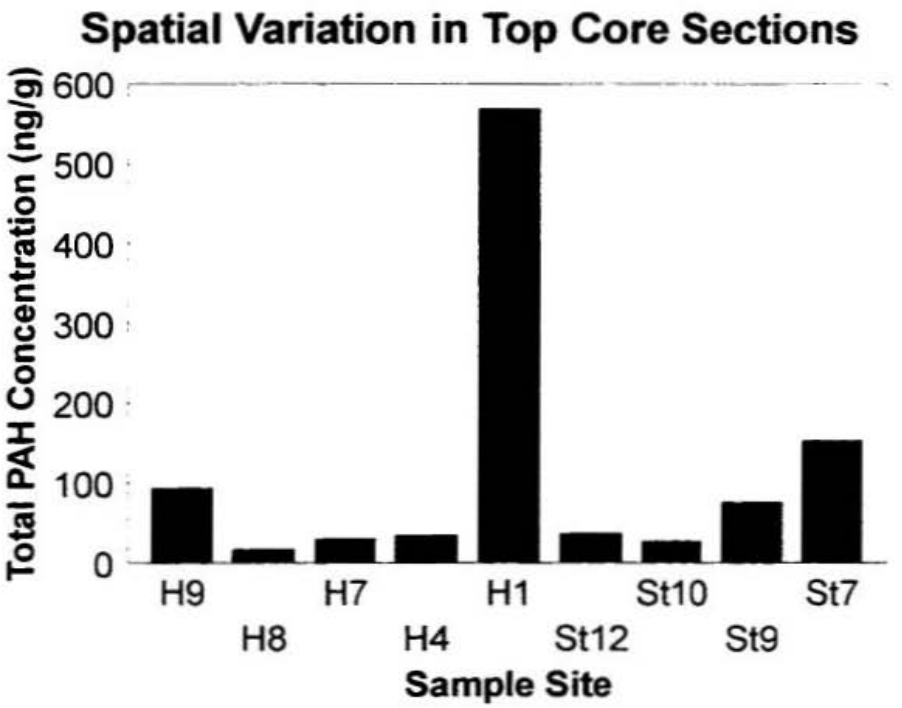


Figure 13: Spatial Variations of PAH in Top Core Sediment Section

and St5 may be located outside the study area. The high levels present at site H1 may also be a direct result of the slow deposition rate. Slightly elevated levels of PAH at site H9, particularly the higher concentration of Chy relative to BaA indicates petroleum contamination in this particular area as well.

Similar molecular distributions of all PAH and consistent isotopic signatures strongly suggest similar PAH sources for the entire study area. Combustion and subsequent atmospheric deposition is the most likely source of PAH in the sediments analyzed.

4.4 Temporal Variations in Sediments:

Sediment cores from sites H9 and H1 indicate that the degree and type of terrestrial influences have changed during the past century. Sediment sections from site H9 show a general decrease in *n*-alkanes with a slight increase at a depth of 24-26 cm, corresponding to the year 1922, as shown in Figure 14. It was expected that the total *n*-alkane concentration would gradually decline with increasing depth as a result of natural degradation in the sediments. The slight increase at a lower depth of the core suggests an additional input of hydrocarbons derived from terrestrial plant material, coinciding with an increase in sawmill activity in the area during the early 1920's. The general increase in deposition of aliphatic hydrocarbons in the upper sediments of site H9 suggests more extensive wood-cutting since the 1950's.

