Chemical Source Attribution at Former MGP Sites

Technical Report

Chemical Source Attribution at Former MGP Sites

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REPORT SUMMARY

This report presents laboratory test results of 45 samples of pyrogenic and petrogenic materials collected at manufactured gas plant (MGP) sites and obtained from commercial sources. Samples were analyzed by several methods and results are tabulated and graphically illustrated. Chemical parameters that can be used to identify sources of these materials during environmental forensic studies are presented and discussed.

Background

Environmental forensic chemistry is a rapidly evolving subdiscipline of environmental analytical chemistry. Based primarily on methods developed for oil exploration and oil spill identification, modern environmental forensic methods are being applied to a wide range of terrestrial and marine environmental problems. Faced with difficult source identification and contaminant allocation problems as part of liability and insurance recovery at MGP sites, companies have increasingly relied on environmental forensic data. EPRI recognized the need for reliable forensic methods and reference data for MGP sites and initiated a study to gather, catalog, and analyze samples from MGP sites using modern forensic methods.

Objectives

To determine chemical or physical parameters of MGP residuals that could be used to identify and allocate sources of contamination at MGP sites and to analyze samples from MGP sites and other commercial sources generating data that show benefits and limitations of those parameters and can be used by utilities in future forensic studies at MGP sites.

Approach

More than 200 samples were collected over several years from MGP sites throughout the country and placed in a refrigerated archive. Of those samples, a subset was analyzed for monocyclic aromatic hydrocarbons (MAHs), polycyclic aromatic hydrocarbons (PAHs), and fingerprint by gas chromatography with flame ionization detection (GC/FID). Selected samples also were analyzed for PAHs and alkylated PAHs, and biomarker compounds by GC with mass spectrometric detection (GC/MS), for infrared spectra by infrared analysis (FTIR), and for compound-specific stable carbon isotope ratios by GC with isotope ratio mass spectrometry (GC/IRMS). The data were checked for quality and summarized in this report.

Results

The organic chemicals commonly found at MGP sites can be separated into petrogenic and pyrogenic substances based on their origin. Petrogenic substances include crude oil and fresh and aged refined petroleum products. Pyrogenic substances include those materials that result when organic matter is subjected to high temperatures with insufficient oxygen for combustion, such as

in MGP processes. A large number of feedstocks, products, and byproducts having a wide range of compositions fall within these two general classifications.

Qualitative GC/FID fingerprinting was shown to distinguish between petrogenic and pyrogenic substances generally and to identify many of the feedstocks, products, and byproducts within these two types of organic substances.Concentrations of alkylated PAHs and biomarker compounds by GC/MS also correlated with the tar process. In addition, GC/MS methods were needed for quantitative analysis of petrogenic substances and weathered and mixed materials where GC/FID could not resolve the target compounds from the sample matrix.

FTIR correctly identified general types of tar and tar products, such as coal carbonization, byproduct coke oven, carburetted water gas, and creosote. FTIR spectral interpretations correlated with other parameters such as GC/FID fingerprints, organic acid content, and biomarker content. Also, the FTIR analysis was especially useful for discriminating crude tars from distillates, such as creosote, and for identifying samples that had degraded oxidatively.

The stable carbon isotope ratios of PAHs in tars from several sources were found to be measurably different and to correlate with the type of tar. Since isotope ratios do not change as petrogenic and pyrogenic materials weather in the environment, GC/IRMS can be used to connect severely weathered to fresh or slightly weathered materials at a site, to determine the source of dissolved phase chemicals, and to investigate sources of low-level PAHs in soil. This capability is complementary to the other techniques because interpretations based on GC/FID, GC/MS, and FTIR analyses become increasingly uncertain as petrogenic and pyrogenic substances weather in the environment.

EPRI Perspective

The information presented in this report can be used in support of source attribution and cost allocation studies at MGP sites. In addition, the data also will be useful for assessing the transport and fate of MGP residuals during site investigations and risk assessments. In particular, the report provides chemical characterization data for 34 samples of MGP materials that can be used as reference samples during site-specific source attribution studies. Further, the report presents methods for assessing and comparing these data and any newly acquired data when determining contamination sources at MGP sites.

Keywords

Manufactured gas plant (MGP) sites
Source identification
Environmental forensic methods
Cost allocation

ABSTRACT

This report presents results of analyses for sampled manufactured gas plant (MGP) residuals, commercial coal tar and coal tar products, crude oil, and refined petroleum products. Samples were analyzed for monocyclic aromatic hydrocarbons (MAHs), polycyclic aromatic hydrocarbons (PAHs), alkylated PAHs, selected organic acids, selected organic bases, and biomarker compounds by gas chromatography with flame ionization detection (GC/FID) and GC with mass spectrometric detection (GC/MS). In addition, GC/FID fingerprints and infrared spectra were collected and reviewed. Finally, the compound-specific stable carbon isotope ratios of selected PAHs in a sample subset were measured using a new method, GC with isotope ratio mass spectrometry (GC/IRMS). The report discusses several approaches for identifying the nature and source of organic contamination at MGP sites and provides chemical composition data and fingerprints for a number of reference samples. Environmental managers can use data provided in this report for source attribution and allocation studies as part of remedial investigations, remedial designs, risk assessments, insurance recovery cases, and third-party liability claims.

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INTRODUCTION

Over the past several years, the electric utility industry has become increasingly aware of potential environmental problems resulting from chemical contamination at former manufactured gas plant (MGP) sites. The magnitude of the problem is easily understood in light of the large number of known MGP sites and the estimated volumes of non-aqueous phase liquids (NAPLs) that exist at some of these sites. Although estimates vary, there are likely 3,000 to 5,000 former MGP sites located throughout the United States (EPA, 2000). Also, an unknown number of disposal sites exist that received MGP wastes at some time (Taylor, 1996). Estimates of free NAPLs at individual MGP sites range from about 3,800 to 190,000 liters (GRI, 1996). These residues, resulting from a variety of historic gas production processes, often were left in holding tanks or placed in trenches or holding ponds many years ago and forgotten (Harkins, 1988, EEI, 1984, Wilson, 1981). In addition to free NAPLs, varying amounts of contaminated soil and sediment exist at former MGP sites.

Numerous regulatory, redevelopment, and liability issues must be managed by owners of former MGP sites. For example, one estimate of the annual expenditure by the U.S. power utility industry for environmental investigations and remediation was between 50 million and 100 million dollars. In addition, the industry spends approximately 30 million dollars annually on environmental litigation and insurance cost recovery (Murarka, 1999). A substantial portion of those costs is expended on former MGP sites. The ability to identify the nature and origins of chemicals in soil, water, and vapors, substantially affects the technical, legal, and economic outcomes. Environmental forensic chemistry has evolved from this need for reliable methods for identifying the nature and origins of chemicals in the environment. EPRI recognized that while environmental forensic chemistry (sometimes called source identification, source attribution, or fingerprinting) was being aggressively developed for oil spill investigations, little effort was being expended on appropriate methods for former MGP site investigations. Therefore, EPRI sponsored research to advance the capabilities of environmental forensics at former MGP sites.

Overview of Environmental Forensic Chemistry at MGP Sites

Environmental forensic chemistry involves scientific testing at a site that allows the investigator to decipher the source(s) and fate of chemicals, and in some instances, determine their age or apportion them to multiple sources (Wait, 1999). Any method that generates reproducible and discriminating chemical data or a diagnostic parameter can be used for forensic investigations. For example, physical/chemical properties such as density, color, or odor might be used to identify NAPLs. The distribution of selected elements might identify a foundry’s signature, or the presence of a certain solvent might indicate impacts by a coatings plant.

One technique used in environmental forensic chemistry consists of analyzing samples and generating chemical “fingerprints” which identify the source of the contaminants. To be successful, chemical fingerprinting requires the identification of compounds or patterns that provide distinguishing or discriminating information. Further, the discriminating information must be reproducible and consistent with basic principles of chemistry. The steps involved in fingerprinting include the selection and/or the development of analytical methods to obtain appropriate and precise data, the development and use of databases from known sources for comparison purposes, and statistical analysis of the data to show significant and consistent similarities or differences.

Several fingerprinting methods have been used to identify the sources of contaminants at utility sites. However, most environmental forensic work is done using only a few methods. By far, the most widely applied methods utilize gas chromatography (GC) coupled to either the flame ionization detector (FID) or the mass spectrometer (MS). Sulfur-specific or nitrogen-specific detectors also have been used for selected purposes, but these applications are infrequent.

Generally, for petroleum and tar products, GC/FID is used to generate a fingerprint of the whole sample because the FID responds to hydrocarbons equivalently. Thus, the relative amount of each compound in a sample can be easily seen by simply comparing the heights of peaks on the chromatogram. However, GC/FID fingerprints often cannot distinguish between samples of similar chemical composition from different sources. In addition, GC/FID fingerprints can be distorted by environmental weathering processes, thereby making source identification difficult (Sauer, 1994). In those cases, techniques based on GC/MS are applied. Using GC/MS, the patterns of certain PAH groups, such as those with attached methyl or ethyl groups, may be used to differentiate between similar petroleum products, even when those materials are severely weathered. Also, certain marker compounds, such as cyclic alkanes, olefins, steranes, and terpanes, can be identified by GC/MS and have been used to differentiate between similar substances under a variety of environmental conditions (Sauer, 1994, Kaplan, 1996, Douglas, 1996).

Other environmental forensic methods are used for selected purposes. For example, infrared spectroscopy (IR) has been used successfully to identify organic liquids. Also, stable carbon, sulfur, hydrogen, and oxygen isotope ratios, long used in geochemistry, are being used more frequently in environmental forensic work (Mansuy, 1997). Other methods, based on liquid chromatography, thin layer chromatography, and nuclear magnetic resonance spectroscopy, have been used by some laboratories to differentiate between sources. However, few of these techniques have been applied systematically to MGP sites.

Environmental Forensic Methods

Four analytical methods were used to characterize the samples included in this report. They were GC/FID, GC/MS, fourier transform infrared spectroscopy (FTIR), and GC with isotope ratio mass spectrometry (GC/IRMS). In addition, the aliphatic, aromatic, and polar portions (fractions) of some samples were isolated using column chromatography. The fractions were then analyzed separately using GC/FID and/or GC/MS. A brief description of the nature of the data generated by each method is included in this subsection.

GC/FID Fingerprinting

All samples and all sample fractions in this study were analyzed by GC/FID. With GC/FID, organic compounds in a sample are vaporized and then separated in a long, narrow fused silica capillary column. Separation approximately follows boiling point with the most volatile compounds exiting the column first, followed by increasingly less volatile compounds. Therefore, certain refined petroleum products generated by the distillation of crude oil and which differ in their boiling point ranges, are distinguishable by where they appear on a chromatogram. Once they exit the column, the compounds are detected using the flame ionization technique. As the compounds exit and are detected their responses are recorded and shown as peaks on a continuous plot. The height and area of a peak is proportional to the concentration of that compound in the sample. When done in a controlled and reproducible manner, the GC/FID method produces a “fingerprint” of a sample where the presence and relative amounts of the compounds are immediately visible as peaks of varying height appearing at different times.

GC/FID methods are commonly used for fingerprinting in a number of forensic fields. It is also an appropriate method for making various petroleum measurements such as total petroleum hydrocarbons (TPH) and diesel range organics (DRO). Two general features of the GC/FID data are used for interpreting the results. First, the patterns of individual peaks and the sizes and shapes of any baseline features are examined qualitatively for similarities and differences among samples. Of particular interest are any features that appear to be correlated to specific MGP processes or to other sources of pyrogenic PAHs.

The instrumental conditions for the GC/FID analyses in this study were adjusted so that compounds with boiling points between about benzene and n-tetracontane (C40) were detectable in one analytical run. This range includes most of the VOCs and all of the SVOCs commonly measured in environmental investigations. In particular, it includes benzene, toluene, ethylbenzene, xylenes, and the 16 parent PAHs that comprise a major portion of MGP tars and other pyrogenic substances. It also includes the range of compounds that are measurable in pyrogenic substances by gas chromatographic methods. Figure 1-1 shows a GC/FID chromatogram for an MGP tar that has target MAHs and PAHs numbered. The other peaks indicate compounds such as aliphatic hydrocarbons, alkylated PAHs, and heterocyclic compounds. The GC/FID pattern seen in Figure 1-1 is typical for MGP tars.

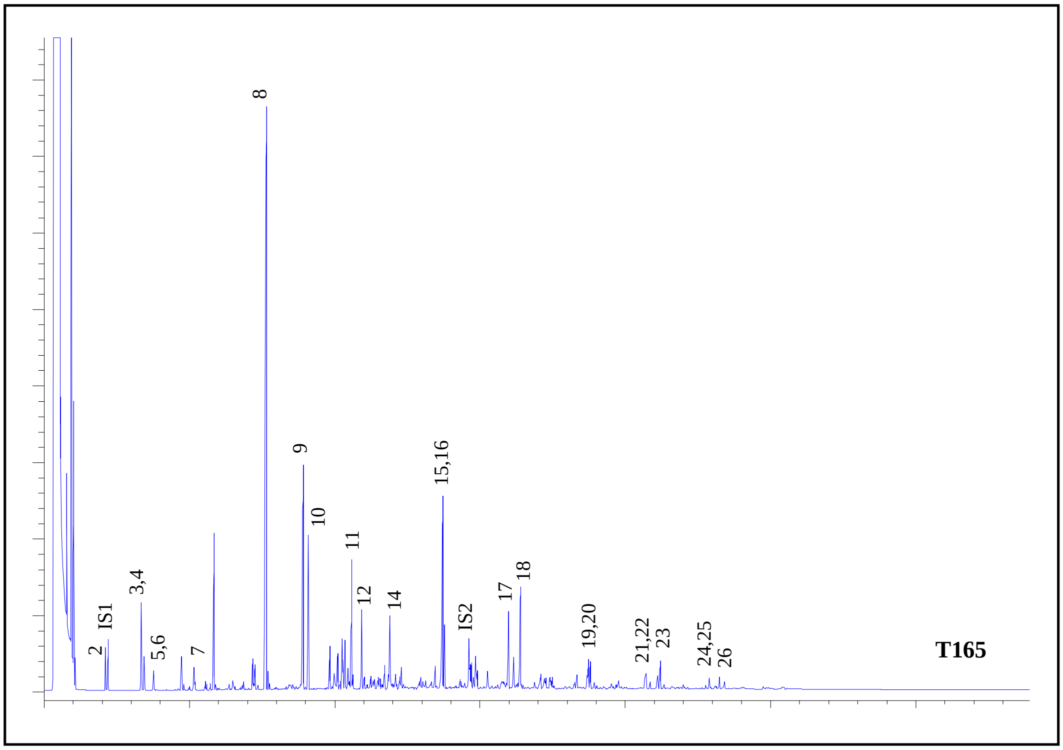


Figure 1-1
GC/FID Chromatogram of MGP Sample T165 (Whole Extract). Peak Numbering Is as Listed in Appendix B.

When sample extracts are fractionated into various chemical classes, such as saturated (aliphatic) hydrocarbons, the GC/FID chromatogram can be used to study the compositional differences among the fractions, including both concentration and pattern differences. This is illustrated in Figure 1-2, where the aliphatic portion of Sample T165 is contrasted to the whole, unfractionated extract. For those samples that have been separated into chemical class fractions, the GC/FID data from each fraction is qualitatively examined. For example, the presence of a bell-shaped baseline “hump”, also called an unresolved complex mixture (UCM), is indicative of petrogenic sources, such as refined petroleum products. Some tar samples exhibit this type of feature in the aliphatic fraction. Also, the presence of a regular series of normal alkanes and certain isoprenoid hydrocarbons, including pristane and phytane, is also indicative of some petroleum products. When these features are present in the aliphatic portion of tar samples, the data suggest that unreacted oil from the process carries over with the gas and the tar. These relatively minor constituents of tars can help to determine whether two samples are from the same source when their major PAH patterns appear similar.

Following the qualitative analysis of the chromatogram, the presence and relative abundance of MAHs and PAHs is examined. These compounds are known to dominate the chromatograms of pyrogenic sources, such as the tars and soot produced by many incomplete combustion and pyrolysis (high temperature) processes including those by former gas manufacturing processes. In contrast, MAHs and PAHs are present at much lower relative amounts in most petrogenic sources, such as refined petroleum products. Certain PAH ratios in the tar samples analyzed for this study appeared to provide a diagnostic tool for the source of those PAHs.

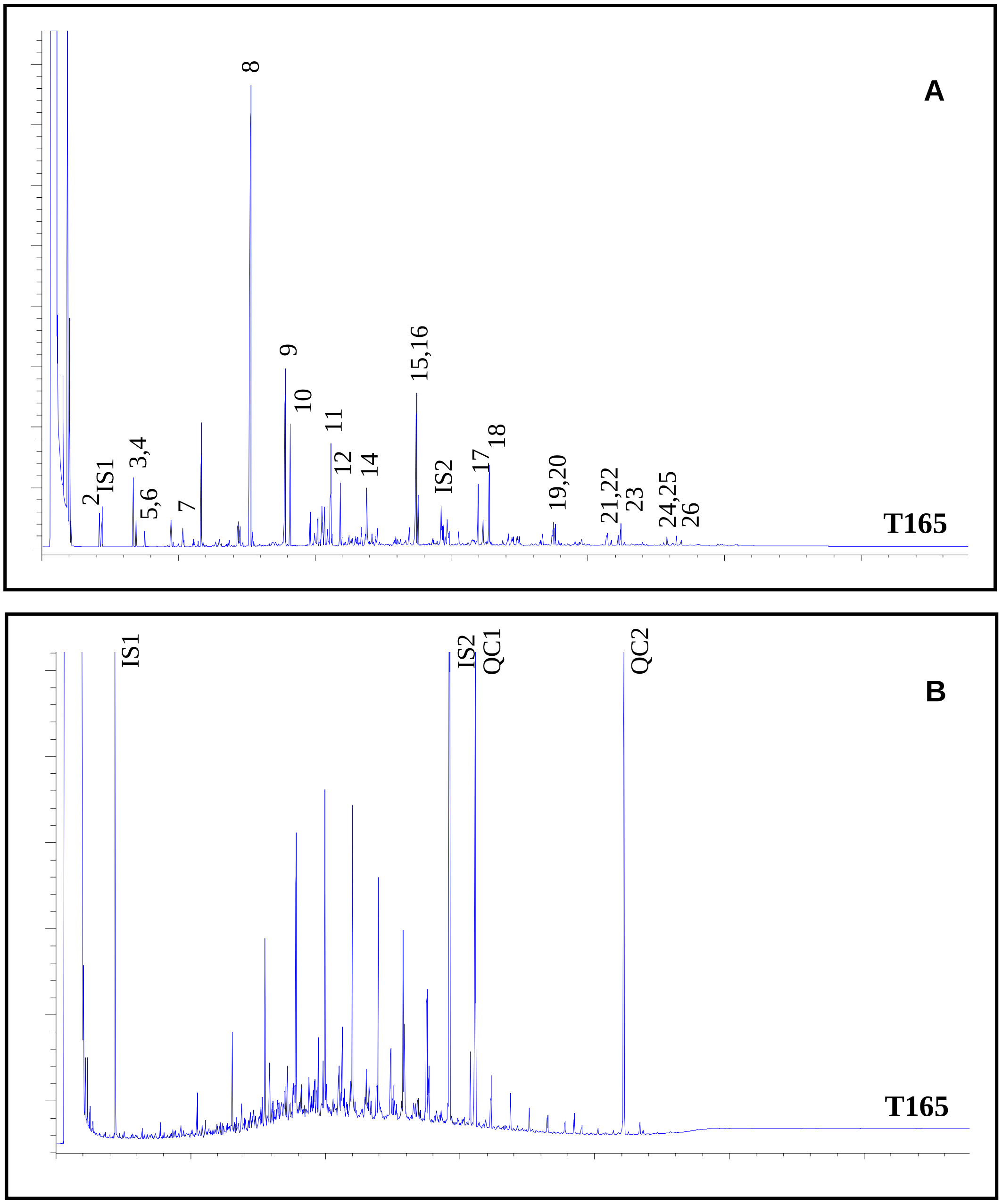


Figure 1-2
Comparison of GC/FID Chromatograms of the Whole Extract (A) and the Aliphatic Fraction (B) of MGP Sample T165. Peak Numbering Is as Listed in Appendix B.

Source identification using GC/FID is mostly qualitatively applied. An experienced chemist compares the chromatograms to those of reference materials, and makes a judgement regarding the nature and source of the contamination in the sample. The chemist may go “peak-by-peak” looking for similarities and differences, comparing peak ratios, and looking for indicator compounds. However, GC/FID data also can be used quantitatively by calculating the concentrations of selected compounds, comparing peak area ratios, or applying chemometric or pattern recognition techniques to the raw or adjusted data.

For some samples, GC/FID fingerprinting is accurate and sufficient. However, the reliability of GC/FID fingerprinting decreases when multiple sources are present in a sample and when the sample composition becomes extensively altered by environmental weathering processes. Other testing methods, such as GC/MS and GC/IRMS, are more appropriate for source identification under these conditions.

GC/MS

Most samples and sample fractions in this study were analyzed by GC/MS. In the same way as GC/FID, organic compounds in a sample are vaporized and then separated in a long, narrow fused silica capillary column. The columns used for GC/MS are the same ones or similar ones as are used for GC/FID analyses. Separation approximately follows boiling point with the most volatile compounds exiting the column first followed by increasingly less volatile compounds. However, in GC/MS, once they exit the column, the compounds are detected using a mass spectrometer. In the mass spectrometer, the molecules of each compound are ionized at high temperature. The ions are unstable and fragment into smaller ions. The ions are then counted and the mass spectrum recorded. Thus, the mass spectrum for a compound is the pattern of ionic fragments that forms when that compound is ionized. Mass spectra vary widely and are characteristic of their source compound. For example, the mass spectrum of hexane is very different from the mass spectrum of benzene.

In GC/MS, one obtains both a chromatogram of peaks that is similar to the chromatogram obtained in GC/FID and additional compound-specific information in the mass spectrum. When done in a controlled and reproducible manner, the GC/MS method produces multiple “fingerprints” of a sample when specific fragment ions are isolated. In particular, the total ion chromatogram of an MGP tar sample looks very similar to the GC/FID chromatogram. In addition, the GC/MS chromatogram having only the ion with a mass/charge of 55 displayed closely resembles the GC/FID chromatogram of the aliphatic fraction for the same sample. Ion 55 is characteristic of aliphatic hydrocarbons and not abundant in aromatic hydrocarbons.

In addition to the analysis of whole extracts, some sample fractions also were analyzed by GC/MS. In these cases, compounds of certain target classes, such as biomarker compounds were selectively measured. Also, by analyzing sample fractions, lower detection limits were possible.

GC/MS is utilized in two general ways in environmental forensic chemistry. First, samples are analyzed under the conditions required by various standard methods, particularly EPA Methods 8260 and 8270 (EPA, 1997). The concentrations of certain target compounds are determined and the mass spectra of each peak in the chromatogram is generated and stored. These mass spectra can be used to identify non-target compounds or to generate extracted ion profiles (EICPs) such as the one for ion 55 discussed previously. Second, various specialty methods are utilized where the GC/MS operating conditions are designed to measure only certain groups of compounds. For example, the method described in 40 CFR Subchapter J Part 300 Subpart L Appendix C for PAHs, alkylated PAHs, and biomarkers is used extensively in oil spill and UST release analyses. This method is similar to ASTM Method D 5739-95, “Standard Practice for Oil Spill Source Identification by Gas Chromatography and Positive Ion Electron Impact Low Resolution Mass Spectrometry.”

GC/MS data are used qualitatively and quantitatively. As with GC/FID, an experienced chemist examines the chromatograms, compares them to those of reference materials, and makes a judgement regarding the nature and source of the contamination in the sample. The chemist may go "peak-by-peak" looking for similarities and differences, comparing peak ratios and looking for indicator compounds. This process is described in detail in ASTM Method D 5739-95.

GC/MS data are more commonly used quantitatively by calculating the concentrations of selected compounds, comparing peak area ratios, or applying chemometric or pattern recognition techniques to the raw or adjusted data. These data analysis methods are used extensively with extended PAH profiles (PAHs and alkylated PAHs) and with biomarker compound data. Various degrees of statistical confidence can be achieved by examining chemical concentrations and compound ratios or patterns from multiple samples and replicate samples. This characteristic of GC/MS quantitative data is particularly valuable when assessing the degree of similarity or difference between samples.

Finally, the mass spectra of selected compounds also can be examined to determine whether any diagnostic or indicator chemicals are present in the sample. For example, the PAHs cadalene and retene (1-methyl-7-isopropylphenanthrene) are present at significant concentrations in coal, but at much lower concentrations in coal tar or petroleum products. Thus, the ratio of retene to chrysene can be used to determine whether coal fines are present in a soil sample and to explain some of the hydrocarbon patterns observed at MGP sites where coal was used extensively. Further, unknown compounds can be identified and their presence used as clues to the source(s) of the chemicals.

GC/MS analyses dramatically increase the amount of data obtained for each sample beyond GC/FID. In many cases, the combination of GC/FID and GC/MS analyses provides a sufficient and reliable source identification. However, for the same reasons as for GC/FID fingerprinting, the reliability of GC/MS forensic methods decreases when multiple sources are present in a sample and when the sample composition becomes extensively altered by environmental weathering processes. For those cases, other methods may provide the additional data needed for a reliable source identification.

FTIR

Infrared spectroscopy has been used as a quality control and forensic tool in many chemical fields. For pure compounds, an IR spectrum reveals information on the chemical structure of the compound. In quality control applications, such as in the pharmaceutical industry, the FTIR spectrum of a product can show the presence of unacceptable levels of contamination. The FTIR spectra of most pure compounds are unique to those compounds. Similarly, the FTIR spectrum of a mixture can be unique to the mixture because it results from the sum of infrared absorbances of the compounds in the mixture. Thus, the FTIR spectra of fuel blends are used to determine batch to batch consistency.

The use of FTIR for tar fingerprinting originated in the quality control laboratories of tar product manufacturers. As with fuel blends and other products, FTIR was used to determine if batches of creosote met product criteria. Over time, peak patterns in the FTIR spectra were correlated with chemical differences in the various products. For example, certain peaks in creosote spectra are sharper than in crude coal tar spectra. This occurs because the heavy weight compounds and free carbon, present in crude coal tar but not present in creosote, influence the peak shapes and intensities. These correlations have been extended to MGP tars by analyzing samples of MGP tars and comparing the FTIR spectra to those of known tar products.

FTIR fingerprinting has distinct advantages and disadvantages. In particular, FTIR is a bulk property measurement. Therefore, compounds present at environmentally significant concentrations (e.g., part per million levels) either will not be detected or will have their spectra masked by the spectra of more abundant compounds in the sample. Thus, interpretation of certain mixture spectra can be problematic. For example, FTIR spectra of sediment samples impacted by significant amounts of urban runoff containing motor fuels and lubricants as well as low concentrations of MGP tar will be interpreted often as containing only heavy petroleum-derived material. The abundant petroleum background masks the MGP tar impact. So if the objective of the testing is to determine the sources of all environmentally significant chemicals in a sample, including those at ppm or ppb concentrations, then FTIR cannot be used alone.

One advantage of FTIR is that it can indicate the presence of materials not detectable by chromatographic methods, such as water, particulate carbon, and polar organic compounds, such as biodegradation byproducts. These data can be important when trying to characterize unknown substances or when trying to distinguish between similar substances such as tars.

Another advantage of the FTIR technique is that it often shows notable differences among basic tar types. Thus, a coal tar spectrum is different from a creosote spectrum, which is different from a carburetted water gas (CWG) tar spectrum. This property of FTIR can be valuable for identifying the source of two or more tars when GC/FID and GC/MS methods cannot do so.

To date, FTIR fingerprinting of tar, tar products, and tar-containing soil and water samples has been qualitative or semiquantitative. No references were found that describe the interpretation of the IR spectra or present the results from multiple samples of known sources. A few reference samples were analyzed by FTIR as part of this study and the results compared to GC/FID and GC/MS data as discussed in Section 3.

GC/IRMS

Stable isotope ratios have been used in geochemistry for many years (Hoefs, 1997). Recently, carbon, hydrogen, sulfur, and oxygen isotope ratios have been found useful for environmental studies (Philp, 1995). A new application of stable isotope ratios, GC/IRMS, can be used to measure the stable carbon isotope ratios of individual compounds in complex mixtures. For industrial by-products, this technique produces fingerprints that are characteristic of the source of the by-product. For example, the stable carbon isotope ratios of pyrolysis byproducts are similar to the organic matter from which they were formed. Figure 1-3 shows the differences in the carbon isotope ratios of PAHs in samples of creosote, combusted grasses, combusted wood, and an MGP tar.

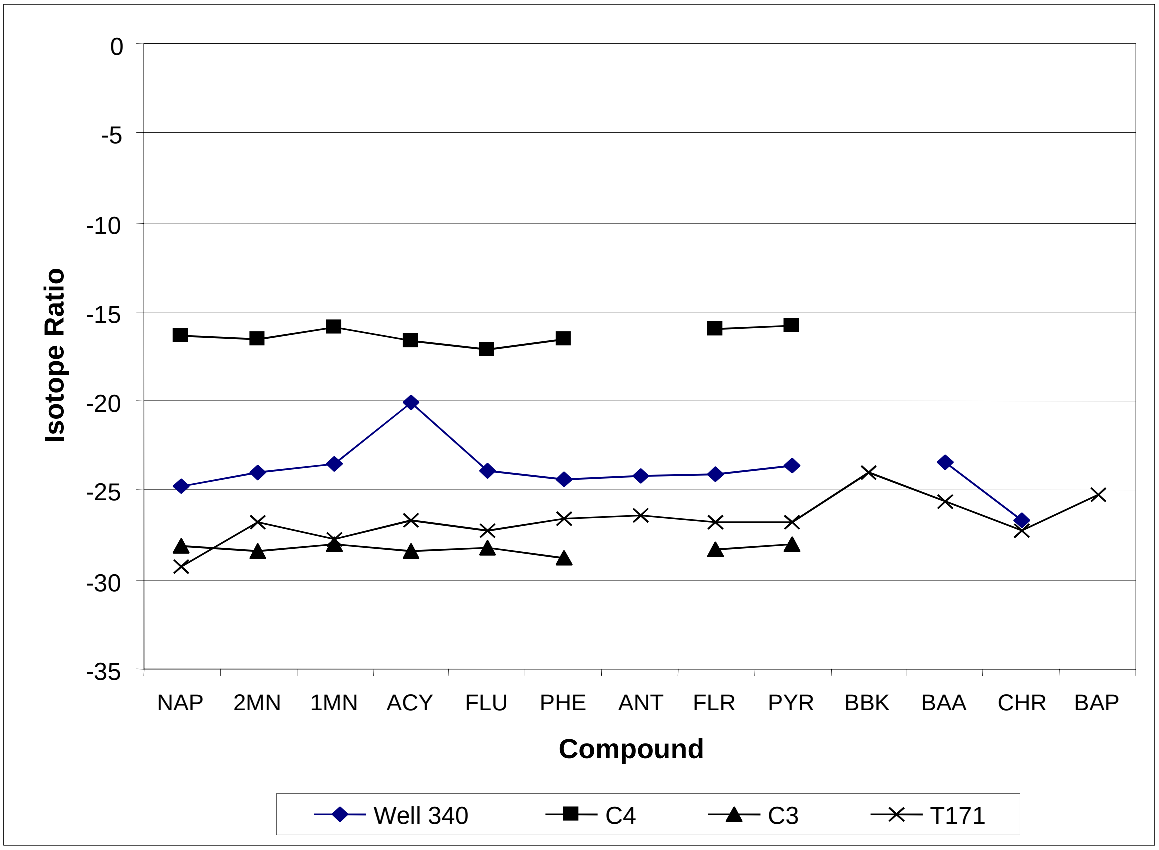


Figure 1-3
GC/IRMS Analysis of Creosote, Combustion Byproducts, and MGP Tar:
Well 340 - Creosote (Hammer, 1998), C4 - Combustion of C4 Grass Species (O'Malley, 1997), C3 - Combustion of C3 Plant Species (O'Malley, 1997), T171 - MGP Tar.

There are several advantages of this technique for environmental forensic studies at former MGP sites. For example, since coal and oil from various sources can have different compound-specific carbon isotope ratios, the tars produced from them should also have different carbon isotope ratios. Thus, fugitive NAPLs can be connected to potential sources.

Also, stable carbon isotope ratios in hydrocarbon compounds resist change as a substance weathers in the environment (Mansuy, 1997, O'Malley, 1996, O'Malley, 1997, Hammer, 1998). Therefore, as oil products or tars weather over time, the carbon isotope ratios of their recalcitrant compounds will stay the same. For this reason, GC/IRMS can connect contaminated samples to their source materials even after their chemical composition has degraded so extensively that other techniques such as GC/MS cannot provide confident source matches. Finally, compound-specific carbon isotope ratios can be used to connect groundwater contamination to its source, since the ratios do not change when the chemicals dissolve in water.

Carbon is a mixture of two stable isotopes, ^{12}C and ^{13}C with an approximate $^{12}C/^{13}C$ ratio of 99:1. Various organic and biochemical processes produce organic matter (plants and animal tissues, oil, coal) slightly enriched in one or the other isotope. These variations in the isotopic composition of organic matter can provide information on the source of the organic material (Philp, 1986).

The isotopic composition of carbon is expressed relative to a reference standard that can be traced to the PDB standard of the University of Chicago (Belemnitella Americana, Cretaceous Peedee Formation, South Carolina) (Faure, 1985). The standard parameter is:

$$\delta^{13}C = \left[\frac{(^{13}C/^{12}C)_{spl} - (^{13}C/^{12}C)_{std}}{(^{13}C/^{12}C)_{std}} \right] \times 1000$$

The results are expressed in parts per thousand (‰). This convention will be used for any data presented in this report.

Classification of Environmental Samples in Forensic Studies

General Classification

In environmental forensic studies, it is often helpful to separate samples based on chemical or physical properties, and draw conclusions regarding their relationships based on the similarity or lack of similarity of one or more of those properties. For example, all of the samples at a site which are shown to contain diesel fuel by chemical analysis could be classified as "containing diesel," and may be related to a common source. Alternatively, all samples at a site that contain an organic phase which is less dense than water (LNAPL), could be classified as "containing LNAPL," possibly originating from multiple sources. The LNAPL group will contain samples with diesel fuel, however the diesel subgroup will not necessarily contain all the LNAPLs. Therefore, using LNAPL as a primary grouping alone may not allow a link to be made between a diesel-containing sample and its source. Thus, the choice of classifications depends as much on the objectives of the study as on the nature of the data.

Hydrocarbons are the principal type of chemicals found at former MGP sites. Hydrocarbons can be divided into three basic classes: petrogenic substances, pyrogenic substances, and diagenetic substances. Each of these are discussed in the following subsections.

Petrogenic Substances

Petrogenic substances can be defined as substances originating from petroleum, including crude oil, fuels, lubricants, and derivatives of those materials. The formation and chemical composition of petrogenic substances, such as crude oil, is complex and discussed in many texts on the subject. For environmental forensic studies at MGP sites it is usually sufficient to know the major types of petrogenic materials that might be found, their compositions, and how they are measured using modern methods.

Aliphatic and aromatic hydrocarbons constitute the vast majority of compounds in petrogenic substances. The aliphatic portion of crude oil consists of numerous straight and branched alkanes along with cyclic alkanes. The key feature of most fresh crude oil is a regular series of normal alkanes clearly visible as a regular progression of evenly-spaced individual peaks in the GC chromatogram. In addition, crude oil contains biomarker compounds and a UCM of compounds evident as a "hump" in the baseline of the chromatogram. Petroleum refining produces a variety of materials having a wide range of compositions.