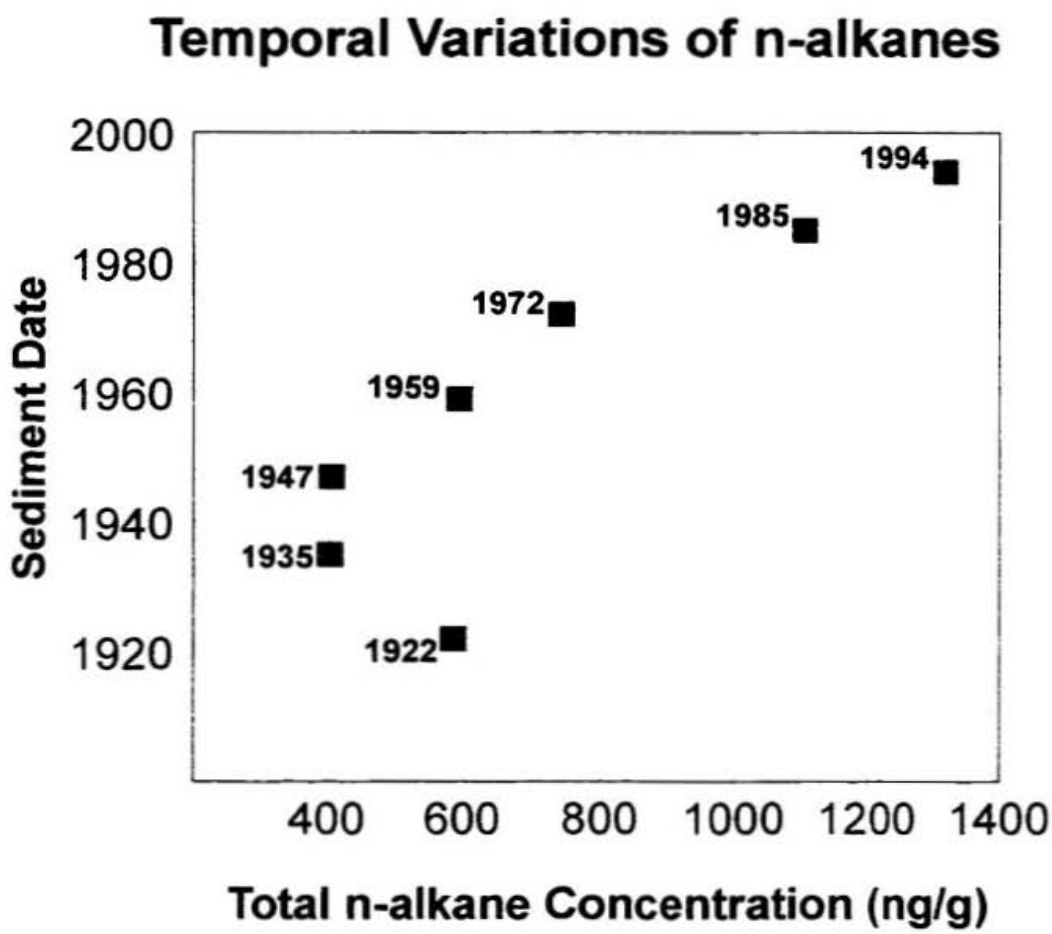


Figure 14: Temporal Variations of *n*-alkanes at Site H9

The temporal variations of PAH in sediments from site H9 are displayed in Figure 15. Maximum total PAH concentrations are observed at sediment depths of 8-10 cm, corresponding to the year 1972; this may be a direct result of increased woodburning with PAH transported through the atmosphere. Decreased concentrations of total PAH in the more recent sections of the core (1985 and 1994) may indicate the shift to alternate sources of heat, particularly electricity. Another slight increase in total PAH concentrations is found at a depth of 16-18 cm in sediments from site H9, corresponding to the year 1947.

4.5 Summary of Results for Related Marine Group Studies:

Analyses of material from net-tows and sediment traps (suspended at various depths) indicate much higher levels of organic material than what appears in the sediments. Fatty acid analyses of sediment trap material indicate terrestrial contributions in the form of pollen. Diatom markers dominate the spring and early summer samples, with terrestrial and zooplankton markers more abundant in late summer and fall.

Additional terrestrial influences on the marine ecosystem have been detected by the presence of phenolic compounds. These play an important role in the production of essential nutrients as they add to the total existing carbon compounds.

Coprostanol, a sterol often used as a marker for sewage input, was targeted for analysis.

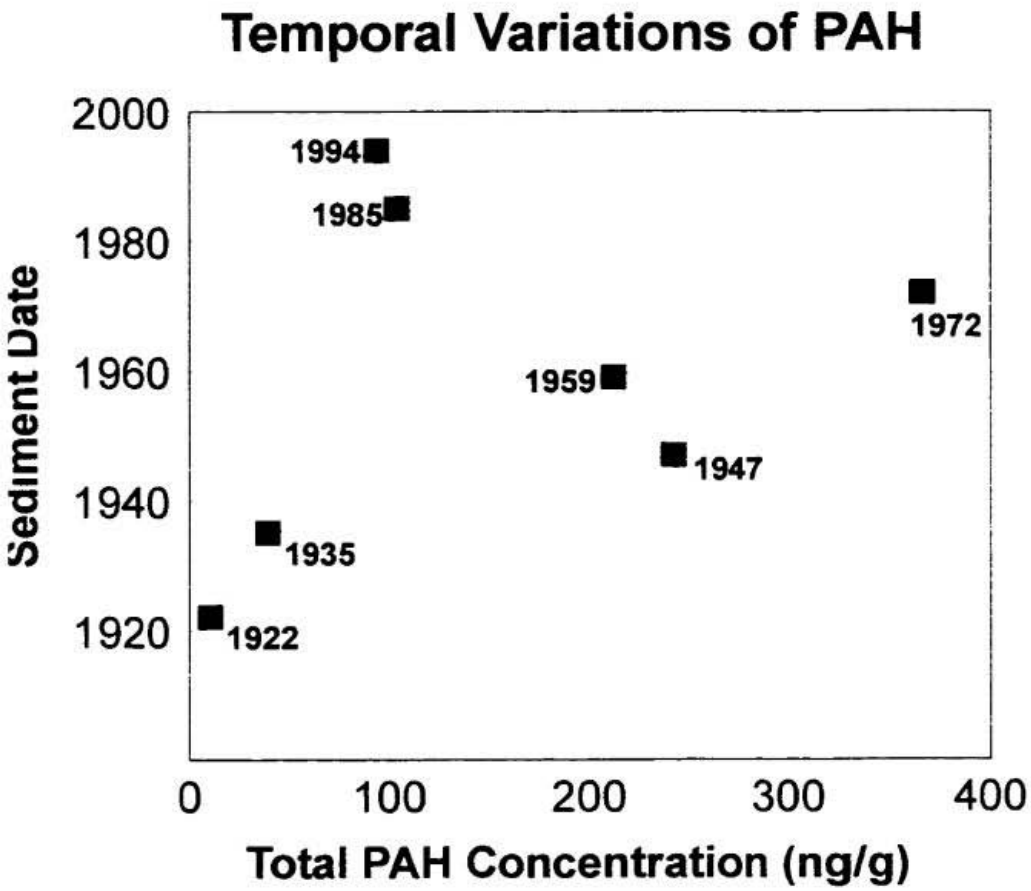


Figure 15: Temporal Variations of PAH at Site H9

Levels of coprostanol ranged from very low to undetectable, suggesting that sewage input is negligible.

According to the results of the Marine Project, the Trinity Bay ecosystem appears to be relatively pristine and healthy. The production of marine biogenic material peaks during the spring bloom, but utilization must be extremely efficient as concentrations in the sediments are low. Anthropogenic influences are also low, which may be a result of low input or rapid decomposition. Results suggest that the decline in the groundfish stocks is not related to supply and cycling of organic material in the ecosystem.

5.0 Conclusions

The sediments of Trinity Bay, Newfoundland reveal large biogenic influences from marine sources on the ecosystem, as indicated by the dominance of C_{25} highly branched isoprenoid alkenes. It is believed that these compounds are produced by a certain species of diatom, present in the cold ocean ecosystem. Further supporting evidence of marine influences is the presence of HEH and pristane. In addition, low CPI values for the straight-chain alkanes and more enriched isotopic values for the smaller *n*-alkanes are attributed to marine sources of hydrocarbons.

The effect of terrestrial influences on the marine environment is illustrated by the predominant odd high molecular weight *n*-alkanes and their corresponding depleted $\delta^{13}C$ values. The presence of the PAH Retene in many sediment samples may also indicate terrestrial plant debris. Elevated levels of *n*-alkanes at sites H9 (near Clarenville) and H1 (near Hickman's Harbour) suggest increased terrestrial input in these regions, likely a result of run-off from the watershed areas of Clarenville and Random Island. A slight increase in total *n*-alkane concentrations near the lower portion of core H9 reflects an increase in sawmill and land-clearing activities in the 1920's.

The dominance of parental PAH over the alkylated analogues, as well as the enhancement of less-stable/kinetic PAH isomers suggests that the major source of

aromatic hydrocarbons is combustion. Isotopic results also suggest pyrolytic sources, although $\delta^{13}C$ values were difficult to obtain for many PAH due to their relatively low concentrations. Consistent molecular distributions and stable carbon isotopic results suggest similar sources of PAH for the entire study area, quite possibly woodburning. Temporal variations of PAH show a slight increase in pyrolytic PAH during the 1940's, with continual decline since that time period. This reflects the decrease in woodburning as a major source of heat for homes in the area during the last fifty years.

Slight petroleum contamination was apparent at sites H9, H1, St7, and St5, as indicated by the enhancement of several more-stable/thermodynamic PAH isomers. This finding is also supported by the presence of diploptene, pristane, and phytane in sediment samples. These petrogenic influences are more apparent at certain areas in-shore, sites H9 and H1, and are likely a result of localized seepage from small outboard motors. Petroleum biomarkers in sediments further off-shore, sites St7 and St5, may reflect spillage from larger ocean vessels.

Based on the low concentrations of PAH, the extent of anthropogenic contamination is extremely low, revealing that the marine environment is relatively pristine and healthy. These research results provide a baseline of hydrocarbons in the marine environment and will be necessary for subsequent monitoring studies, particularly with future exploitation of petroleum resources along the eastern coast of Newfoundland.

By combining molecular characterization with stable carbon isotopic analysis, sources of hydrocarbons in the marine environment have been identified. Specific distinctions between marine, terrestrial, pyrolytic, and petrogenic sources of hydrocarbons could also be made. By analyzing aliphatic and aromatic hydrocarbons, more information can be assessed, leading to a better understanding of the cycling of organic material in this cold ocean ecosystem.

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Appendix 1

Sediment Grab Sample Data
Hydrocarbons in Fraction 1
Concentration (ng/g)

Sample Site	H10	H6	H5	H3	H2	St11	St5
Compound							
n-alkanes							
nC15	2.0	13.5	4.6	1.5	1.2	–	2.5
nC16	1.9	15.0	4.2	2.1	1.4	4.3	2.7
nC17	2.8	19.2	5.6	2.8	1.7	5.1	3.4
nC18	1.7	14.4	3.6	2.1	1.7	4.7	2.7
nC19	3.5	18.8	6.2	2.4	1.7	4.6	4.7
nC20	3.1	32.0	7.8	3.1	3.5	10.5	6.0
nC21	4.4	36.0	10.1	4.0	3.5	11.0	8.7
nC22	3.3	32.0	8.4	3.6	3.5	10.8	6.5
nC23	9.5	89.0	24.3	10.2	8.9	28.7	20.1
nC24	7.5	81.6	21.2	8.3	8.8	27.0	15.3
nC25	10.3	96.2	30.3	13.8	9.3	30.8	24.8
nC26	7.8	86.3	21.6	9.2	9.0	28.2	16.4
nC27	13.8	121.4	38.0	21.7	9.4	33.4	43.5
nC28	8.0	86.3	22.0	8.9	9.0	27.8	16.3
nC29	12.3	109.4	34.9	20.4	9.2	33.7	46.5
nC30	7.7	83.7	20.9	8.1	8.9	27.3	15.5
nC31	11.2	107.2	31.8	17.8	9.0	32.1	40.6
nC32	7.5	82.1	–	7.5	8.9	–	14.1
nC33	8.6	87.3	22.8	10.5	8.9	28.1	22.6
nC34	–	–	–	6.8	–	–	–
isoprenoids							
pristane	10.2	44.1	23.7	13.9	4.9	12.2	30.8
phytane	7.0	42.5	–	9.2	4.3	14.3	–
brC20:0	–	66.6	–	–	–	12.6	–
brC20:1	43.0	74.4	22.4	7.2	–	–	38.7
brC20:1'	5.4	38.8	–	–	–	–	17.1
brC25:3	41.7	501.8	417.2	66.4	35.9	32.7	45.1
brC25:3'	27.6	177.9	154.1	43.4	15.4	40.3	–
brC25:4a	–	193.4	126.2	22.7	15.9	–	–
brC25:4b	15.4	209.1	191.5	26.1	19.8	–	–
brC25:4a'	–	–	44.5	–	–	–	–
brC25:4b'	53.9	186.8	38.5	13.6	–	–	–
brC25:5	18.1	–	–	–	–	–	–
brC25:5'	31.5	186.0	–	11.6	–	–	–
CPI	1.8	1.5	2.4	2.1	1.3	1.9	2.9
Total n-alkane*	126.6	1211.6	318.4	164.6	117.5	348.2	312.8
Total aliphatic*	380.3	2933.1	1336.5	378.7	213.7	460.4	444.5

*Total is the sum of those compounds which have been identified above.

Appendix 2

Sediment Grab Sample Data
Hydrocarbons in Fraction 2
Concentration (ng/g)

Sample Site	H10	H6	H5	H3	H2	St11	St5
Compound							
PAH							
F	1 4	–	0 8	0 3	–	–	–
Pa	3 8	4 8	2 7	1 6	0 8	1 4	18 5
A	3 2	3 8	1 4	0 7	0 5	–	5 2
MPa's	2 3	5 1	1 8	1 2	0 9	–	12 2
Fl	7 7	2 9	2 2	2 6	2 7	0 1	34 2
Py	3 1	0 8	0 9	1 6	1 9	0 4	24 7
Ret	0 3	2 9	–	0 3	0 4	–	28 3
BaA	6 3	–	5 1	2 9	2 9	–	41 4
Chy	3 8	–	–	2 1	2 1	–	23 7
BbF	4 2	–	–	3 9	–	–	12 8
BkF	2 6	–	–	–	–	–	8 1
BeP	3 6	–	–	3 1	–	–	13 3
BaP	3 6	–	–	3 2	–	–	19 0
Per	3 5	–	–	4 4	–	–	12 9
In	–	–	–	2 8	–	–	–
DBA	–	–	–	–	–	–	–
BPer	–	–	–	3 0	–	–	–
Total PAH	49 4	20 3	14 8	33 7	12 1	2 0	254 1