Some of the important characteristics of refined petroleum products and petrogenic substances in general are:

- Fresh crude oil and distillate products, such as diesel fuel, contain a homologous series of normal alkanes. These compounds biodegrade relatively quickly in the environment and can be used as an indication of the age of the material.
- Fresh crude oil and distillate products also contain a homologous series of cyclic alkanes. These compounds resist biodegradation and can be used to identify the source of aged samples.
- Crude oil and some petroleum products contain biomarker compounds that are derived from biochemicals from the organic debris that became the oil. Some of these biomarker compounds include the isoprenoid hydrocarbons pristane and phytane, terpanes, stearanes, and aromatic hydrocarbons. The relative amounts of some of these compounds have been found to be source-specific. In addition, many of these compounds resist biodegradation and other weathering processes, and have been useful in identifying oil sources in weathered samples. However, it is important to note that many biomarker compounds have limited usefulness for releases of common petroleum products because they are removed during refining.
- In addition to hydrocarbons, numerous organic compounds containing oxygen, nitrogen, and sulfur are present at low relative proportions. Some of these, such as dibenzothiophene and alkyalted dibenzothiophenes have been used to group samples of petrogenic substances according to their sources.

Pyrogenic Substances

Pyrogenic substances can be defined as those organic substances originating from oxygen-depleted high temperature processes, including: incomplete combustion, pyrolysis, cracking, and destructive distillation. They can be generated from numerous organic starting materials, such as oil, coal, and vegetation. Pyrogenic materials consist primarily of aromatic hydrocarbons. However, significant amounts of oxygen, nitrogen, and sulfur-containing compounds are present in some pyrogenic materials.

By definition, tar is a pyrogenic material, and MGP tar includes several types of tar produced from coal or oil as a by-product of gas production at former MGPs. Tars are a mixture of liquid hydrocarbons, suspended carbon, and some water. Tars are usually liquids at room temperature. For the purposes of this report, tar includes only these types of pyrogenic materials. It should not be confused with other common uses of the term tar such as for asphalt paving which is a petrogenic substance.

MGP tars are complex hydrocarbon mixtures that contain relatively high amounts of MAHs and parent PAHs, with naphthalene often being the most dominant PAH compound. While there is some variability in the chemical composition of MGP tars because of the coal or oil used as the starting material and the conditions of gas manufacture, the GC/FID chromatograms of MGP tars are generally alike. MGP tars are also similar to some other pyrogenic substances, such as by-product coke oven tars, which are used for a variety of products, such as roofing materials, road tars, driveway sealers, pharmaceuticals, creosote, and organic chemicals.

While overwhelmingly aromatic, tars also contain aliphatic hydrocarbons such as straight and branched alkanes, cyclic alkanes, and isoprenoid hydrocarbons. Other biomarker compounds, including steranes and terpanes, are usually absent from tars.

Diagenetic Substances

Diagenetic substances include PAHs from natural sources. These sources include plants and buried organic materials in their early stages of maturation. The concentrations of diagenetic PAHs are typically very low and not important at MGP sites. Diagenetic PAHs are not discussed further in this report.

Mixed Materials

Occasionally, a sample will contain both petrogenic and pyrogenic signatures. The composition of these samples can be categorized as “mixed.” One of the challenges of environmental forensic study is to recognize mixed sources and to quantify the contributions of each source. A wide range of potential mixed materials is found at MGP sites, as discussed in the next section.

Other Materials or Unknown

Sometimes samples at MGP sites contain synthetic compounds, natural organic materials, or other substances that are unknown. While present at some MGP sites, these chemicals will not be considered in this report. The methods for source attribution of contaminants that are not petrogenic or pyrogenic are often different from those described in this report.

Specific Classification of Samples

Often is it important to classify samples more narrowly. For example, within the petrogenic group, samples may contain gasoline, heating oil, or lubricating oil. These classifications are determined by matching the composition and resulting chromatographic patterns to those of known materials. This level of classification is often successful for refined petroleum products.

However, further classifying pyrogenic materials into groups such as MGP tar, coke oven tar, wood tar, and others is more challenging because the variability among pyrogenic materials can be both less than, as well as greater than that of petrogenic substances. For example, gasoline and diesel fuel, two petrogenic substances, have clearly different chemical compositions, which are notable in their chromatographic patterns. In contrast, the chemical compositions of many pyrogenic substances are largely the same. However, the chemical compositions and chromatographic patterns of diesel fuels from different sources are quite similar, and distinguishing among several sources of diesel fuel can be difficult. Again in contrast, a number of notably different tar patterns can be found at a single MGP site. Other chemical or physical properties may be used to further classify samples as needed.

Sources of PAHs

PAHs are major constituents of MGP site contamination. Also, they form the basis for source attribution for many forensic studies at sites with petrogenic or pyrogenic materials. The pattern of PAHs clearly distinguishes petrogenic from pyrogenic substances. Therefore, a more detailed discussion of the sources and nature of PAHs in the environment are presented in this section.

PAHs are formed whenever organic substances are exposed to high temperatures under low oxygen or no oxygen conditions in a process called pyrolysis (Blumer, 1976). Pyrolytic processes occur intentionally, such as the destructive distillation of coal into coke and coal tar, or the thermal cracking of petroleum residuals into lighter hydrocarbons. Similar processes occur unintentionally such as the incomplete combustion of motor fuels in cars and trucks, the incomplete combustion of wood in forest fires and fireplaces, and the incomplete combustion of fuel oils in heating systems. These processes occur at temperatures that range from about 350°C to more than 1200°C and their products are called pyrogenic.

PAHs also can be formed at lower temperatures. In particular, crude oils contain PAHs that formed over millions of years at temperatures as low as 100°C to 150°C (Blumer, 1976). PAHs formed during crude oil maturation and similar processes are called petrogenic.

Both pyrogenic and petrogenic sources of PAHs have been found to contain hundreds of individual PAH compounds in generally predictable patterns. For example, it is known that the temperature of formation of PAHs largely determines the distribution of the various parent and alkylated PAHs (Figure 1-4) (Blumer, 1976). Variations in these PAH distributions are measured using GC methods, particularly GC/MS, and are used to identify the sources of those PAHs. For example, Figure 1-5 shows the PAH profile for a sample of coal tar (a pyrogenic or high temperature substance) and for crude oil (a petrogenic or low temperature substance). The differences between these two substances are manifested in the patterns of alkylated PAHs.

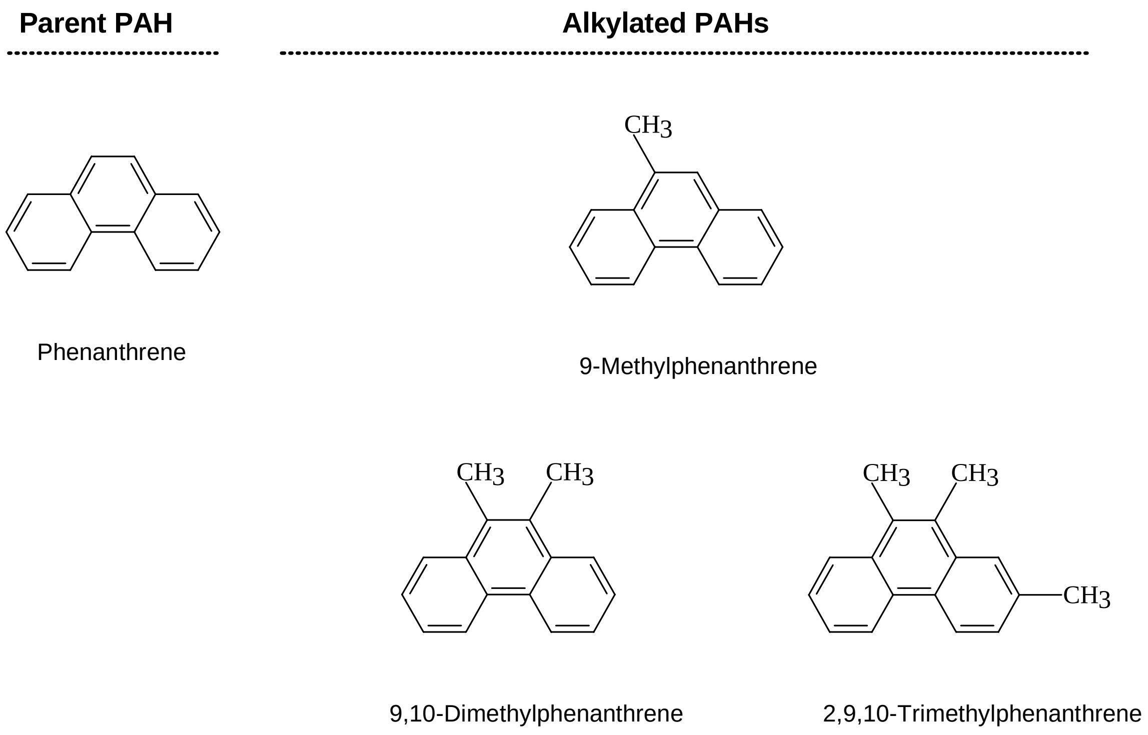


Figure 1-4
Examples of Parent and Alkylated PAHs

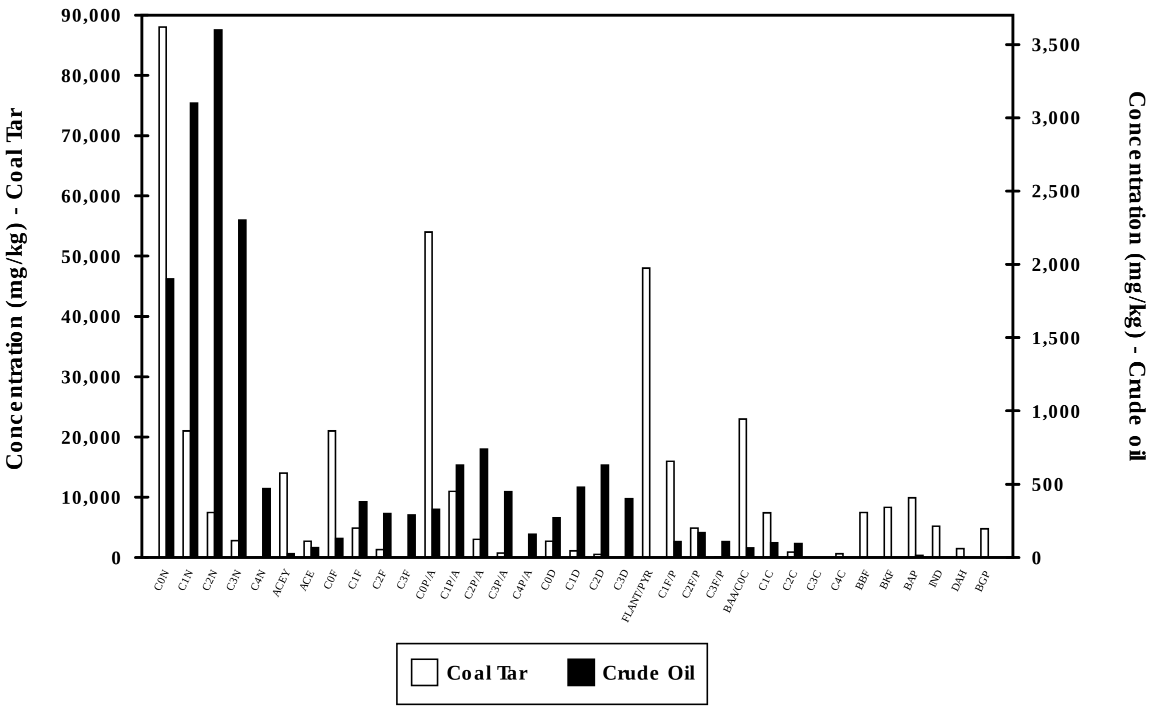


Figure 1-5
Extended PAH Profiles (EPPs) for a Petrogenic and a Pyrogenic Substance

Of particular importance to environmental forensic study is the fact that petrogenic and pyrogenic substances from different sources can have measurably different amounts of PAHs. For example, crude oils from different reservoirs can exhibit notably different ratios of trialkylated dibenzothiophenes to trialkylated phenathrenes. Similarly, the ratios of dialkylated chrysene to chrysene varies among certain pyrogenic sources.

Thus, a list of 48 parent MAHs and PAHs and alkylated MAH and PAH groups were measured routinely in the EPRI samples. In addition, dibenzofuran, dibenzothiophene, and alkylated dibenzothiophenes were determined. A list of these compounds is shown in Appendix A.

MGP Chemistry and Environmental Forensic Investigations

Recently, as former MGP sites have been investigated and undergone redevelopment, the owner utilities and owners of other sites have become aware of the potential complexity of the contaminant profiles at these sites. For example, several different types of NAPL may be found on a site. Each type of NAPL may or may not be physically associated with a former MGP structure. Soil or sediment samples may contain MGP residuals that may or may not resemble NAPLs found on site. Also, various petroleum products may be present. In some cases, environmental weathering processes may have severely altered the chemical composition of MGP-impacted media, confounding the interpretation of those results.

A careful review of the history of former MGP sites reveals a considerable list of potential waste products. Coal tar, CWG tar, oil gas (OG) tar, light oil, pitch, creosote, crude oil, refined tars and oils, coal, and many others were used or produced at gas plants. Fortunately, extensive literature on MGP processes and the chemistry of its raw and product materials exists. Some discriminating physical and chemical characteristics can be found in the literature for some materials (Harkins, 1988, McNeil, 1981, Rhodes, 1979, Morgan, 1931, Gas Engineers Handbook, 1965). However, little of the data in these references was generated using modern environmental forensic analytical techniques such as high resolution capillary column gas chromatography, GC/MS, or GC/IRMS.

In addition to the substantial list of fuels, products, and wastes associated with MGPs, many MGP sites were used subsequently for other purposes. As a result, there may be secondary wastes present such as polychlorinated biphenyls (PCBs) and transformer oils from a substation or gasoline or heating oil from leaking underground storage tanks (USTs).

Finally, chemicals from unrelated sources off-site may have been migrated onto the site or MGP wastes may have migrated off-site and mingled with non-MGP wastes. This latter case is frequently encountered in urban sediments.

A brief description of each of the major MGP processes is presented in the following subsections with a discussion of the potential types of substances that might be encountered at each plant type.

Coal Carbonization (CC)

Coal gas was produced in a relatively simple process in which bituminous coal was heated in an oven in the absence of air. In the process, light hydrocarbons (the gas) and heavier hydrocarbons (the tar) were driven off and subsequently separated. Impurities in the gas were removed by a variety of processes.

The types of MGP materials that might be encountered on a CC site included coal, coke, ash, coal tar, light oil, drip oils, naphthalene oil, and purifier wastes such as iron cyanide complexes. MAHs and PAHs can be detected in coal and coal tar-containing soil. Light oil, drip oil, and naphthalene oil are fractions of the coal tar and also contain MAHs and PAHs. For example, light oil is primarily benzene, toluene, xylenes, but also contains alkylated MAHs and some PAHs at low relative abundances.

Carburetted Water Gas (CWG)

In the CWG process, water gas was produced by passing steam over a bed of incandescent coal or coke. The resulting gas was rich in hydrogen but did not burn very brightly. To improve the illuminating power of the finished gas, the water gas was directed through a carburetor where oil was cracked to produce light hydrocarbons (methane, ethane, etc.) and tars. The oil/gas mix was cracked again in a superheater to complete the reaction. Impurities in the gas were removed by a variety of processes.

The use of petroleum products in CWG plants is the important difference between CC and CWG. Feedstock oils were stored and in some cases released at the site. The feedstock oils used at CWG plants were primarily middle distillate oils called gas oil. These oils were similar to modern diesel fuels. However, petroleum naphtha was used in the early years of gas manufacture and heavier oils and oil/tar blends were used at various times, particularly in the middle 1900s.

The tars produced from the CWG process had somewhat different chemical compositions as compared to CC tars. Further, CWG plants were known to generate tar/oil/water emulsions that contained substantial amounts of unreacted feedstock oil in addition to the pyrogenic tar. Therefore, the chemical compositions of CWG tars and emulsions are different from those generated at CC plants.

Finally, coal, coke, ash, coal tar, light oil, drip oils, naphthalene oil, and purifier wastes can also be found at CWG plant sites.

Oil Gas (OG)

The oil gas process was similar to CWG in that a petroleum feedstock was cracked to produce the gas with the simultaneous production of tar. However, the process involved the direct cracking of oil at high temperatures without the initial production of water gas. Therefore, coal or coke were not used.

OG wastes were similar to CWG wastes with the exception that significant amounts of lampblack were also produced. Lampblack consists mostly of small particles of carbon with some tar and some water.

Report Organization

This report is divided into four additional sections. Section 2 provides a description of the sources of the samples analyzed and the analytical methods used. Section 3 presents summaries of the results and discusses how the results can be used for forensic studies at MGP sites. Section 4 contains a summary of the conclusions and major findings. The references are given in Section 5.

In addition, there are three appendices. Appendix A shows the target analyte lists for the GC and GC/MS methods. Appendix B shows the GC/FID fingerprints generated for each sample. Appendix C contains the concentration data for all of the samples by each method.

2
METHODS AND MATERIALS

Materials

Samples of pyrogenic materials were obtained from former MGP sites, from commercial sources, and other verified sources. Some samples were collected by META Environmental, Inc. (META) personnel. Others were collected by participating utilities or their contractors and sent to META. Once at META, the samples were logged and stored in refrigerators at 4°C until sample preparation and analysis. Most samples were received in standard glass jars with Teflon™-lined screw caps or Teflon™-lined, septum-sealed screw caps used for environmental sampling. However, a few samples were received in metal cans, plastic buckets, or other types of jars. In those cases, the sample or a portion of the sample was transferred in the laboratory to a QC-acceptable glass jar with a Teflon™-lined, septum-sealed screw cap prior to placement in the refrigerated sample archive.