Appendix 3
Sediment Core (Top Section 0-2cm) Data
Hydrocarbons in Fraction 1
Concentration (ng/g)

Sample Site	H9	H8	H7	H4	H1	St12	St10	St9	St7
Compound									
n-alkanes									
nC15	–	–	–	–	–	–	–	–	2.5
nC16	–	–	3.0	2.8	–	4.0	–	–	2.9
nC17	13.6	10.9	12.9	11.8	19.5	18.6	12.4	10.1	14.2
nC18	12.8	10.5	11.9	11.3	18.9	17.5	11.9	10.0	11.0
nC19	24.6	12.6	13.8	11.9	34.7	16.1	12.2	10.9	13.4
nC20	33.2	28.1	32.2	29.2	42.8	39.8	32.9	26.8	28.2
nC21	42.1	30.0	33.4	29.6	56.6	40.3	33.4	27.3	29.4
nC22	34.5	28.5	32.2	29.4	43.7	40.0	33.2	26.7	27.9
nC23	99.3	75.4	85.4	76.8	124.6	104.6	87.0	71.0	75.7
nC24	85.4	73.0	82.8	75.0	103.4	102.5	86.1	69.3	72.4
nC25	107.0	78.5	88.7	79.1	130.6	108.7	91.0	76.9	83.9
nC26	89.7	75.3	85.7	76.4	107.9	105.6	89.3	70.6	73.7
nC27	124.4	81.3	91.1	81.3	154.3	113.1	91.4	78.5	89.6
nC28	89.1	74.7	85.6	–	108.7	–	88.3	70.0	71.9
nC29	115.1	78.4	89.0	78.5	150.2	108.2	89.4	77.0	87.4
nC30	86.2	74.6	84.7	–	103.6	–	–	69.3	71.8
nC31	105.2	76.0	87.7	76.8	128.3	107.1	88.2	74.0	82.2
nC32	83.8	–	–	–	100.1	–	–	68.0	70.7
nC33	88.6	73.9	85.2	–	108.4	–	–	69.1	71.2
nC34	83.4	–	–	–	98.5	–	–	–	–
isoprenoids									
pristane	46.5	31.9	36.8	39.7	177.3	56.9	–	29.3	45.4
phytane	–	–	–	36.0	79.5	60.4	37.9	–	–
brC20:0	–	–	–	–	–	–	–	–	38.7
brC20:1	55.4	32.0	37.2	34.0	141.1	–	–	–	–
brC20:1'	–	–	–	–	74.8	–	–	–	–
brC25:3	145.3	117.1	170.8	234.2	192.8	141.5	216.7	206.1	213.7
brC25:3'	155.5	–	–	130.7	–	–	128.8	129.0	139.4
brC25:4a	–	–	106.2	115.9	–	–	105.9	89.3	–
brC25:4b	–	–	105.1	130.8	221.0	–	132.7	115.4	125.2
brC25:4a'	–	–	–	–	–	–	–	–	–
brC25:4b'	–	–	–	–	–	–	–	–	–
brC25:5	–	–	–	139.2	–	–	–	–	–
brC25:5'	155.6	–	–	–	–	–	–	–	–
CPI	1.3	1.7	1.7	4.1	1.3	4.1	2.0	1.4	1.4
Total n-alkane*	1318.0	881.6	1005.1	669.8	1634.9	926.0	846.6	905.5	980.1
Total aliphatic*	1876.3	1062.6	1461.2	1530.5	2521.4	1184.8	1468.6	1474.6	1542.6

*Total is the sum of those compounds which have been identified above.

Appendix 4
Sediment Core (Top Section 0-2cm) Data
Hydrocarbons in Fraction 2
Concentration (ng/g)

Sample Site	H9	H8	H7	H4	H1	St12	St10	St9	St7
Compound									
PAH									
F	–	–	3.3	–	–	–	–	–	–
Pa	4.0	2.7	7.4	3.9	80.9	4.1	3.5	3.6	5.8
A	3.5	2.5	4.7	3.1	29.6	–	–	2.9	4.0
MPa's	3.6	3.7	6.5	5.1	70.2	5.5	3.5	3.4	4.9
Fl	2.0	3.7	3.8	3.9	206.1	3.9	0.4	2.7	6.1
Py	1.1	1.3	1.2	1.8	158.9	2.4	–	1.5	3.6
Ret	3.1	2.8	3.2	2.8	22.8	3.9	3.4	2.5	2.6
BaA	–	–	–	–	–	–	–	18.7	20.3
Chy	16.3	–	–	14.1	–	16.4	16.0	11.4	13.7
BbF	–	–	–	–	–	–	–	–	–
BkF	24.5	–	–	–	–	–	–	–	–
BeP	–	–	–	–	–	–	–	–	29.8
BaP	–	–	–	–	–	–	–	–	29.7
Per	35.6	–	–	–	–	–	–	29.3	32.4
In	–	–	–	–	–	–	–	–	–
DBA	–	–	–	–	–	–	–	–	–
BPer	–	–	–	–	–	–	–	–	–
Total PAH	93.6	16.8	30.1	34.7	568.6	36.2	26.8	76.0	152.9

Appendix 5

Sediment Core Data - Down core H9
Hydrocarbons in Fraction 1
Concentration (ng/g)

Sample Depth	0-2cm	4-6cm	8-10cm	12-14cm	16-18cm	20-22cm	24-26cm	28-30cm
Compound								
n-alkanes								
nC15	–	10.3	6.5	8.8	12.1	7.6	8.9	4.6
nC16	–	8.2	7.1	8.5	9.0	7.0	8.7	5.0
nC17	13.6	13.3	11.1	13.5	13.5	13.9	18.3	11.6
nC18	12.8	6.7	7.2	7.4	7.1	7.0	8.4	6.6
nC19	24.6	22.9	19.4	24.3	17.7	24.6	35.7	29.4
nC20	33.2	13.3	14.8	12.4	11.8	11.4	15.0	11.6
nC21	42.1	26.6	23.7	22.4	17.4	19.6	28.7	23.8
nC22	34.5	16.7	16.5	13.8	12.4	12.2	17.0	13.4
nC23	99.3	61.1	53.7	45.2	34.9	36.3	53.9	42.0
nC24	85.4	38.1	38.6	29.6	27.8	26.6	37.0	27.4
nC25	107.0	87.8	63.3	52.4	34.5	35.4	56.3	40.7
nC26	89.7	48.3	42.7	32.1	28.1	27.0	37.9	27.3
nC27	124.4	187.7	92.4	76.5	37.6	39.0	65.4	45.7
nC28	89.1	56.4	41.5	31.4	27.4	25.5	34.7	25.4
nC29	115.1	176.7	80.8	65.7	32.3	32.6	50.4	35.7
nC30	86.2	48.0	39.3	28.6	26.4	24.8	32.7	24.1
nC31	105.2	135.9	67.8	57.3	29.7	28.6	42.6	30.3
nC32	83.8	42.0	36.9	27.1	–	–	–	–
nC33	88.6	64.6	46.6	36.7	27.1	25.1	33.6	24.8
nC34	83.4	40.2	34.7	–	–	–	–	–
isoprenoids								
pristane	46.5	47.9	41.6	63.1	47.3	46.5	60.3	35.4
phytane	–	–	–	–	23.8	21.6	21.9	23.9
brC20:0	–	–	–	–	–	–	–	–
brC20:1	55.4	133.6	91.1	102.8	79.1	88.1	111.7	63.5
brC20:1'	–	–	–	21.4	–	18.5	24.0	15.3
brC25:3	145.3	151.2	195.0	54.7	62.1	125.8	89.6	164.6
brC25:3'	155.5	123.9	106.1	75.9	54.6	70.3	77.6	61.4
brC25:4a	–	–	–	–	–	–	–	–
brC25:4b	–	–	78.0	–	–	46.3	49.5	57.1
brC25:4a'	–	–	84.1	–	–	–	–	–
brC25:4b'	–	–	58.3	–	–	56.1	–	–
brC25:5	–	–	–	–	–	–	–	–
brC25:5'	155.6	–	–	–	–	–	–	–
CPI	1.3	2.8	1.8	2.4	2.0	2.1	2.4	2.3
Total n-alkane*	1318.0	1104.8	744.6	593.6	406.6	404.2	585.0	429.4
Total aliphatic*	1876.3	1561.4	1398.8	911.5	673.4	877.3	1019.5	850.6

*Total is the sum of those compounds which have been identified above.

Appendix 6

Sediment Core Data - Down core H9
Hydrocarbons in Fraction 2
Concentration (ng/g)

Sample Depth	0-2cm	4-6cm	8-10cm	12-14cm	16-18cm	20-22cm	24-26cm	28-30cm
Compound								
PAH								
F	–	1.5	–	–	5.2	–	–	–
Pa	4.0	20.3	36.9	22.7	46.8	5.6	1.7	1.5
A	3.5	11.8	25.4	9.8	26.4	2.7	1.4	1.1
MPa's	3.6	10.3	31.6	20.0	35.2	6.2	3.0	3.8
Fl	2.0	29.3	102.5	60.8	54.5	6.6	1.3	1.1
Py	1.1	15.6	52.7	33.0	35.2	4.3	1.4	0.9
Ret	3.1	1.6	4.7	3.0	4.1	1.3	1.5	1.4
BaA	–	8.2	70.3	38.6	20.8	7.5	–	–
Chy	16.2	5.0	41.2	24.1	13.3	4.6	–	–
BbF	–	–	–	–	–	–	–	–
BkF	24.5	–	–	–	–	–	–	–
BeP	–	–	–	–	–	–	–	–
BaP	–	–	–	–	–	–	–	–
Per	35.6	–	–	–	–	–	–	–
In	–	–	–	–	–	–	–	–
DBA	–	–	–	–	–	–	–	–
BPer	–	–	–	–	–	–	–	–
Total PAH	93.5	103.7	365.2	212.1	241.4	38.9	10.4	9.8

Appendix 7
Sediment Core Data - Down core H1
Hydrocarbons in Fraction 1
Concentration (ng/g)

Sample Depth	0-2cm	4-6cm	8-10cm	12-14cm	16-18cm	20-22cm	24-26cm	28-30cm
Compound								
n-alkanes								
nC15	–	15.2	8.6	6.3	–	5.9	–	–
nC16	–	16.5	9.3	7.1	6.5	6.4	6.0	5.7
nC17	19.5	24.5	15.2	13.4	9.9	8.7	7.9	7.4
nC18	18.9	19.1	11.1	9.2	7.9	8.2	6.7	5.9
nC19	34.7	74.2	58.3	63.6	43.9	17.1	20.6	21.5
nC20	42.8	45.4	25.3	19.7	19.8	17.0	16.5	16.2
nC21	56.6	76.6	48.1	46.7	38.6	22.8	25.4	27.1
nC22	43.7	46.7	25.7	20.4	20.7	17.0	17.0	17.2
nC23	124.6	147.2	83.2	71.5	66.3	48.2	49.9	52.8
nC24	103.4	109.1	60.3	45.1	47.7	41.4	41.1	40.9
nC25	130.6	153.0	81.6	65.6	63.4	47.5	48.2	52.6
nC26	107.9	114.3	62.2	45.4	48.6	42.6	42.1	42.1
nC27	154.3	187.5	97.7	76.2	76.2	51.7	50.1	61.5
nC28	108.7	110.9	61.6	43.8	48.5	42.1	41.4	41.8
nC29	150.2	174.8	92.7	69.3	68.4	50.1	46.0	58.0
nC30	103.6	107.0	58.9	41.9	46.1	41.5	–	40.1
nC31	128.3	142.0	77.4	55.6	58.0	46.0	43.3	51.5
nC32	100.1	102.5	–	–	45.1	–	–	39.4
nC33	108.4	109.0	60.4	43.2	46.9	41.4	40.5	42.4
nC34	98.5	–	–	–	–	–	–	–
isoprenoids								
pristane	177.3	308.0	174.6	184.7	90.4	49.7	44.9	50.0
phytane	79.5	60.7	28.7	33.1	–	26.1	–	–
brC20:0	–	–	–	–	–	–	–	–
brC20:1	141.1	661.3	497.7	345.4	118.9	37.7	57.6	81.7
brC20:1'	74.8	234.2	167.9	94.8	48.5	30.0	25.6	35.6
brC25:3	192.8	163.0	–	–	–	–	–	–
brC25:3'	–	–	–	–	–	–	–	–
brC25:4a	–	–	–	–	–	–	–	–
brC25:4b	221.0	–	–	–	–	–	–	–
brC25:4a'	–	–	–	–	–	–	–	–
brC25:4b'	–	–	–	–	–	–	–	–
brC25:5	–	–	–	–	–	–	–	–
brC25:5'	–	–	–	–	–	–	–	–
CPI	1.3	1.8	2.2	2.4	1.7	1.9	2.7	1.6
Total n-alkane*	1634.9	1775.5	937.7	744.1	762.5	555.6	502.5	624.2
Total aliphatic*	2521.5	3202.7	1806.4	1402.1	1020.2	699.1	630.7	791.6