More than 200 samples were received over several years for this study. However, only a subset of those samples was analyzed for the various forensic parameters discussed in this report. Several factors were used to select samples for analysis. Most importantly, samples for which the nature and source of the material were reasonably known were desirable. Also, it was important to include a group of samples that covered the range of MGP processes, other coal tar sources, and some common refined petroleum products. For example, the data set could include samples of MGP tar from CWG and CC processes, as well as tar from commercial generators of coal tar products.

Tables 2-1 and 2-2 list the samples that are included in this report. A brief description of the source of each sample has been included in the table, as has the formation process when known. Thirty-four samples of tar or tarry soil were analyzed for selected parameters. The samples include former MGP tars from CWG and CC plants, as well as samples of commercial tar and tar products. In addition, two coal samples and nine petroleum product samples have been included. One of the objectives of the EPRI research was to correlate the chemical composition of MGP residuals with the type of plant or equipment that produced it. Based on the histories of the samples and the MGP site from which they were collected, Table 2-3 summarizes the known or suspected sources of the samples. These source classifications are used in Section 3 as part of the data interpretation.

Table 2-1
Tars and Tarry Materials

Sample Code	Sample Type and Source
T004	Stiff, taffy like tar from excavation at an MGP site in the northeast. The plant reportedly utilized the CWG and some oil gas processing.
T005	Fluid tar pumped from a well at an MGP tar disposal site in the northeast. Both CC and CWG were used at the plant. However, CWG was the dominant and more recent process.
T006	Fluid tar pumped from a well at an MGP site in the midwest. Both CC and CWG were used at the plant, with CWG reported as the dominant process.
T008	Fluid tar bailed from a holder or vault at an MGP site in the midwest. Both CC and CWG were used at the plant, with CC reported as the dominant process.
T009	Stiff, thick tar scooped from a holding tank at an MGP site in the midwest. CC was reported as the dominant and likely process.
T016	Fluid tar from a well at an MGP site in the northeast. CWG was the likely process, but was not confirmed.
T017	Fluid tar from a catch basin at an MGP site in the northeast. CWG was the only reported process at that plant.
T031	Tarry soil from an MGP site in the midwest. CC was the dominant process at that site.
T044	Fluid tar pumped from a well at an MGP site in the northeast. Both CC and CWG were used extensively at the site.
T045	Fluid tar pumped from a second well at the same MGP site as T044. The wells were located in different areas of the site.
T049	Coal tar obtained from a commercial source.
T060	Taffy-like tar collected with a shovel from an MGP site in the northeast. CC was the dominant process at the site.
T095	Tarry sediment collected near T044 and T045.
T124	Creosote obtained from a commercial source.
T125	Coal tar oil obtained from a commercial source.
T126	Fluid tar from a well at an MGP site in the midwest. The well was located in the area of the site where the CWG plant operated.
T136	Coal tar pitch from an MGP site in the northeast that included a tar distillation plant. The sample was a hard, black, amorphous mass.
T140	Very tarry soil from a tar separator at a small MGP site in the northeast. CWG was the only process reported at that plant.
T165	Fluid tar pumped from a well at a small MGP site in the midwest. CWG was the only process reported at that plant.

Sample Code	Sample Type and Source
T171	Fluid tar from a well at an MGP site in the mid-Atlantic. CC, CWG, and oil gas were practiced at the site.
T174	Fluid tar pumped from a well at an MGP site in the northwest. CC was the principal process at the site, however some OG was generated late in the plant's operating history. The well was located near a neighboring tar processing plant.
T175	Tarry soil from a gas holder at a small MGP site in the northeast. CC appeared to have been the only process used at that plant.
T176	Tarry soil from the same gas holder as T175.
T185	Fluid tar from the initial condenser of a commercial coke plant in the midwest.
T192	Fluid tar from a tar tank at an MGP site in the northwest. The plant was primarily a CC plant, but was later modified to an oil gas plant.
T198	Fluid tar pumped from a well at an MGP site in the mid-Atlantic. Both CC and CWG were practiced at the site.
T199	Fluid tar pumped from a well in a gas holder at the same MGP site as T198.
T201	Thick tar from tar separator at an MGP site in the midwest. The tar separator was associated with the CC portion of the plant.
T202	Thick tar from a second tar separator at the same MGP site as T201. The second tar separator also was associated with the CC portion of the plant.
T203	Fluid tar pumped from a well at the same MGP site as samples T198 and T199, but located some distance away from the gas holder.
T204	Second fluid tar sample collected from a well near T203.
T206	Fluid tar bailed from a tar separator at an MGP site in the northeast. The process could not be confirmed.
T207	Tarry soil from an MGP site in the northeast. CC was the primary process at that site.
T208	Fluid tar from a tar tank at an MGP site in the northeast. The tar tank appeared to have been associated with the CWG portion of the plant.

Table 2-2
Coal and Petroleum Samples

Sample Codes	Sample Type and Source
M006	Coal sample from utility in the northeast
M007	Coal sample from utility in the midwest
M018	Hot road patch asphalt from municipal public works
P013	High sulfur gas oil feed from commercial source
P063	No. 2 fuel oil from commercial source
P065	Bunker C oil from commercial source
P066	Prudhoe Bay crude oil from commercial source
P123	Kerosene composite from commercial source
P126	Diesel fuel composite from commercial source
P127	Fuel oil #4 from commercial source
P128	Fuel oil #6 from commercial source

Table 2-3
Known or Suspected Tar Processes

Sample	Source	Sample	Source	Sample	Source
T004	CWG	T095	UNK	T185	CO
T005	CWG	T124	CR	T192	UNK
T006	CWG	T125	CR	T198	CWG
T008	UNK	T126	CWG	T199	CWG
T009	CC	T136	CC	T201	CC
T016	CWG	T140	CWG	T202	CC
T017	CWG	T165	CWG	T203	CC
T031	CC	T171	CWG	T204	CC
T044	UNK	T174	CC	T206	UNK
T045	UNK	T175	CC	T207	CC
T049	CO	T176	CC	T208	CWG
T060	CC				

CWG – carburetted water gas; CC – coal carbonization; CO – coke oven; CR – creosote; UNK – unknown process

Methods

Sample Preparation

Samples were prepared for analysis using several methods. Tar and oil samples were diluted using EPA Method 3580A, Waste Dilution (SW-846). Sample weights and solvent volumes were adjusted as needed to achieve detection limits or to bring concentrations within the linear range of the instrument. Soil samples were extracted using EPA Method 3540C, Soxhlet Extraction. No water samples or other matrices were included in this study.

Class Fractionation

Some samples were fractionated into aliphatic, aromatic, or polar fractions. Two methods were used for the fractionation. Organic acids and organic bases were separated from the principal hydrocarbon mass using EPA Method 3650B, Acid-Base Partition Cleanup. In that procedure, a portion of the extract generated by waste dilution or Soxhlet extraction was spiked with surrogate compounds and washed with aqueous solutions of sodium hydroxide or sulfuric acid to isolate the organic acids and organic bases, respectively. Following pH adjustment, the aqueous solutions were back-extracted with methylene chloride to recover the organic compounds.

EPA Method 3630C, Silica Gel Cleanup, was used to separate the aliphatic, aromatic, and polar fractions of the diluted samples. The aliphatic fractions contained compounds such as normal alkanes, isoprenoid hydrocarbons, and biomarker compounds. The aromatic fractions contained the MAHs and PAHs, as well as certain heterocyclic compounds such as dibenzofuran and dibenzothiophene. The polar fraction contained compounds such as phenol, quinoline, and carbazole. Each fraction was collected, concentrated, and stored in a refrigerator until instrumental analysis.

Sample Analysis

Sample extracts prepared as described above were analyzed by up to three instrumental methods. Most unfractionated extracts as well as each fraction were analyzed by high resolution capillary column GC/FID using a modification of EPA Method 8100. GC/FID was used to generate fingerprints, to quantify total extractable compounds, and to quantify MAHs, PAHs, and selected aliphatic compounds.

Some extracts were analyzed by full scan GC/MS using EPA Method 8270. These analyses were used to quantify selected semivolatile organic compounds (SVOCs) and to tentatively identify unknown compounds.

Finally, some fractionated extracts were analyzed by GC/MS in the selected ion monitoring (SIM) mode for PAHs, alkylated PAHs, and biomarker compounds. This method is a modification of EPA Method 8270 and ASTM Method D 5739-95.

Gas Chromatography With Ion Ratio Mass Spectrometry (GC/IRMS)

Selected samples were analyzed by GC/IRMS for stable carbon isotope ratios of selected PAHs. The sample extracts were prepared by EPA Methods 3580A, 3540C, and 3630C along with those for the other GC/MS analyses. The extracts were then shipped to the University of Oklahoma where they were analyzed using a Varian 3410 GC coupled with a Finnigan MAT 252 isotope ratio mass spectrometer via a combustion furnace heated at 1050 °C and a water trap. A 30 meter by 0.25 mm, 5% phenylmethylsilicone capillary GC column was used so that the GC/IRMS chromatography conditions would be similar to standard GC/MS conditions.

There are no standardized methods for GC/IRMS. The accuracy and reproducibility of GC/IRMS data are mainly affected by chromatographic resolution (coeluting compounds bias the true isotope ratio of the target compound) and background material from column bleed and any UCM of the sample. The accuracy of the data was initially monitored with a set of standard compounds of known isotopic composition. Internal standards (fully deuterated n-alkanes C9, C10, C16, C19, C24, and C32) were added to the samples to provide a second control of the data. Each sample was analyzed at least two times, and standard deviations (1 σ) of the replicates were calculated for each internal standard and each PAH compound to estimate reproducibility. Analytes that showed unexpectedly high standard deviations (typically greater than 1) were examined for coelutions and their isotopic values determined from a portion of the peak with minimum interference (Mansuy, 1997).

Fourier Transform Infrared Spectroscopy (FTIR)

The infrared spectra of a few tar samples were measured. In each case, a thin film of the raw tar was placed on a silver chloride cell and a full infrared scan was collected from 4000 to 450 wavenumbers (cm^{-1}) using a fourier transform infrared spectrophotometer. Centre Analytical Laboratories, Inc conducted the FTIR analyses.

3

RESULTS AND DISCUSSION

This section presents the results of comprehensive analyses of 34 pyrogenic and 11 petrogenic samples. Table 2-1 shows the sample codes and sources of these samples. Also included are selected results from EPRI-sponsored field studies at former MGP sites. These additional data were chosen to illustrate applications of the data generated from the EPRI reference materials.

GC/FID Fingerprinting

The GC/FID chromatograms of the whole extract (unfractionated) of 34 MGP tars, MGP soils, and commercial tars are included in Appendix B. Also included in Appendix B are the GC/FID chromatograms of the whole extracts of two coal samples and seven petroleum product samples. In addition, the GC/FID chromatograms of the saturated hydrocarbon, acid, and base fractions of 19 MGP tars, MGP soils, and commercial tars, two coal samples, and seven petroleum product samples are shown.

GC/FID data were examined both qualitatively and quantitatively with the objective of finding patterns that correlated with the sources of the samples. The discussion that follows refers to the figures in Appendix B.

The hydrocarbon chemistry of refined petroleum products is well known and an extensive literature of information on petroleum products exists. The GC/FID chromatograms for seven common petroleum products were included in this report to illustrate the differences among petroleum products and between refined petroleum products and MGP wastes. For example, the chromatogram of the whole extract of the kerosene composite (P123, p. B-5) shows the typical distillate pattern consisting of a regular series of peaks corresponding to normal alkanes from about octane (C8) to about octadecane (C18). The chromatogram also includes a UCM within the same range. The UCM is “bell-shaped” reflecting the effects of the distillation process. Since kerosene consists mostly of saturated hydrocarbons, the whole extract chromatogram closely resembles the saturated hydrocarbon chromatogram (p. B-27).

In contrast, the chromatogram of the whole extract of MGP tar sample T165 (p. B-16) shows the typical CWG tar pattern. MAHs and PAHs dominate the chromatogram. Naphthalene (peak 8) is present at the highest concentration, while dibenzofuran (peak 13) is a minor constituent. No UCM is visible in the figure. In contrast to most petroleum products, the saturated hydrocarbon chromatogram of Sample T165 (p. B-36) is dramatically different from the whole extract chromatogram. For sample T165, the saturated hydrocarbon pattern closely resembles a No. 2 fuel oil or gas oil product and may be an artifact of the petroleum feedstock used at that plant.

Other MAH and PAH patterns that can be characteristic of MGP tars include the fluoranthene/pyrene (Fl/Py) ratio (peaks 17 and 18), the acenaphthylene/acenaphthene (ACY/ACE) ratio (peaks 11 and 12), and the ethylbenzene/m/p-xylene ratio (peaks 3 and 4). Figure 3-1 illustrates the use of peak ratios in GC/FID fingerprints to classify tars and tarry soil at MGP sites. The relative abundance of several peaks in two potential source samples, Site Tar A and Site Tar B, are clearly different. For example in Site Tar A, ACY is present at substantially higher concentration than ACE. In contrast, ACY is at a much lower concentration than ACE in Site Tar B. The ratio of these compounds in a NAPL seep sample near the site match Site Tar A closely.

Figure 3-2 illustrates another application of GC/FID fingerprinting. Three distinct sources are visible in the chromatograms of Figure 3-2. The top chromatogram shows a pyrogenic material with a pattern that is typical of CWG tars. Chromatogram B shows a severely weathered petroleum product. Sample B was collected near the former oil storage tank for the MGP and is most likely an old release of gas oil or other feedstock for carburetion. In contrast, chromatograms C, D, and E show varying mixtures of the MGP tar and a relatively fresh petroleum product. These samples were collected downgradient of leaking underground storage tanks that contained No. 4 fuel oil.

The fingerprints in Appendix B and the examples in Figures 3-1 and 3-2 show that GC/FID fingerprints can provide substantial discriminating power for both pyrogenic and petrogenic substances. When combined with sample preparation methods that isolate subsets of compounds, detailed compositional information is obtained by simple examination of the chromatograms.

Aromatic Hydrocarbon Composition

MAHs and PAHs were measured in 34 samples of MGP tars, MGP soils, and commercial tars by GC/FID. In addition, MAHs, PAHs, and alkylated MAHs and PAHs were measured in 21 samples of MGP tars, MGP soils, and commercial tars by GC/MS. Finally, MAHs, PAHs, and alkylated MAHs and PAHs were measured in 10 samples of petroleum products by GC/MS. The data are provided in Appendix C.

The following subsections summarize the Appendix C data and examine some of the trends and correlations that can be used for source attribution studies.

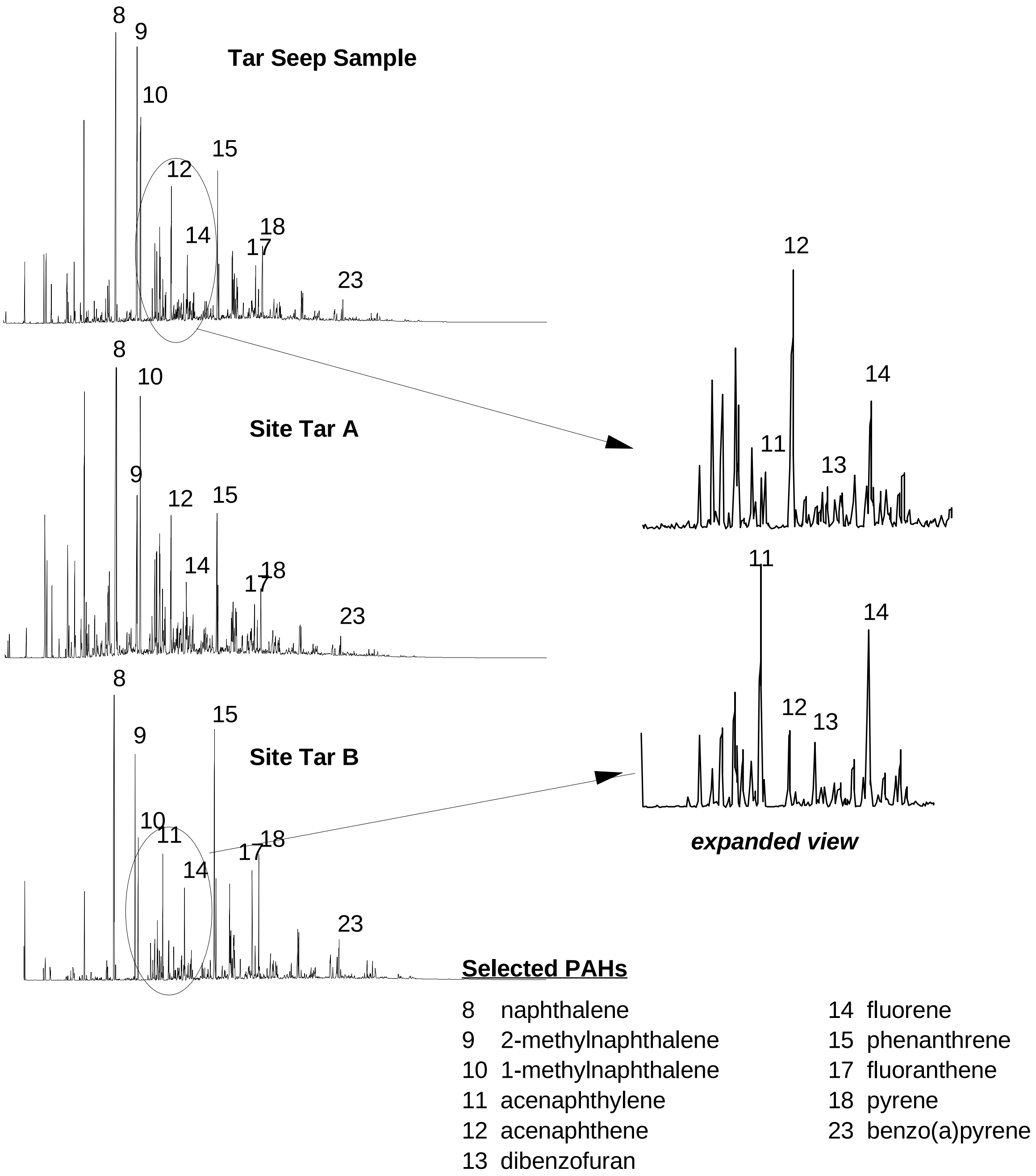
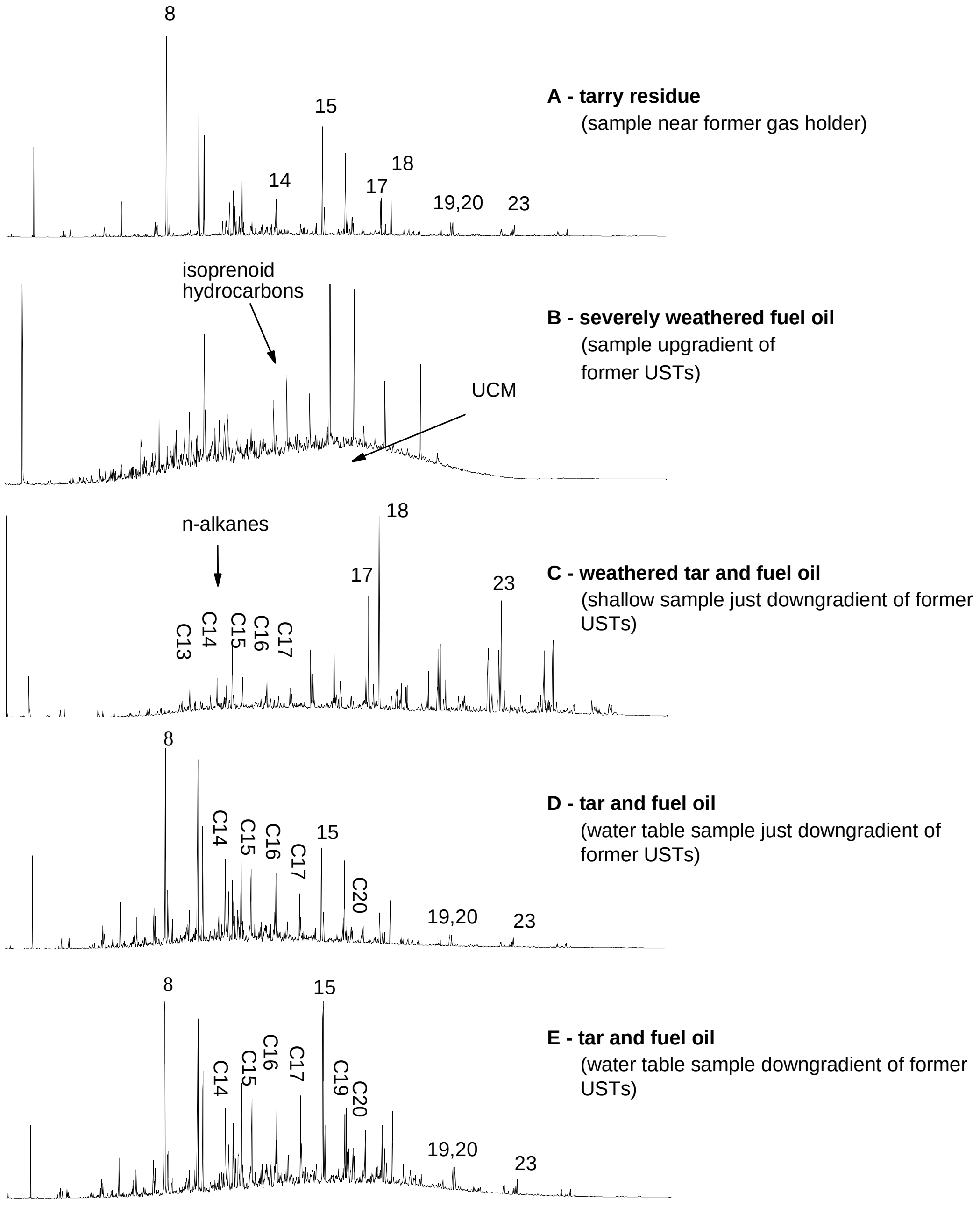


Figure 3-1
Variability in GC/FID Fingerprints of Tar Samples From an MGP Site



A - tarry residue
(sample near former gas holder)

B - severely weathered fuel oil
(sample upgradient of former USTs)

C - weathered tar and fuel oil
(shallow sample just downgradient of former USTs)

D - tar and fuel oil
(water table sample just downgradient of former USTs)

E - tar and fuel oil
(water table sample downgradient of former USTs)

Figure 3-2
Source Attribution of Co-Mingled Wastes at an MGP Site

PAHs and Alkylated PAHs

MGP tars are pyrogenic substances with a composition dominated by aromatic compounds. Within the aromatic compounds group, the parent PAHs are present at higher concentrations than their alkylated homologues. For example, the naphthalene (C0N) concentration is greater than that for the singly alkylated methylnaphthalenes (C1N), and much greater than those for the doubly alkylated dimethyl- and ethylnaphthalenes (C2N). This pattern is repeated for fluorene, phenanthrene, fluoranthene and pyrene, and the other parent PAHs. The data are commonly reported in tables and bar graphs. For example, Figure 3-3 shows a bar graph representing the EPP for MGP tar T165. The pyrogenic pattern is immediately apparent using the bar graph representation of the data. In addition, when the data are normalized and then plotted, the bar graphs can be compared by overlap.

In contrast, the characteristic pattern of PAHs and alkylated PAHs in petrogenic substances consists of alkylated homolog groups at higher concentrations than the parent PAH compound. This pattern is illustrated in Figure 1-5 for crude oil.

An EPP bar graph for a sample shows whether the sample is pyrogenic or petrogenic and can suggest whether the material has degraded from its fresh condition. Degradation is indicated by the depletion of parent compounds verses their alkylated homologues. PAHs with lower numbers of attached alkyl carbons degrade more rapidly than those with larger numbers of attached alkyl carbons. The EPPs for the pyrogenic samples analyzed in this study are all very similar except for the samples of pitch and weathered soil. They have not been reproduced for this report, but can be readily generated from the data in Appendix C.

Compound Ratios

The ratios of the PAHs and alkylated PAHs can be used as indicators of the source of the material. For example, CWG tars commonly have fluoranthene/pyrene (Fl/Py) ratios of between about 0.5 and 0.9. In contrast CC, CO, and CR type tars have Fl/Py ratios greater than about 1.0. This is illustrated in Figure 3-4 where the FL/Py ratios of the tars are plotted verses the dibenzofuran/fluorene ratios (D/F). Table 3-1 lists the Fl/Py ratios for those samples analyzed by GC/MS while Table 3-2 supplements the Table 3-1 results with data from GC/FID analyses. All the CWG tars tested had Fl/Py ratios between 0.58 and 0.87, while all of the CC, CO, and CR type tars had Fl/Py ratios from 0.87 to 1.46. Based on this indicator, most or all of the other samples with uncertain sources are CWG residues.

The D/F ratio also is useful for determining the source of the tar. As shown in Figure 3-4 and Tables 3-1 and 3-2, the CWG tars had D/F ratios between 0.12 and 0.46 while the CC, CO, and CR type tars had F/D ratios between 0.39 and 1.11. This indicator ratio also suggests that the unknown samples were CWG residues.

The data shown in Figure 3-4 and Tables 3-1 and 3-2 also indicate measurable variability in the compound ratios among all the samples tested. Therefore, ratios like Fl/Py can be used to group samples by source even for pyrogenic substances produced by the same process. Other ratios that have been used to classify pyrogenic materials include ethylbenzene/xylenes, acenaphthylene/acenaphthene, phenanthrene/anthracene, and benz(a)anthracene/chrysene.

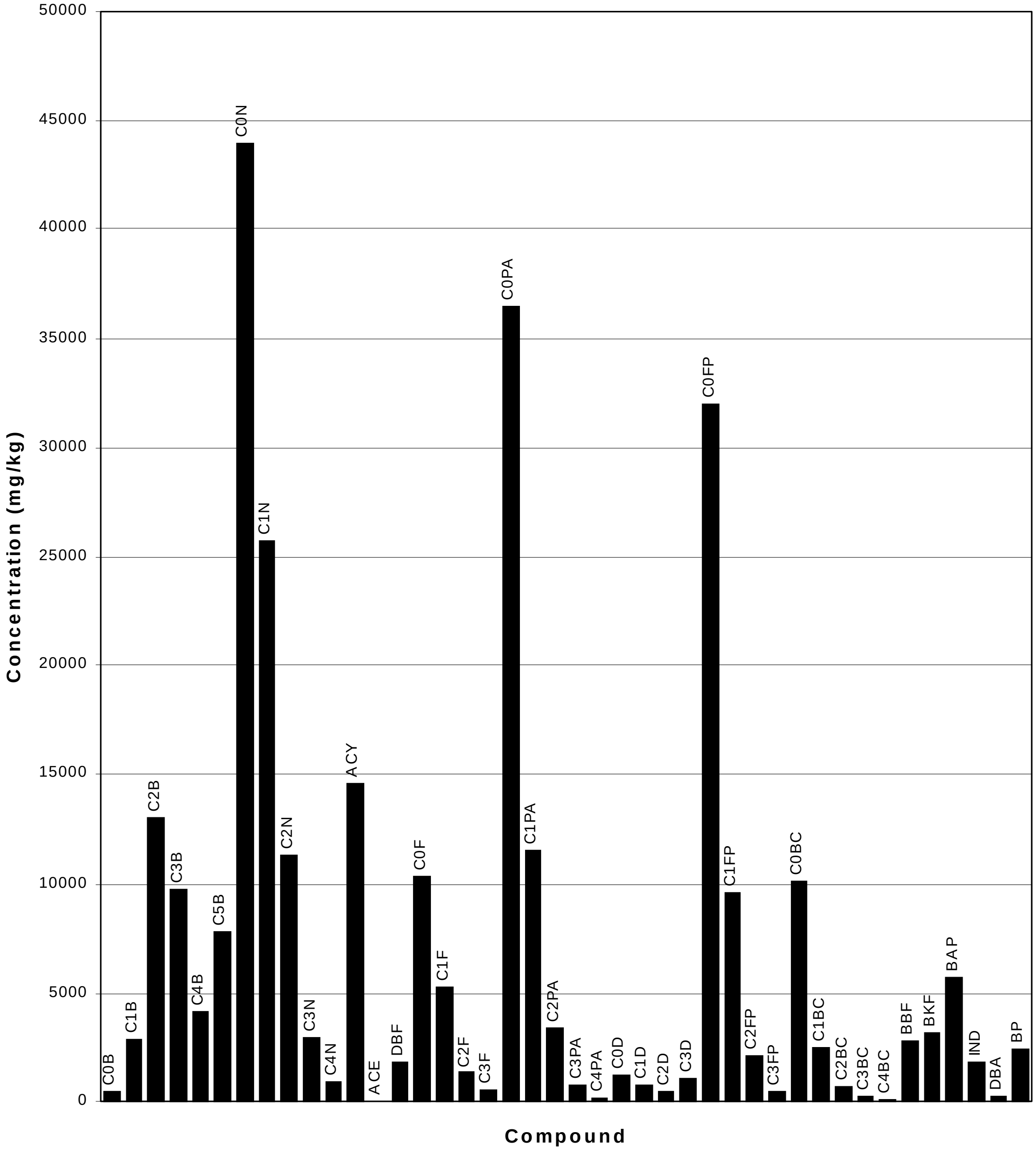


Figure 3-3
Extended PAH Profile (EPP) for Sample T165

Table 3-1
Selected Compound Ratios by GC/MS

Sample	C2D:C0D	C2PA:C0PA	Fl/Py	D/F	Source
T004	0.91	0.32	0.72	0.11	CWG
T006	0.38	0.07	0.84	0.34	CWG
T009	0.44	0.20	1.00	0.72	CC
T045	0.57	0.19	0.89	0.34	UKN
T049	0.09	0.04	1.39	0.84	CO
T060	0.26	0.08	1.27	0.86	CC
T095	2.98	0.68	0.58	0.25	UNK
T124	0.19	0.06	1.34	0.58	CR
T136	0.10	0.05	1.22	0.52	CC
T140	0.20	0.05	0.70	0.11	CWG
T165	0.39	0.09	0.73	0.18	CWG
T171	0.63	0.16	0.69	0.08	CWG
T174	0.41	0.10	0.99	0.61	CC
T175	1.35	0.26	1.04	0.48	CC
T176	0.68	0.18	0.86	0.31	CC
T185	0.11	0.03	1.27	0.75	CO
T192	0.42	0.11	0.82	0.15	UNK
T198	0.69	0.17	0.96	0.41	CWG
T199	1.68	0.40	0.73	0.17	CWG
T202	0.26	0.06	1.30	1.25	CC

Table 3-2
Selected Compound Ratios by GC/FID

Sample	Fl/Py	D/F	Source
T005	0.77	0.31	CWG
T008	0.79	0.22	UNK
T016	0.58	0.33	CWG
T017	0.74	0.19	CWG
T031	1.31	1.06	CC
T044	0.61	0.19	UNK
T125	1.42	0.76	CC
T126	0.8	0.25	CWG
T201	1.1	0.91	CC
T203	1.08	0.8	CC
T204	1.02	0.57	CC
T206	0.76	0.34	UNK
T207	1.15	0.73	CC
T208	0.77	0.28	CWG

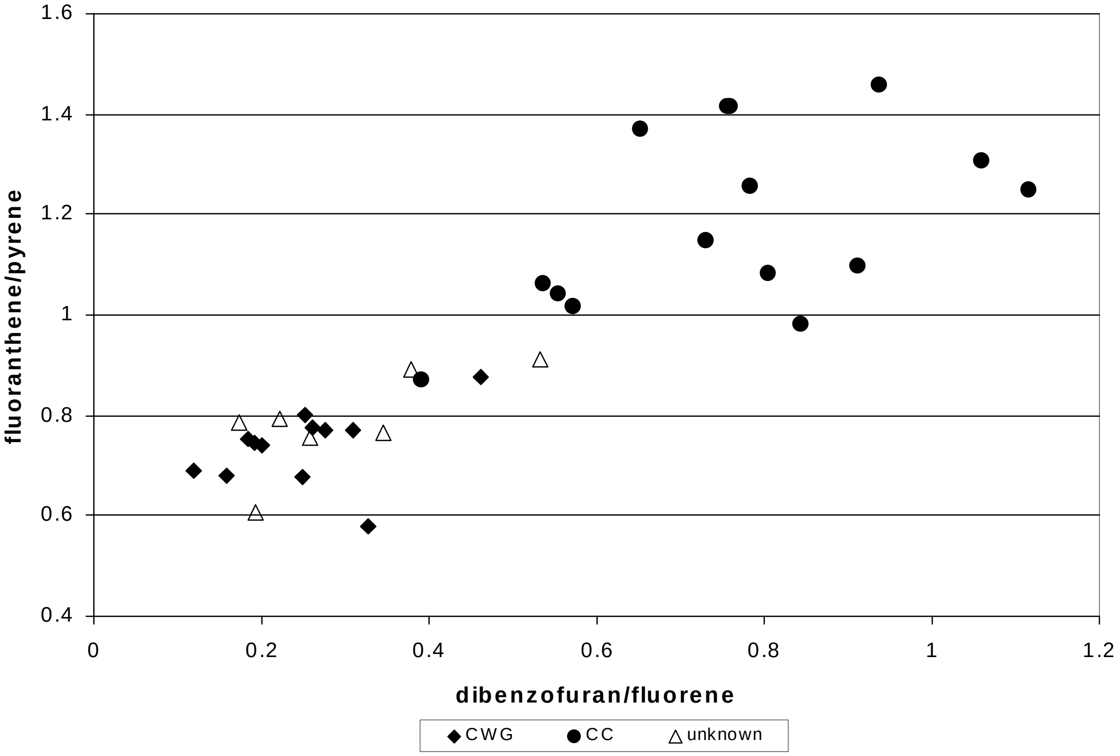


Figure 3-4
Double Ratio Plot of Tar Process Indicators

However, care must be used when using compound ratios for source attribution because some ratios can change as a substance ages in the environment. Also, systematic differences in compound ratios due to the analytical process can be misinterpreted as differences in source. All analyses performed for forensic purposes should be as accurate and precise as possible. A thorough system of quality control checks should be included with each batch of samples. For example, the Fl/Py ratios calculated from typical remedial investigation data are commonly incorrect because of the way in which many laboratories calculate the concentrations of the certain compounds. In particular, the concentration of fluoranthene is usually determined relative to the response of the internal standard, phenanthrene-d10. However, the concentration of pyrene is usually determined using the internal standard, chrysene-d12. Sample-to-sample variations in the relative recovery of these two internal standards affects the concentrations of fluoranthene and pyrene and thus their ratio. For forensic studies these two compounds should be determined relative to the same internal standard so that the basis of their ratios is consistent from sample to sample. Similarly, extreme care must be exercised to assure that variations observed in any diagnostic ratio or pattern is not caused by analytical variability.

In addition to ratios of parent PAHs, the ratios of certain alkylated PAHs have been used to classify samples and track hydrocarbon degradation in petroleum spill analyses. These compounds have not been used much for the characterization of pyrogenic substances. Figure 3-5 shows a double ratio plot of pyrogenic samples from this study. In particular, the ratio of dialkylated dibenzothiophenes (C2D) to dialkylated phenanthrenes (C2PA) is plotted verses the ratio of trialkylated dibenzothiophenes (C3D) to trialkylated phenanthrenes (C3PA). This is a common diagnostic for petroleum spills. The data indicate a substantial difference in both ratios between CWG tars and CC tars for most samples, indicating that it can be used as a diagnostic parameter for pyrogenic substances also. Other PAH/alkyl PAH ratios provide discriminating power that may be complementary to the C3D:C3PA ratio.