*Total is the sum of those compounds which have been identified above.

Appendix 8

Sediment Core Data - Down core H1
Hydrocarbons in Fraction 2
Concentration (ng/g)

Sample Depth	0-2cm	4-6cm	8-10cm	12-14cm	16-18cm	20-22cm	24-26cm	28-30cm
Compound								
PAH								
F	–	3.7	–	–	–	–	–	–
Pa	80.9	58.8	13.8	4.5	5.8	12.5	3.0	2.3
A	29.6	17.5	6.3	2.7	3.3	4.8	2.1	2.0
MPa's	70.2	34.6	15.6	5.4	8.5	11.4	3.7	3.4
Fl	206.1	89.9	46.6	9.1	22.6	19.6	1.7	–
Py	158.9	59.9	32.1	6.3	15.9	14.3	1.0	–
Ret	22.8	6.4	5.8	2.0	3.2	3.5	2.0	1.7
BaA	–	88.8	55.0	18.3	33.1	25.0	12.6	–
Chy	–	52.7	34.5	11.9	21.1	14.9	7.4	–
BbF	–	36.6	28.4	–	–	–	–	–
BkF	–	24.5	18.1	–	–	–	–	–
BeP	–	34.4	26.8	–	–	–	–	–
BaP	–	46.0	30.0	–	–	–	–	–
Per	–	28.8	25.9	–	–	–	–	–
In	–	–	–	–	–	–	–	–
DBA	–	–	–	–	–	–	–	–
BPer	–	–	–	–	–	–	–	–
Total PAH	568.6	582.8	339.0	60.1	113.5	106.1	33.4	9.3

Appendix 9

Sediment Core Data - Down core St7
Hydrocarbons in Fraction 1
Concentration (ng/g)

Sample Depth	0-2cm	4-6cm	8-10cm	12-14cm	16-18cm	20-22cm	24-26cm	28-30cm
Compound								
n-alkanes								
nC15	10.1	8.1	3.3	4.4	3.6	6.4	2.9	3.5
nC16	11.4	10.5	4.4	5.2	5.0	8.9	3.8	4.1
nC17	14.2	13.0	6.8	7.1	8.0	11.1	5.5	6.2
nC18	11.0	10.5	4.9	5.1	5.8	8.9	4.2	4.0
nC19	13.4	11.0	5.4	5.6	6.6	8.1	5.0	4.6
nC20	28.2	18.5	7.8	9.6	9.9	12.6	7.8	8.7
nC21	29.4	20.4	9.3	11.0	11.9	13.9	9.5	9.7
nC22	27.9	19.1	8.4	10.0	10.6	13.2	8.4	9.1
nC23	75.7	52.6	24.2	28.3	30.6	35.9	24.7	26.1
nC24	72.4	46.4	19.8	24.2	25.1	31.5	20.0	22.7
nC25	83.9	57.9	28.4	30.8	34.2	39.9	27.7	28.9
nC26	73.7	47.8	21.1	24.8	26.1	34.6	20.9	24.0
nC27	89.6	59.1	33.0	31.5	36.7	43.8	29.8	32.0
nC28	71.9	45.9	20.1	23.7	24.9	31.7	19.3	23.0
nC29	87.4	56.3	33.6	30.0	34.1	38.4	28.3	32.0
nC30	71.8	44.0	19.2	22.7	23.1	29.4	18.3	22.3
nC31	82.2	51.3	30.2	26.0	29.5	34.2	24.2	29.2
nC32	70.7	–	18.2	–	–	–	–	–
nC33	71.2	22.5	20.9	23.1	23.6	29.3	19.1	23.5
nC34	–	–	–	–	–	–	–	–
isoprenoids								
pristane	45.4	73.1	85.8	99.6	100.6	131.3	69.3	38.1
phytane	–	40.0	36.8	32.6	34.8	72.2	–	22.3
brC20:0	38.7	–	–	–	–	–	–	–
brC20:1	–	–	–	–	–	–	–	–
brC20:1'	–	–	–	–	–	–	–	–
brC25:3	213.7	241.2	388.0	380.2	509.6	331.4	354.2	138.2
brC25:3'	139.4	139.5	190.4	217.0	279.0	204.6	229.7	128.4
brC25:4a	–	88.6	126.8	127.0	149.9	120.6	86.1	57.2
brC25:4b	125.2	135.0	220.8	204.8	260.1	198.8	172.5	83.4
brC25:4a'	–	–	–	–	–	–	–	–
brC25:4b'	–	–	–	–	–	–	–	–
brC25:5	–	92.1	116.9	118.8	149.2	114.7	92.5	62.2
brC25:5'	–	–	–	–	–	–	–	–
CPI	1.4	1.8	1.9	2.0	2.1	1.9	2.2	2.1
Total n-alkane*	996.2	594.9	319.0	323.1	349.3	431.9	279.3	313.8
Total aliphatic*	1558.7	1404.3	1484.5	1503.1	1832.4	1605.5	1283.6	843.5

*Total is the sum of those compounds which have been identified above.