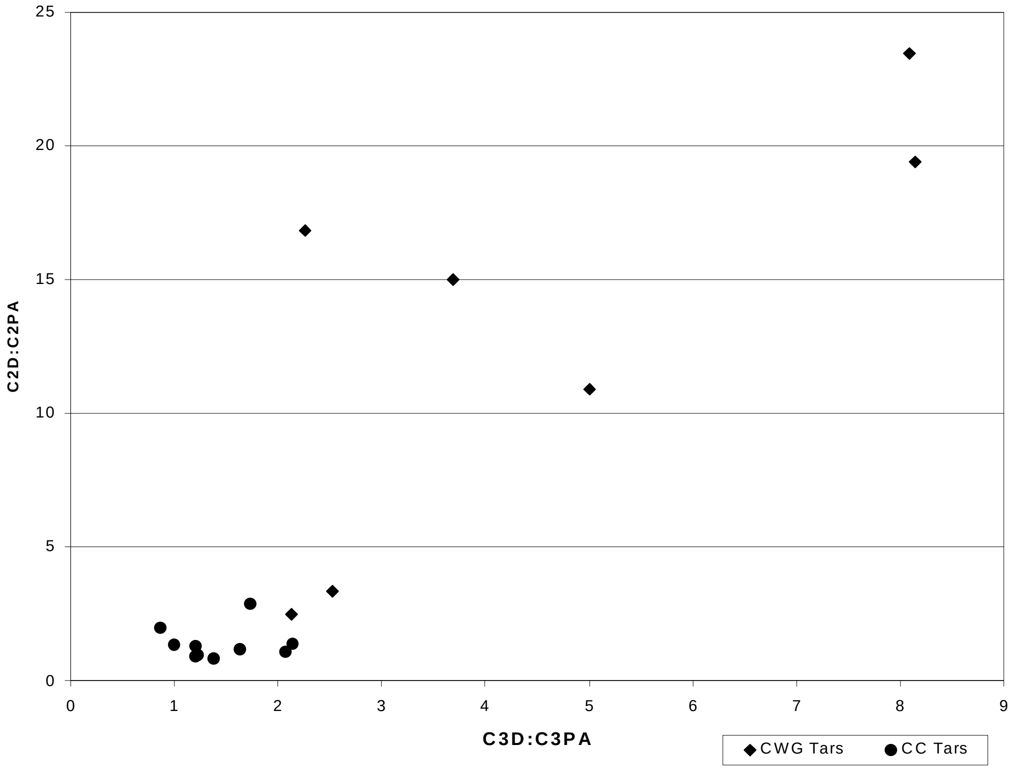


Figure 3-5
Double Ratio Plot for Pyrogenic Samples

Saturated Hydrocarbons and Biomarker Compounds

Chemical biomarkers are compounds found in some natural materials, such as crude petroleum, which can be traced to biological precursor compounds. The presence and relative abundances of the various biomarker compounds can be characteristic for each source of crude petroleum. Also, some refined petroleum products retain the biomarker compounds from the source oil, and therefore they are often useful in determining whether samples contaminated with petroleum had a common source (Philp, 1986).

In some cases, these compounds also are helpful for estimating the degree of weathering of petroleum. For example, C30 17α (H) 21β(H) hopane was found to degrade only very slowly in spilled oil and could be used with other more rapidly degraded compounds as the base compound for degradation ratios. When the appropriate number and types of samples are available, these ratios provide the relative degree of weathering for a particular petroleum substance released to the environment. However, a sample of the fresh petroleum is needed to establish the starting conditions and thus the degree of degradation from initial conditions (Butler, 1991).

Biomarker compounds have limited usefulness for pyrogenic materials, such as coal tar, because the high temperature formation conditions destroy them. Several authors report that no biomarker compounds can be detected in coal tar samples and therefore, if pyrogenic sources are present in a sample, they will not interfere with the identification of petroleum sources using biomarker compounds (Sauer, 1994). EPRI research has shown that the situation at MGP sites is more complex. Some MGP tars, especially from CWG plants contained biomarker compounds.

The sample of byproduct coke tar (T049) had one biomarker compound detected at the detection limit. Also, very few biomarker compounds were detected in a sample of commercial creosote, T124 (Appendix C). Both of these samples were generated from coal at high temperatures.

Table 3-3
Comparison of Biomarker Compound Concentrations (mg/kg) in Selected Samples

Compound[1]	M006	P013	T049	T165	T176	T004
T1	0.032	25.0	1.05			
T2	0.003	4.4			I	33
T3	0.016	54.0			0.04	12
T4	0.005	79.1			0.02	14
T5	0.007	186				29
T6	0.002	118				14
T7	0.012	100			I	10
T8	0.04	51.6			0.07	4.6
T9	0.006	40.4				2.2
T10	0.014	39.7				2.8
T11	0.005	42.2				9.0
T12	0.010	44.9				4.7
T13	0.014	74.5			0.04	20
T14	0.04	35.7			0.04	1.7
T15	0.47	102			0.51	15
T16	0.03	8.16			0.08	11
T17	0.69	205			0.82	42
T18	0.11	44.4			0.82	6.8
T19	0.08	24.8			0.24	8.5
T20	1.39	311			0.77	50
T21	0.23	60.4			0.30	9.0
T22	0.44	127			0.22	9.8
T23	0.29	77.3			0.17	7.1
T24	0.10	10.2			0.09	
T25	0.28	70.3			0.15	4.9
T26	0.20	55.4			0.11	4.7
T27	0.12	56.1			0.05	3.0
T28	0.08	44.5			0.04	2.5
T29	0.06	30.1			0.03	
T30	0.04	17.0			0.02	
T31	0.016	36.4				5.4
T32	0.02	20.2				8.1
Detection limit			1.0	1.0		1.0

1 – See Appendix A for full compound names.
I – Interference
A blank space denoted not detected at the detection limit shown.

However, as discussed previously, many MGPs did not use coal as a primary feedstock and did not operate at the same high temperatures as commercial byproduct coking facilities. In particular, some CWG and OG units utilized various petroleum products as feedstocks and operated at lower temperatures (Harkins, 1988). Further, MGP plant operators struggled to operate their plants at optimum conditions using manual controls and under a wide range of weather conditions. Consequently, tars were produced that contained various amounts of unreacted petroleum fuels. CWG plants frequently had difficulties with tar/water emulsions not encountered at CC plants, illustrating the chemical differences between coal tars and tars produced from petroleum (GRI, 1996). As seen in Table 3-3, some of these petroleum-derived tars contain the same biomarker compounds found in coal and in gas oil.

Samples T004 and T176, collected at MGP sites known to have used the CWG process, contained low levels of biomarker compounds. In contrast, sample T165, collected at a former CWG site had no detectable biomarker compounds. The lack of biomarker compounds in sample T165 might be explained by the limited boiling point range of the underlying saturated hydrocarbon fraction. As seen in Figure 3-6, the aliphatic fraction of sample T165 closely resembles diesel fuel with few detectable compounds having boiling points greater than that of n-hexacosane (C26). In contrast, most biomarker compounds have boiling points greater than C26.

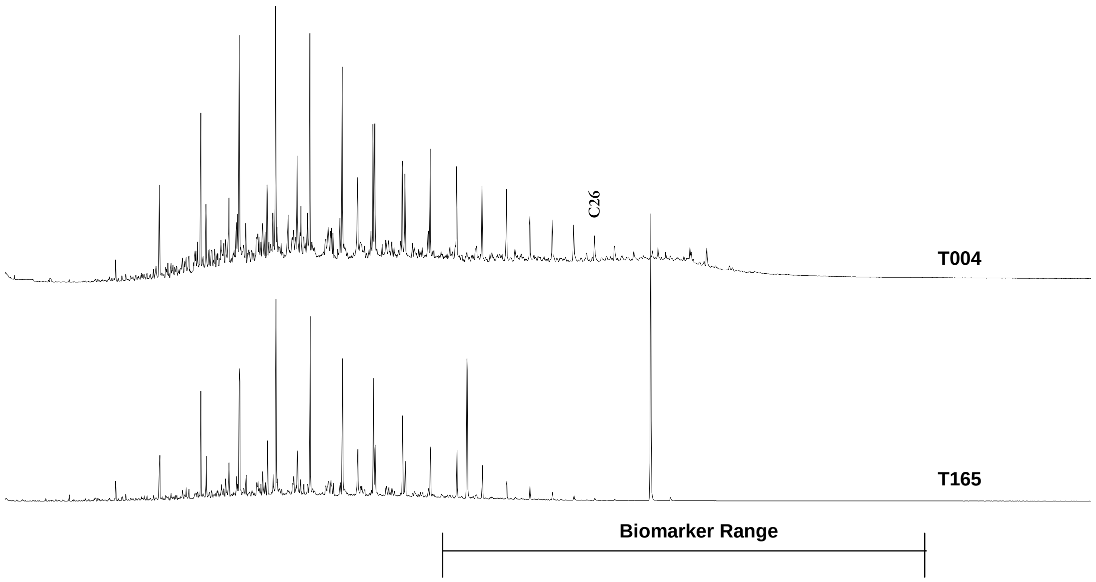


Figure 3-6
Comparison of Chromatographic Range of Common Biomarker Compounds With Saturated Hydrocarbons in Tar

The detectability of biomarker compounds in MGP tars also is influenced by analytical detection limits. For crude oil and heavy petroleum products, aliphatic hydrocarbons can comprise 50 percent or more of the total mass of the oil. Biomarker compounds are components of this major fraction of the material. In contrast, the aliphatic hydrocarbon fraction of MGP tars are typically less than 10% (EPRI, 1999) of the total mass. Since biomarker compounds are minor constituents of the aliphatic fraction, their detectability in tars is challenging.

Biomarker compounds were also detected in samples of coal (Table 3-3). The concentrations were low but measurable. Since coal was used extensively at MGP sites and coal fines frequently are found in soil samples, it is important to determine whether the coal or the MGP tar is the source of any biomarker compounds.

While many tars and other pyrogenic substances have no measurable biomarker compounds, most have detectable saturated hydrocarbon fractions. Pages B-24 to B-37 of Appendix B show the saturated hydrocarbon fractions of 19 tars or tarry soils, two coal samples, and seven common petroleum products. The GC/FID fingerprints show a range of saturated hydrocarbon patterns from no distinct saturated hydrocarbon pattern in creosote to middle weight petroleum distillate pattern in sample T165. No trend in pattern appears to distinguish CC tars from CWG tars.

However, as seen in Table 3-4, CWG tars appear to have more saturated hydrocarbons than CC, CO, and CR tars as a group. For example, the saturated hydrocarbon content of the CWG tars ranged from 3.1 to 47.2 percent with an average content of 14.5 percent. The saturated hydrocarbon content of the CC, CO, and CR tars ranged from 1.3 to 10.8 percent with an average content of 4.9 percent. The range for the CWG tars is wide and one or two outliers appear to skew the statistics. However, the trend is maintained if the median is used instead of the mean. The median for the CWG tars is 10.8 while the median for the CC, CO, and CR tars is 4.4.

As discussed in the next section, FTIR analysis of bulk tar samples shows substantially more saturated hydrocarbon character in CWG tars than in CC, CO, and CR tars. However, the FTIR technique measures saturated hydrocarbon functional groups attached to aromatic compounds as well as free saturated hydrocarbons such as decane. As stated previously, CWG tars contain more alkylated PAHs than CC, CO, and CR tars that can contribute to the FTIR response.

Table 3-4
Saturated and Aromatic Hydrocarbons in Tars and Oil

	Concentration (mg/kg)				
Library ID	**Straight**	**Saturated**	**Aromatic**	**% Saturated**	**% Aromatic**
M006	1,330	125,000	531,000	19.1	80.9
M007	2,620	197,000	267,000	42.4	57.6
M018	52,500	2,150	2,420	47.0	53.0
P013	729,000	315,000	262,000	54.6	45.4
P063	898,000	206,000	408,000	33.5	66.5
P065	296,000	192,000	161,000	54.3	45.7
P066	572,000	396,000	215,000	64.8	35.2
P123	916,000	923,000	159,000	85.3	14.7
P128	183,000	234,000	187,000	55.5	44.5
T004	317,000	69,600	2,100,000*	3.1	96.9
T005	766,000	76,400	459,000	14.3	85.7
T008	341,000	10,800	230,000	4.5	95.5
T009	285,000	22,100	182,000	10.8	89.2
T016	663,000	321,000	359,000	47.2	52.8
T017	744,000	56,800	576,000	9.0	91.0
T031	148,000	1,160	21,600	5.1	94.9
T044	482,000	43,900	453,000	8.8	91.2
T045	349,000	22,900	225,000	9.2	90.8
T049	829,000	25,600	732,000	3.4	96.6
T124	675,000	8,670	659,000	1.3	98.7
T125	662,000	23,200	476,000	4.7	95.3
T126	702,000	73,400	542,000	11.9	88.1
T136	168,000	6,050	143,000	4.1	95.9
T140	297,000	36,200	338,000	9.7	90.3
T165	683,000	40,800	521,000	7.3	92.7
T171	682,000	69,400	442,000	13.6	86.4
T175	6,730	657	5,120	11.4	88.6
T176	30,400	2,610	23,400	10.0	90.0

Sample is an outlier: Percentages calculated from the saturated fraction only

Organic Acids and Organic Bases

The concentrations of organic acids and organic bases in tars depend on the process and the feedstock (Harkins, 1988, GRI, 1996, Rhodes, 1979). In general, CC tars contain organic acids and bases, while CWG tars and OG tars do not. This reported compositional difference was tested by isolating the organic acids and organic bases from the tar matrix by extracting them with basic and acidic solutions, respectively. The resulting extracts were analyzed by GC/FID. This technique is specific for those compounds that have a significant solubility in acidic or caustic aqueous solution. For example, the organic acids phenol, cresols, xylenols, naphthalenols, and benzoic acid are readily recovered by this method. However, some higher molecular weight compounds with weakly acidic functional groups will not fractionate into the aqueous solution because of their limited solubilities. Also, the method is limited to those organic acids and organic bases that could be determined by GC under the operating conditions of this study.

The percent of total acid extractable and total base extractable compounds verses total extractable compounds was determined for 19 tar, seven petroleum and two coal samples. This was done by integrating the entire chromatogram for each of the whole, the acidic, and the basic extracts and calculating the concentrations relative to the internal standard o-terphenyl. Table 3-5 shows the calculated percentages and the known or suspected source of each sample.

The organic acid content of the known or suspected CWG tars ranged from 0.03 to 0.15 percent with an average organic acid content of 0.08±0.06 percent (n=8). In contrast, the organic acid content of CC, CO, and CR tars as a group ranged from 0.15 to 4.17 percent with an average organic acid content of 1.65±1.32 percent (n=8). It is important to note that one sample, T136, was a coal tar pitch that had had most of the light hydrocarbons including phenols, cresols, and xylenols removed by distillation. When this sample is removed from the statistics, the organic acid content of the CC, CO, and CR tars is 1.86±1.26 percent (n=7). The data in Table 3-5 do not suggest any consistent difference between CC and CO tars or creosote.

The organic base content of the known or suspected CWG tars ranged from <DL to 0.19 percent with an average organic base content of 0.06±0.06 percent (n=6). In contrast, the organic base content of the CC, CO, and CR tars ranged from 0.18 to 2.49 percent with an average organic base content of 0.97±0.68 percent (n=8). When sample T136, the coal tar pitch sample, is removed, the average base content is 1.03±0.70 percent (n=7). As with the organic acids, there does not appear to be a difference between CC and CO tars.

The two coal samples had an average organic acid content of 2.3 percent and an average organic base content of 0.17 percent. In contrast the petroleum products had almost no measurable organic acids and bases.

In addition to total organic acids by GC/FID, selected individual acid compounds were determined in the samples by GC/MS. Table 3-6 shows the concentrations of the compounds measured. Phenols were present in the CC, CO, CR, and coal samples, and absent from the CWG samples and the petroleum samples. Also, phenols were present in the soil samples from the CC sites, but at much lower concentrations.

No individual organic base compounds were quantified in this study. However, a qualitative examination of the samples showed the presence of compounds such as aniline, quinoline, and carbazole in the CC, CO, CR, and coal samples. Alkylated homologues of those compounds were detectable also. Organic base compounds were not present in CWG tars and petroleum products.

The presence or absence of organic and basic compounds in CWG tars and the petroleum products is reflected in the GC/FID chromatograms (Appendix B) where numerous compounds are visible in CC, CO, CR, and coal samples. The patterns of organic acids and organic bases vary among the samples, indicating that these chemical groups can be used to further fingerprint tars with similar PAH profiles. Figure 3-7 illustrates the differences between the organic acid fraction of a CWG tar (T199), a CC tar (T203), and a fresh CO tar (T185). Both samples T203 and T185 contain detectable levels of organic acids spanning a wide boiling point range. However, Sample T203 is depleted of phenol and alkylphenols, but contains similar concentrations of higher molecular weight compounds. These results indicate that the substantially soluble phenol, cresols, and xylenols have migrated out of the released tar, represented by T203, into the groundwater. Similar trends in contaminant weathering are observed with hydrocarbons and organic bases.

- Organic acids present at 0.15 to 4.17% in CC, CO, and CR tars
- Organic acids present at 0.03 to 0.15% in CWG tars
- phenols and alkylated phenols have been lost from the field sample (T203) relative to the fresh tar (T185)

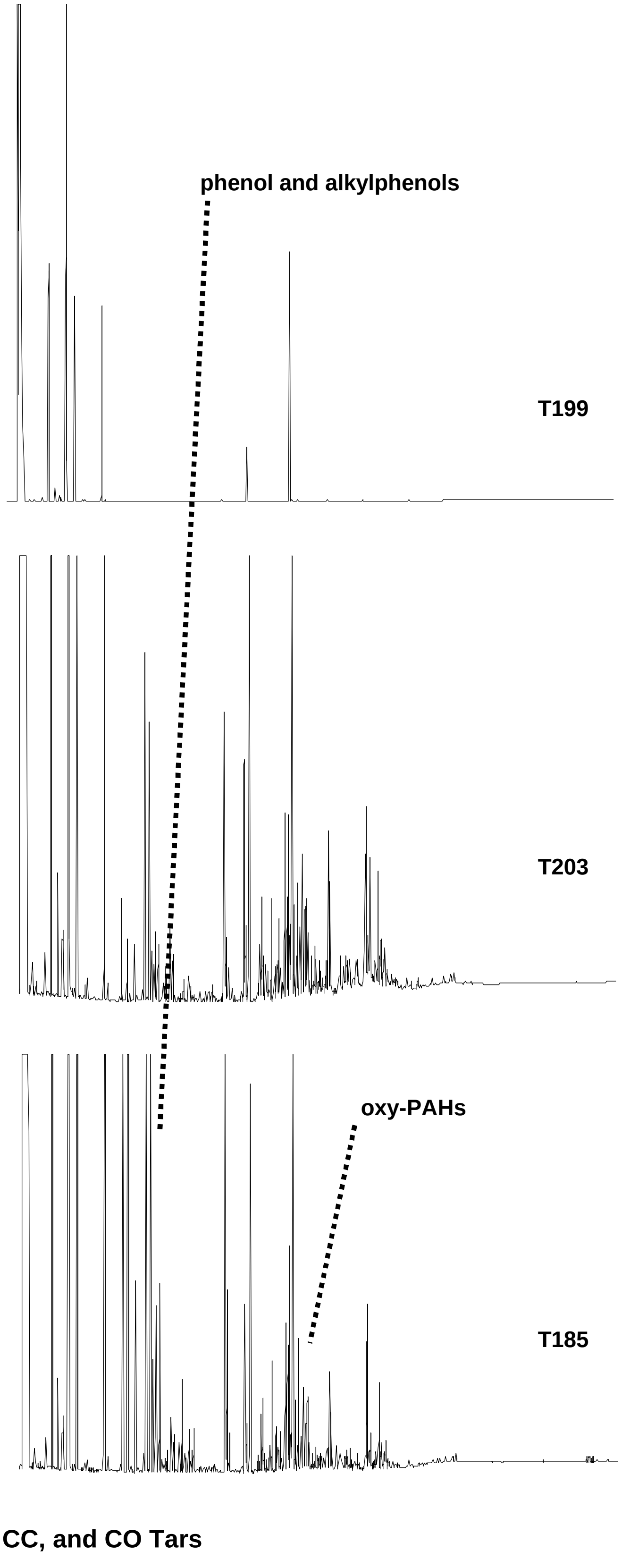


Figure 3-7
Organic Acid Content of CWG, CC, and CO Tars

Table 3-5
Concentrations and Percentages of Total Hydrocarbons, Organic Acids, and Organic Bases in Tars, Coal, and Oils

Sample	Concentration (mg/kg)			%Acid	%Base	Source
	Whole	Acid	Base			
T004	327,000	490	623	0.15	0.19	CWG
T005	775,000	463	290	0.06	0.04	CWG
T008	347,000	871	308	.25	.09	UNK
T009	288,000	12,000	3,100	4.17	1.08	CC
T016	672,000	395	132	0.06	0.02	CWG
T017	752,000	224	279	0.03	0.04	CWG
T31	157,000	2,210	1,260	1.41	0.81	CC
T044	493,000	243	262	0.05	0.05	UNK
T045	360,000	2,460	540	0.68	0.15	UNK
T049	841,000	7,820	20,900	0.93	2.49	CO
T124	687,000	15,400	6,150	2.24	0.89	CR
T125	674,000	12,600	6,900	1.87	1.02	CR
T126	714,000	500	128	0.07	0.02	CWG
T136	169,000	255	842	0.15	0.5	CC
T140	310,000	555	155	0.18	0.05	CWG
T165	695,000	330	<DL	0.05		CWG
T171	693,000	225	<DL	0.03		CWG
T175	3,292	74.2	25.9	2.25	0.79	CC
T176	27,800	44.0	51.2	0.16	0.18	CC
M006	1,350	18.7	1.07	1.39	0.08	
M007	2.650	84.6	6.89	3.2	0.26	
M018	9.940	<DL	<DL			
P013	741,000	461	135	0.06	0.02	
P063	910,000	704	426	0.08	0.05	
P065	306,000	<DL	177		0.06	
P066	583,000	190	138	0.03	0.02	
P123	1,020,000	<DL	2,310		0.23	
P128	297,000	<DL	1,340		0.45	

CWG – carburetted water gas; CC – coal carbonization; CO – coke oven; CR – creosote;
UNK – unknown process
A blank space denotes not detected.

Table 3-6
Concentrations of Selected Organic Acid Compounds

Sample	Concentration (mg/kg)				Source
	Phenol	2-Methyphenol	3&4-Methylphenol	2,4-Dimethylphenol	
T004					CWG
T005					CWG
T008		27.6	36.2	45.4	UNK
T009	941	1000	1950	1090	CC
T016					CWG
T017					CWG
T31	134	155	246	191	CC
T044					UNK
T045	114	185	293	218	UNK
T049	1200	652	1670	426	CO
T124	2980	2210	4400	1370	CR
T125	2800	2060	4140	1250	CR
T126				6.2	CWG
T136	4.0	2.6	4.6	2.0	CC
T140					CWG
T165					CWG
T171					CWG
T175	0.6	0.6	1.4	0.7	CC
T176	0.3	0.3	1.2	0.5	CC
M006	0.2	0.7	0.6	0.9	
M007			0.02	0.02	
M018					
P013					
P063					
P065					
P066				6.1	
P123					
P128					

CWG – carburetted water gas; CC – coal carbonization; CO – coke oven; CR – creosote;
UNK – unknown process
A blank space denotes not detected.

FTIR Spectroscopy

The FTIR spectra of four MGP tar samples (T198, T199, T203, T204), one sample of crude coke oven tar (T185), and one sample of commercial creosote (T124) were recorded. Figure 3-8 shows the spectra and notes some of the features that are used to identify the samples.

Petrogenic and pyrogenic substances are readily identified using the FTIR spectra. However, the method is particularly useful for identifying the source process of tars and other pyrogenic substances.

Substantial information is present on the infrared spectra of complex mixtures such as tars and oils. However, when interpreting the spectra of pyrogenic substances such as MGP tar, a few key features are important. For example, a high baseline can indicate the presence of substantial amounts of carbon and carbonaceous matter. Free carbon particles are found at significant amounts in crude CC and CO tars, and in lampblack. Less free carbon is present in CWG tars.

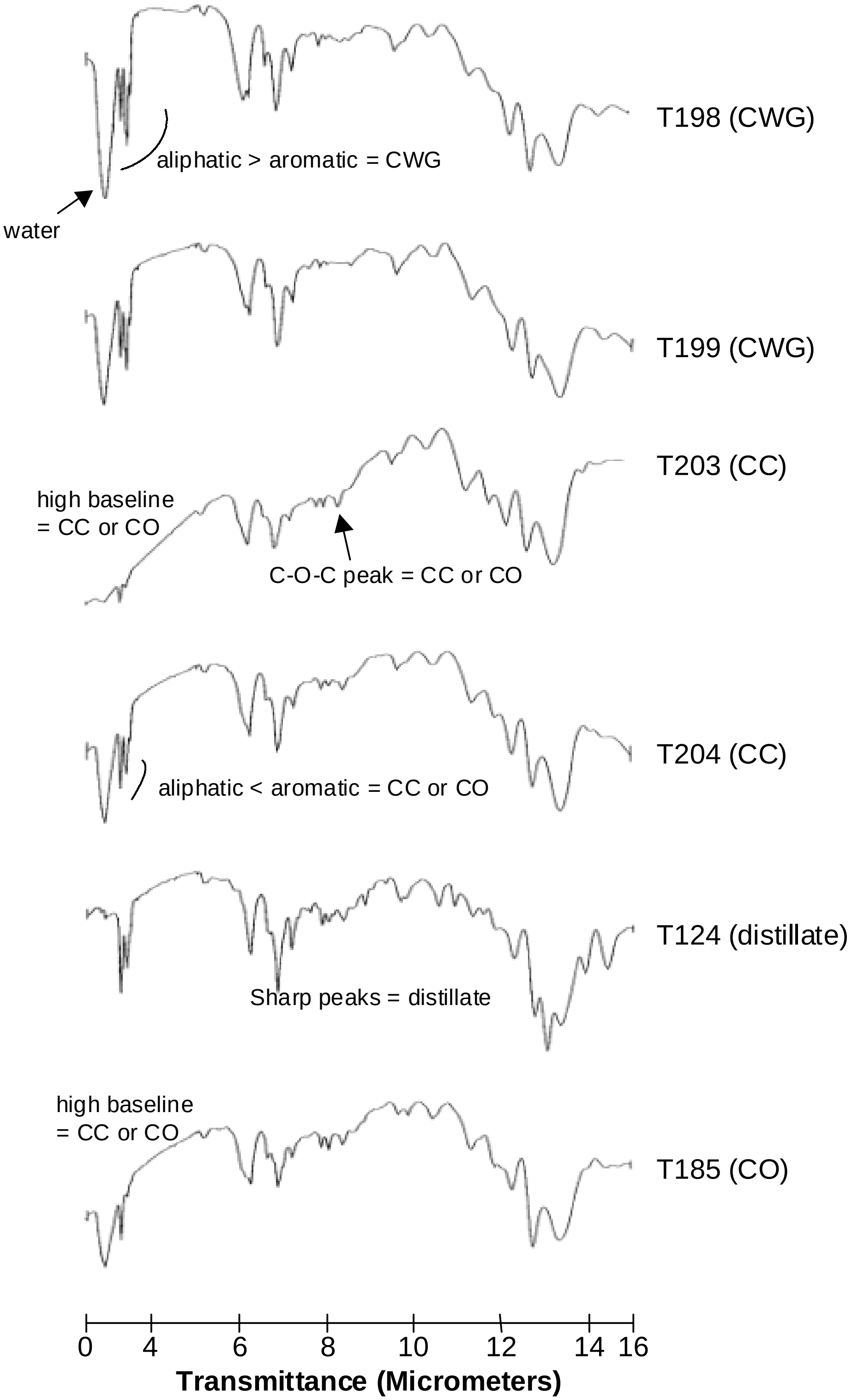


Figure 3-8
Comparison of FTIR Spectra of Tar Samples

Finally, even less free carbon is present in creosote and other coal tar products that are produced from the distillation of coal tar. Conversely, pitch and pitch products (the distillation residue) contain high levels of free carbon.

Certain peaks in the FTIR spectra show the relative amount of saturated hydrocarbons in a sample. As was observed with the GC/FID and GC/MS data, higher levels of saturated hydrocarbons indicates CWG tars, while little or no detectable saturated hydrocarbons indicates a CC tar, CO tar, or tar distillate.

Oxygen-containing compounds in the tar give peaks in the spectrum. Relatively high amounts of some oxygen-containing compounds indicate CC and CO tars and their products. The peaks for these compounds are typically absent from CWG tar spectra. The presence of other oxygen-containing compounds indicate oxidative degradation of the organic matter in the sample. These peaks are characteristic of weathered soil samples containing lower concentrations of pyrogenic or petrogenic substances.

Table 3-7 correlates the results obtained by FTIR spectroscopy with those obtained by various other forensic methods. The other methods included: examination of the ratios of D/F and Fl/Py by GC/FID; partitioning and analysis for organic acids; and analysis for biomarker compounds.

Good correlation was obtained between the FTIR results and the known or suspected tar source. Also, good correlation was obtained among the methods tested. Only two test results appeared to be incorrect. First, no biomarker compounds were detected in sample T199, a suspected CWG tar. However, as stated in an earlier section, while the presence of biomarker compounds suggests a CWG or OG tar, the absence of biomarker compounds do not eliminate CWG and OG tars as possible sources.

Second, no organic acids were detected in sample T204, a suspected CC tar. In fact, while no low molecular weight organic acid compounds, such as phenol and cresol were detectable, numerous unidentified high molecular weight acidic compounds were present. Since phenol and its alkylated homologues are quite water soluble and biodegradable, it is possible that those compounds have been depleted over time, leaving only the high molecular weight compounds. Thus, after careful consideration of the data, it appears that there is perfect agreement among the forensic methods used in this case study.

As stated in the introduction section of this report, no publication exists that systematically presents the FTIR analysis of pyrogenic and petrogenic substances potentially present at MGP sites. These data indicate that FTIR is a useful forensic method for MGP site studies and that more comparative studies of this type would be valuable.

Table 3-7
Comparison of FTIR Results to Other Forensic Methods for Six Tar Samples

Sample	GC/FID	Acids	Biomarkers	FTIR	Known or Suspected Source
T199	CWG	CWG	CC	CWG	CWG
T198	CWG	CWG	CWG	CWG	CWG
T203	CC	CC	CC	CC or CO	CC
T204	CC	CWG	CC	CC or CO	CC
T124	CC	CC	CC	Tar distillate	Creosote
T185	CC	CC	CC	CC or CO	CO

Stable Carbon Isotope Ratios

The previous subsections show that several methods are available for determining the source of pyrogenic substances at MGP sites. All of the methods, including the GC and FITR methods, measure some portion of the molecular composition of the sample and compare the results to known references. Also, the results of all of the methods become less certain as the degree of environmental degradation increases, as the concentrations of target compounds decrease, and as the number of different sources in the sample increases. Complementary methods are needed that are less susceptible to compositional changes and concentration. Stable carbon isotope ratios by GC/IRMS is one method that meets these needs.

No systematic analysis by GC/IRMS of samples from former MGP sites was found in the literature. In response, 19 samples of tar or tarry soil were analyzed. The analyses were done in three batches over a two-year period. The stable carbon isotope ratios of many MAHs, PAHs, and other compounds were measured in one batch or the other. From these data, this report presents the results of a subset of 13 PAHs for which data were available in most samples. Appendix C, pages C-19 to C-22, list all of the results.

The data have several characteristics that are important to understand when applying this method to environmental forensic studies.

- The range of $\delta^{13}C$ (‰) values obtained for tar samples from diverse sources was small. In general, $\delta^{13}C$ (‰) values ranged from about –21 to –30 ‰, a difference of only 9‰. The difference between the stable carbon isotope values for PAHs in other pyrogenic sources is somewhat greater, as illustrated by the two combustion byproducts shown in Figure 1-3. Therefore, the GC/IRMS technique involves the measurement of small differences between samples. Consequently, the measurements must be very precise, they must be reproducible from batch to batch, and they must be traceable to known standard materials.
- Within the narrow range of $\delta^{13}C$ (‰) values for the MGP materials tested, some samples were well separated. For example, Figure 3-9 shows the carbon isotope ratio profiles for a

CC tar from an MGP site in the northeast and a CWG tar from an MGP site in the midwest. The carbon isotope ratio profiles for the samples are distinctly different and the differences are much greater than the variance of repeated measurements of each sample. Clearly, soil or water impacts by one of these two sources could be distinguished from the other source. Because the carbon isotope ratio profiles are independent of concentration, this capability is especially useful for investigations of low level soil contamination and background PAH determinations.

- In contrast to tars T060 and T165, shown in Figure 3-9, the carbon isotope ratio profiles of other tars were not different. Figure 3-10 shows the carbon isotope ratio profiles of two CWG tars, one from an MGP site in the midwest and one from a second MGP site in a different midwest city. The carbon isotope ratio profiles for these samples are nearly identical. Separating impacts by these two materials would be difficult or impossible using GC/IRMS alone.
- A distinct difference in ^{13}C enrichment was found between CC, CO, and CR samples and CWG samples. Table 3-8 Lists the mean δ^{13}C (‰) values for each of the samples tested. The values for the CC, CO, and CR samples ranged from -22.5 to –24.175 ‰ with an average value of –23.31 ‰. The values for CWG samples ranged from –22.83 to –28.76 ‰, with an average value of –26.56 ‰. While small, there is a consistent difference between coal tars and CWG tars.

Table 3-8
Average Carbon Isotope Ratios, δ^{13}C (‰), for PAHs in Tars

Sample	Mean Ratio	Source	Sample	Mean Ratio	Source
T006	-28.76	CWG	T185	-23.26	CO
T044	-26.14	UNK	T192	-22.8	UNK
T045	-25.389	UNK	T198	-22.83	CWG
T060	-23.297	CC	T199	-25.65	CWG
T124	-24.175	CR	T201	-22.93	CC
T136	-23.298	CC	T202	-22.5	CC
T140	-27.06	CWG	T203	-22.845	CC
T165	-28.38	CWG	T204	-23.854	CC
T171	-26.66	CWG	T206	-26.032	UNK
T174	-23.62	CC			

CWG – carburetted water gas; CC – coal carbonization; CO – coke oven; CR – creosote; UNK – unknown process

Some MGP forensic studies are interested in whether a particular tar or contaminated soil contains CC or CWG residues. This might be important for estimating the age of the material for insurance recovery, tracking the migration of MGP tar from known sources, or allocating the contributions among various parties that operated on or near the site.

Samples T044 and T045 were two tars collected from distant monitoring wells on a large MGP site. The GC/FID fingerprinting and organic acid content data indicated that Sample T044 was CWG tar while sample T045 was CC tar. However, the saturated hydrocarbon profiles and FTIR results indicated that both samples were CWG tars, and were “qualitatively identical.” The compositions of these two samples were investigated further using GC/IRMS. Figure 3-11 shows the carbon isotope profiles for the two samples as compared to a known CWG tar and CC tar. Based on the GC/IRMS data, samples T044 and T045 were from similar sources. However, several isotope ratio differences, such as for naphthalene, chrysene, and benzo(a)pyrene indicate that the tars were not identical and that they were not from the same batch. For example, they may have been produced at different times from different feedstocks. Also, the carbon isotope profiles of both tars were measurably different from the reference CWG and CC tars, again suggesting differences in feedstocks. Based on the ranges for CWG and CC tars, samples T044 and T045 are both CWG tars.

The GC/IRMS method and EPRI reference data were used at another MGP site where tar was observed seeping out of the ground some distance away from several potential sources. Tars from the seeps and from each of the sources were analyzed by GC/IRMS. Figure 3-12 shows results indicating that the tar found near Sample 9, in area 1, was most similar to the tar seep.

As shown by the data generated for this report, the determination of stable carbon isotope ratios by GC/IRMS can be used as a complementary method for identifying the source of pyrogenic substances at MGP sites.