Appendix 10

Sediment Core Data - Down core St7
Hydrocarbons in Fraction 2
Concentration (ng/g)

Sample Depth	0-2cm	4-6cm	8-10cm	12-14cm	16-18cm	20-22cm	24-26cm
Compound							
PAH							
F	–	–	–	–	–	–	–
Pa	5.8	1.6	2.5	–	2.7	–	–
A	4.0	1.0	1.2	–	1.6	–	–
MPa's	4.9	1.3	3.9	2.4	3.6	2.3	3.0
Fl	6.1	1.9	3.1	8.2	9.7	9.6	8.0
Py	3.6	2.0	2.8	6.1	6.4	7.0	5.3
Ret	2.6	1.7	1.4	1.6	1.6	1.8	1.2
BaA	20.3	–	–	7.7	8.2	–	–
Chy	13.7	–	–	6.0	7.5	–	–
BbF	–	–	–	–	–	–	–
BkF	–	–	–	–	–	–	–
BeP	29.8	–	–	–	–	–	–
BaP	29.7	–	–	–	–	–	–
Per	32.4	–	–	–	–	–	–
In	–	–	–	–	–	–	–
DBA	–	–	–	–	–	–	–
BPer	–	–	–	–	–	–	–

Total PAH	152.9	9.5	14.9	32.0	41.3	20.6	17.5

Appendix 11

Stable Carbon Isotopic Analysis - Sediment Grab Sample Data
Hydrocarbons in Fraction 1
13C composition (per mil)

Sample Site	H10	H6	H5	H3	St11	St 5
Compound						
n-alkanes						
nC15	–	–	–	–	–	–
nC16	–	–	–	-30.9	–	–
nC17	-22.5	–	-21.8	-27.2	–	–
nC18	–	–	–	-29.7	-23.9	–
nC19	-23.7	-26.7	-22.2	-25.4	-26.4	–
nC20	-31.8	–	–	-30.3	–	–
nC21	–	-26.0	–	-29.3	-27.2	-24.9
nC22	–	-23.3	–	-27.0	-26.0	–
nC23	-25.9	-28.6	-24.7	-28.9	-28.9	-30.4
nC24	–	-30.3	–	-30.8	-30.3	–
nC25	-18.1	-28.1	–	-27.0	-29.5	-25.1
nC26	–	-31.2	–	-29.5	-30.7	–
nC27	-31.4	-31.8	-30.2	-31.3	-30.8	-31.3
nC28	–	–	–	–	-31.4	-33.0
nC29	-30.4	-32.6	–	-30.1	-31.2	-32.7
nC30	–	–	–	–	–	–
nC31	-32.9	-33.5	–	-31.6	-31.6	-33.7
nC32	–	–	–	–	–	–
nC33	–	–	–	–	–	–
nC34	–	–	–	–	–	–
isoprenoids						
pristane	–	-22.7	–	–	-26.3	-20.9
phytane	–	–	–	–	–	–
brC20:0	–	–	–	–	–	–
brC20:1	-14.6	–	–	–	–	–
brC20:1'	–	–	–	–	–	–
brC25:3	-31.2	-32.3	-36.4	-33.5	–	–
brC25:3'	-17.1	–	–	–	–	–
brC25:4a	–	–	–	–	–	–
brC25:4b	–	–	–	–	–	–
brC25:4a'	–	–	–	–	–	–
brC25:4b'	–	–	–	–	–	–
brC25:5	–	–	–	–	–	–
brC25:5'	–	–	–	–	–	–

Appendix 12
Stable Carbon Isotopic Analysis - Sediment Core Data
Hydrocarbons in Fraction 1
13C composition (per mil)

Sample Site	H9 0-2	H9 24-26	H8 0-2	H4 0-2	H1 0-2	H1 28-30	St12 0-2	St9 0-2	St7 0-2	St7 20-22
Compound										
n-alkanes										
nC15	–	–	–	–	–	–	–	–	–	–
nC16	–	–	–	–	–	–	–	–	–	–
nC17	–	–	–	–	–	–	–	–	-26.4	-19.9
nC18	–	–	–	–	–	–	-26.8	–	-29.9	–
nC19	-22.1	-18.4	-21.6	–	-24.5	-17.6	-26.7	–	-27.8	-26.1
nC20	–	–	–	–	–	–	–	–	-28.5	–
nC21	-19.3	-19.6	-21.7	-28.9	–	-19.6	-25.8	–	-28.4	-31.3
nC22	-24.3	-22.8	-25.4	-32.9	–	-22.0	-25.3	–	-28.5	-28.7
nC23	-26.1	-23.8	-29.0	-32.4	-25.7	-23.3	-28.8	-30.3	-29.5	-29.9
nC24	-32.9	-27.6	–	-34.8	-29.8	-30.3	-31.4	–	-30.2	-30.0
nC25	-27.5	-23.8	-29.3	-30.6	-31.0	-29.0	-30.4	-29.3	-30.1	-29.7
nC26	-34.0	-26.2	–	–	-36.1	–	-31.7	–	-31.0	-29.1
nC27	-32.5	-29.1	-32.8	-30.1	-32.5	-33.0	-31.7	-30.6	-30.4	-29.7
nC28	-33.4	–	–	–	–	–	-29.8	–	–	-29.1
nC29	-32.4	-29.4	-31.2	-31.8	-33.2	-32.9	-31.4	-31.1	-30.3	-31.0
nC30	-25.2	–	–	–	–	–	–	–	–	–
nC31	-32.9	-32.9	-30.7	-31.8	-33.1	-32.9	-30.7	-30.2	-32.2	-31.7
nC32	–	–	–	–	–	–	–	–	–	–
nC33	–	–	–	–	–	–	–	–	–	–
nC34	–	–	–	–	–	–	–	–	–	–
isoprenoids										
pristane	-25.1	-23.1	-23.2	–	-27.9	-23.6	-27.5	–	–	-30.0
phytane	–	–	–	–	–	–	–	–	–	–
brC20:0	–	–	–	–	–	–	–	–	–	–
brC20:1	–	–	–	–	–	–	–	–	–	–
brC20:1'	–	–	–	–	–	–	–	–	–	–
brC25:3	–	–	–	–	–	–	-27.7	-35.8	-34.2	-31.2
brC25:3'	–	–	–	–	–	–	–	–	–	–
brC25:4a	–	–	–	–	–	–	–	–	–	–
brC25:4b	–	–	–	–	–	–	–	–	-25.7	–
brC25:4a'	–	–	–	–	–	–	–	–	–	–
brC25:4b'	–	–	–	–	–	–	–	–	–	–
brC25:5	–	–	–	–	–	–	–	–	–	–
brC25:5'	–	–	–	–	–	–	–	–	–	–

Appendix 13

Stable Carbon Isotopic Analysis - Sediment Grab Sample Data
Hydrocarbons in Fraction 2
13C composition (per mil)

Sample Site	H10	H5	H3	St5
Compound				
PAH				
F	-25.3	–	–	–
Pa	-24.1	-25.9	–	-23.8
A	-23.3	-29.2	–	–
MPa's	–	–	–	–
Fl	-24.0	-26.6	-25.0	-25.2
Py	-23.9	-24.7	-24.4	-25.0
Ret	–	–	–	–
BaA	-23.6	–	–	-24.9
Chy	-23.9	–	–	–
BbF	–	–	–	–
BkF	–	–	–	–
BeP	–	–	–	–
BaP	–	–	–	–
Per	–	–	–	–
In	–	–	–	–
DBA	–	–	–	–
BPer	–	–	–	–

Appendix 14
Stable Carbon Isotopic Analysis - Sediment Core Data
Hydrocarbons in Fraction 2
13C composition (per mil)

Sample Site	H9 0-2	H9 20-22	H4 0-2	H1 0-2	St12 0-2	St9 0-2	St7 0-2	St7 16-18
Compound								
PAH								
F	–	–	–	–	–	–	–	–
Pa	–	-21.3	–	-26.5	–	–	–	–
A	–	–	–	-25.3	–	–	–	–
MPa's	–	–	–	–	–	–	–	–
Fl	-23.1	-25.2	-30.0	-25.0	-26.5	–	–	-25.2
Py	-23.4	-26.1	-23.5	-24.6	-26.9	-23.1	-24.0	-20.4
Ret	–	–	–	-25.2	–	–	–	–
BaA	–	–	–	–	–	–	–	–
Chy	–	–	–	–	–	–	–	–
BbF	–	–	–	–	–	–	–	–
BkF	–	–	–	–	–	–	–	–
BeP	–	–	–	–	–	–	–	–
BaP	–	–	–	–	–	–	–	–
Per	–	–	–	–	–	–	–	–
In	–	–	–	–	–	–	–	–
DBA	–	–	–	–	–	–	–	–
BPer	–	–	–	–	–	–	–	–

Appendix 15
210Pb Dating: Down Core Sediments

Sample Site	Core section	Age (Year)	Sed Rate (g/m2/yr)
H1	0-2cm	1995	44.38
H1	2-4cm	1978	23.63
H1	4-6cm	1928	18.69
H9	0-2cm	1994	138.72
H9	2-4cm	1991	120.69
H9	4-6cm	1985	99.45
H9	6-8cm	1979	99.83
H9	8-10cm	1972	108.95
H9	10-12cm	1966	99.03
H9	12-14cm	1959	110.71
H9	14-16cm	1953	105.63
H9	16-18cm	1947	92.06
H9	18-20cm	1940	128.15
H9	20-22cm	1935	113.18
H9	22-24cm	1929	97.82
H9	24-26cm	1922	90.73
H9	28-30cm	N/a	N/a

Appendix 16
Standard n-alkanes - Data for Calibration Curves

Compound	Conc (ng/uL)	Area Counts
Heptadecane	62.50	30934366
	25.00	11835514
	18.75	9030025
	9.38	4173274
Octadecane	47.50	26772827
	19.00	10747882
	14.25	8084009
	7.13	2949200
Eicosane	52.50	34259014
	21.00	13124680
	15.75	9128492
	7.88	2820797
Tetracosane	45.00	16839710
	18.00	3618952
	13.50	1578209
	6.75	984426
Pentacosane	47.50	12728490
	19.00	2835976
	14.25	1093118
	7.13	871368

Appendix 17
Standard PAH - Data for Calibration Curves

Compound	Conc (ng/uL)	Area Counts
Fluorene	15.00	10470459
	10.00	8438037
	7.50	5569761
	2.50	1034261
	0.50	272703
	0.25	30114
Phenanthrene	15.00	12749628
	10.00	8438037
	7.50	5077871
	2.50	1162970
	0.50	1101523
	0.25	97872
Anthracene	15.00	13318465
	10.00	9655255
	7.50	5613797
	2.50	1794351
	0.50	1536727
	0.25	189477
Fluoranthene	2.50	1907254
	0.50	926078
	0.25	173910
Pyrene	2.50	2190995
	0.50	959516
	0.25	215148
Benzo(a)anthracene	15.00	1142170
	10.00	614341
	7.50	174729
	0.25	44854
Chrysene	15.00	2016075
	10.00	1324868
	7.50	760966
	0.25	12120
Benzo(b)fluoranthene	15.00	1931101
	10.00	981504
	7.50	307383
	2.50	92444
Benzo(k)fluoranthene	15.00	1659129
	10.00	1020804
	7.50	514825
	2.50	203587
Benzo(a)pyrene	15.00	1511161
	7.50	279553
	10.00	903960
	2.50	87852

Appendix 18
Deuterated Standards - Data for Calibration Curves

Compound	Conc (ng/uL)	Area Counts
phenanthrene-d10	50	24072987
	125	59260820
		40131406
		33058856
	250	62509411
		88297513
		67716101
	375	107579204
		104404258
		89490989
	500	116343665
		108610011

Compound	Conc (ng/uL)	Area Counts
pyrene-d10	50	15671243
	125	37509538
		33838745
		25339845
	250	53982398
		56622252
		54524618
	375	85540327
		91430156
		65490217
	500	86384091
		61143310

Compound	Conc (ng/uL)	Area Counts
tetracosane-d50	50	10236940
	125	27232912
		14317669
		7770998
	250	17177651
		24475196
		22980495
	375	31717211
		35086428
		24704448
	500	28458905
		15142752