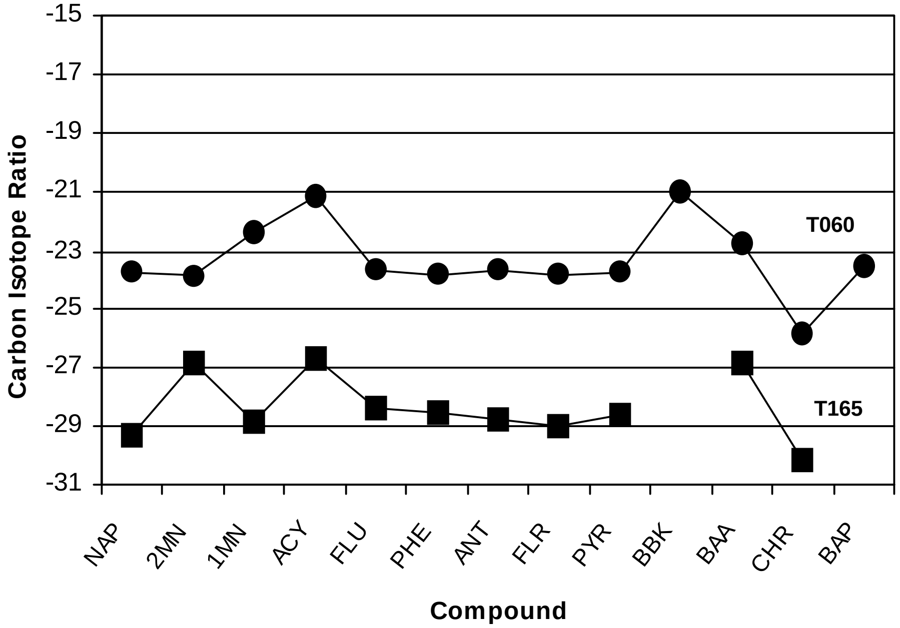


Figure 3-9
Comparison of the Stable Carbon Isotope Ratio Profiles of Two MGP Tars

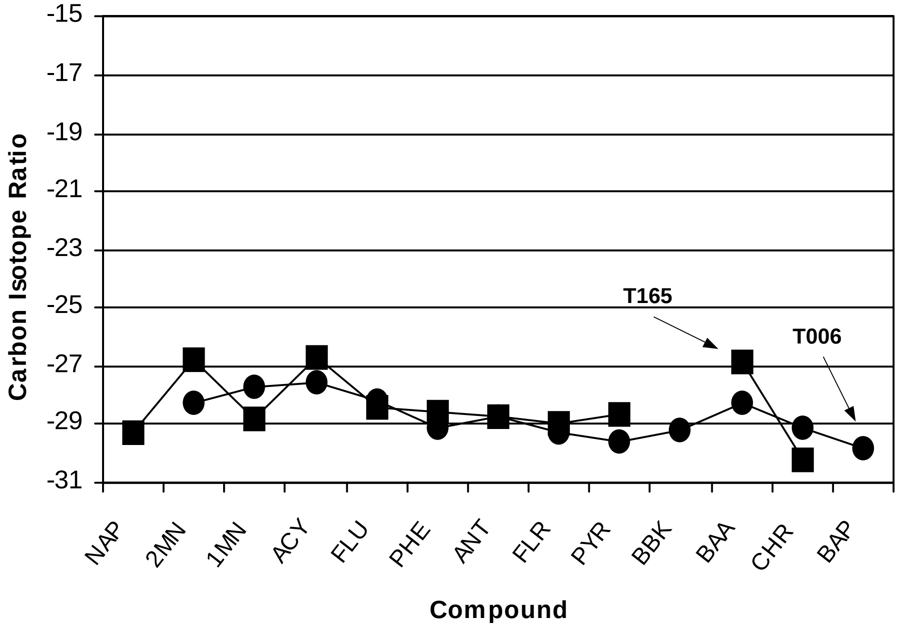


Figure 3-10
Comparison of the Stable Carbon Isotope Profiles of Two Tars From CWG Plants

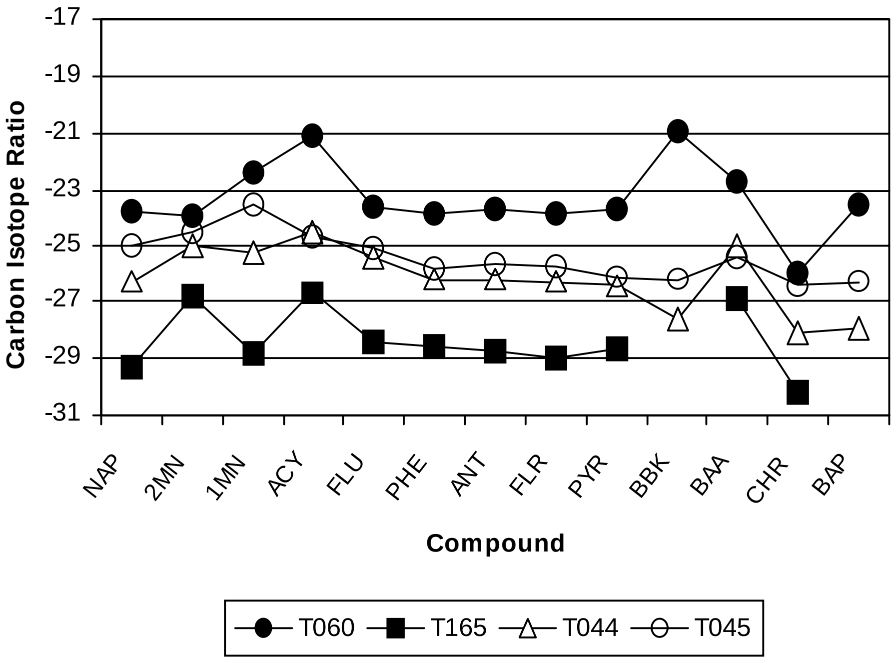


Figure 3-11
Comparison of the Stable Carbon Isotope Ratio Profiles for Two Suspected CWG Tars to Known CWG Tar and CC Tar

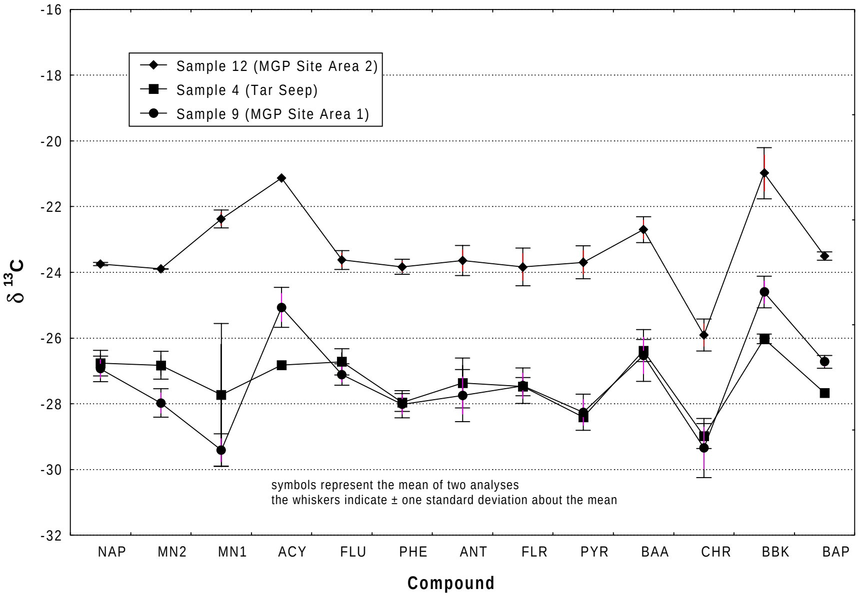


Figure 3-12
Comparison of δ^{13}C Values of PAHs at an MGP Site

4

CONCLUSIONS

As part of on-going EPRI research on MGP site investigation methods and chemical transport and fate, a study was conducted to examine the limits of environmental forensic methods for MGP source attribution. For this purpose, 34 samples of MGP tars, MGP soils, and commercial tar products were characterized chemically for MAHs, PAHs, alkylated PAHs and chemical fingerprints. Also analyzed were two coal samples and seven petroleum product samples. Four analytical methods were used to characterize the samples, GC/FID, GC/MS, FTIR, and GC/IRMS. Additionally, a subset of the samples were fractionated into saturated hydrocarbon, aromatic hydrocarbons, organic acids, and organic bases prior to analysis to examine their compositions more closely. These methods are commonly used in environmental forensic chemistry to identify the types of chemicals in a sample, to determine the source of the chemicals, and to classify or group samples by their source. Based on the results obtained in this study, the following conclusions were reached.

1. Both pyrogenic and petrogenic substances are found at MGP sites. However, pyrogenic substances, primarily tars and tar-impacted soil, are the major type of contamination present. The tars and tar-derived materials at MGP sites fall into to major categories by their formation process, CC and CWG residuals. The composition of MGP tars can be used to determine the formation process and to identify samples with common sources. For example, the values of compound ratios such as fluoranthene/pyrene (Fl/Py), dibenzofuran/fluorene (D/F), and alkylated dibenzothiophenes and alkylated phenanthrenes (C3D/C3PA) correlate with the source of the tar. For example, CWG tars have Fl/Py ratios between about 0.5 and 0.9, while CC tars have Fl/Py ratios between about 0.9 and 1.5. In addition, compound ratios are independent of concentration and many remain stable as MGP residuals weather in the environment.

2. CWG tars have very low to non-detectable amounts of organic acids and organic bases. Conversely, CC tars have measurable amounts of those compounds. Both CWG tars and CC tars contain saturated hydrocarbons. However, the concentration of total saturated hydrocarbons is consistently higher in CWG tars than in CC tars. Further, several saturated hydrocarbon patterns were observed in the samples reflecting the feedstock and formation process of the tar.

3. Pyrogenic substances reportedly contain no detectable biomarker compounds. However, some CWG tars were found to have low but measurable concentrations of those compounds. These features can be used to deduce the source of pyrogenic material in a sample and to group samples.

4. All of the analytical methods tested provided information that could be used for environmental forensic studies. The methods were complementary, with no one method providing all of the information all of the time. GC/FID fingerprints show visibly the differences between pyrogenic and petrogenic materials, provide the concentrations of certain key parameters, such as fluoranthene and pyrene, or total organic acids. However, GC/FID analyses cannot provide the concentrations of PAHs in petrogenic materials or the concentrations of alkylated PAHs, organic acids, and organic bases in petrogenic and pyrogenic materials. Also, GC/FID fingerprinting becomes increasingly uncertain as the number of contamination types in the samples increases or as the degree of weathering increases.

5. GC/MS provides fingerprints and the concentrations of a wide range of diagnostic compounds. It is the only method that can accurately determine the concentrations of alkylated PAHs and biomarkers. However, source attribution with GC/MS also breaks down as the number of contamination types in the samples increases or as the degree of weathering increases.

6. By making measurements on the whole sample, FTIR spectroscopy was effective at discriminating different tar types. Components of the sample that are not measured by chromatographic methods, such as the free carbon content, could be used to differentiate crude tar from distillates. However, FTIR spectroscopy is less effective for soil extracts than for pure NAPLs, is not very sensitive, becomes increasingly uncertain as the mixture complexity increases, and often cannot identify minor, but important, components of the sample in the presence of larger amounts of other substances.

7. One of the more difficult problems for environmental forensics at MGP sites is determining the source of PAHs at low concentrations or when severely weathered. In some cases, GC/IRMS can provide the complementary data needed to determine if low level or weathered contamination originated at an MGP. Because stable carbon isotope ratios appear to remain the same as pyrogenic and petrogenic substances weather, the isotope profiles of fresh and aged materials can be compared. However, in many cases, the carbon isotope ratio differences between sources are small and measurements have to be very precise to differentiate reliably.

8. Many of the diagnostic parameters identified in this report rely on small differences between like samples. Therefore, measurements made for environmental forensic purposes must be accurate and very precise. This requirement applies to all of the analytical methods. An extensive quality control system must be implemented to minimize batch-to-batch variability and therefore minimize misinterpretations.

5
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A

TARGET COMPOUNDS

Table A-1
SVOCs by EPA Method 8270C

pentachloroethane
phenol
bis(2-chloroethyl)ether
aniline
2-chlorophenol
benzy alcohol
2-methylphenol
4-methylphenol
bis(2-chloroisopropyl)ether
3-methylphenol
N-nitrosopyrolidine
N-nitroso-di-n-propylamine
N-nitrosomorpholine
hexachloroethane
N-nitrosopiperidine
2-nitrophenol
2,4-dimethylphenol
bis(2-chloroethoxy)methane
2,6-dichlorophenol
1,2,4-trichlorobenzene
naphthalene
4-chloroaniline
2,4-dichlorophenol
hexachloropropene
hexachlorobutadiene
1,2,3-trichlorobenzene
N-nitrosodi-n-butylamine
4-chloro-3-methylphenol
2-methylnaphthalene
1,2,4,5-tetrachlorobenzene
hexachlorocyclopentadiene
2,4,6-trichlorophenol
2,4,5-trichlorophenol
2-nitroaniline
dimethylphthalate
acenaphthylene
4-nitrophenol
dibenzofuran
pentachlorobenzene
2,3,4,6-tetrachlorophenol
diethylphthalate
4-chlorophenyl-phenylether
fluorene
4-nitroaniline
4,6-dinitro-2-methylphenol
N-nitrosodiphenylamine
4-bromophenyl-phenylether
hexachlorobenzene
pentachlorophenol
phenanthrene
dinoseb (DNBP)
anthracene
di-n-butylphthalate
fluoranthene
pyrene
butylbenzylphthalate
benz(a)anthracene
chrysene
bis(2-ethylhexyl)phthalate
di-n-octylphthalate
benzo(b)fluoranthene
benzo(k)fluoranthene
benzo(a)pyrene
indeno(1,2,3-cd)pyrene
dibenz(a,h)anthracene
benzo(g,h,i)perylene
2-chloronaphthalene

Table A-2
PAHs and Alkylated PAHs by GC/MS/SIM

Code	Compound	Code	Compound
C0B	benzene	C1PA	C1-phenanthrene/anthracene
C1B	C1-benzene	C2PA	C2-phenanthrene/anthracene
C2B	C2-benzene	C3PA	C3-phenanthrene/anthracene
C3B	C3-benzene	C4PA	C4-phenanthrene/anthracene
C4B	C4-benzene	C0D	dibenzothiophene
C5B	C5-benzene	C1D	C1-dibenzothiophene
	toluene	C2D	C2-dibenzothiophene
	ethylbenzene	C3D	C3-dibenzothiophene
	m/p-xylene		fluoranthene
	styrene		pyrene
	o-xylene	C0FP	C0-fluoranthene/pyrene
	1,2,4-trimethylbenzene	C1FP	C1-fluoranthene/pyrene
C0N	naphthalene	C2FP	C2-fluoranthene/pyrene
C1N	C1-naphthalene	C3FP	C3-fluoranthene/pyrene
C2N	C2-naphthalene		benz(a)anthracene
C3N	C3-naphthalene		chrysene
C4N	C4-naphthalene	C0BC	C0-benz(a)anthracene/chrysene
	2-methylnaphthalene	C1BC	C1-benz(a)anthracene/chrysene
	1-methylnaphthalene	C2BC	C2-benz(a)anthracene/chrysene
	acenaphthylene	C3BC	C3-benz(a)anthracene/chrysene
	acenaphthene	C4BC	C4-benz(a)anthracene/chrysene
	dibenzofuran		benzo(b)fluoranthene
C0F	fluorene		benzo(k)fluoranthene
C1F	C1-fluorene		benzo(a)pyrene
C2F	C2-fluorene		indeno(1,2,3-cd)pyrene
C3F	C3-fluorene		dibenz(a,h)anthracene
	phenanthrene		benzo(g,h,i)perylene
	anthracene		
C0PA	C0-phenanthrene/anthracene		

Table A-3
Biomarker Compounds by GC/MS/SIM

Code	Compound	Code	Compound
C12	decane	T23	22R-17α(*H*),21β(*H*)-30-homohopane
C16	heptadecane	T24	17β(*H*),21β(*H*)-hopane (Hopane)
C18	octadecane	T25	22S-17α(*H*),21β(*H*)-30,31-bishomohopane
C20	eicosane	T26	22R-17α(*H*),21β(*H*)-30,31-bishomohopane
C30	triacontane	T27	22S-17α(*H*),21β(*H*)-30,31,32-trishomohopane
I1	2,4,10-Trimethyldodecane (Farnesane)	T28	22R-17α(*H*),21β(*H*)-30,31,32-trishomohopane
I2	2,4,10-Trimethyltridecane	T29	22S-17α(*H*),21β(*H*)-30,31,32,33-tetrakishomohopane
I3	2,6,10-Trimethylpentadecane (Norpristane)	T30	22R-17α(*H*),21β(*H*)-30,31,32,33-tetrakishomohopane
Pr	2,6,10,14-Tetramethylpentadecane (Pristane)	T31	22S-17α(*H*),21β(*H*)-30,31,32,33,34-pentakishomohopane
Ph	2,6,10,14-Tetramethylhexadecane (Phytane)	T32	22R-17α(*H*),21β(*H*)-30,31,32,33,34-pentakishomohopane
T1	C_{19} tricyclic terpane	S1	C_{20} 5α(*H*),14α(*H*),17α(*H*)-sterane
T2	C_{20} tricyclic terpane	S2	C_{21} 5α(*H*),14β(*H*),17β(*H*)-sterane
T2	C_{21} tricyclic terpane	S3	C_{22} 5α(*H*),14β(*H*),17β(*H*)-sterane
T4	C_{22} tricyclic terpane	S4	C_{27} 20S-13β(*H*),17α(*H*)-diasterane
T5	C_{23} tricyclic terpane	S5	C_{27} 20R-13β(*H*),17α(*H*)-diasterane
T6	C_{24} tricyclic terpane	S6	C_{27} 20S-13α(*H*),17β(*H*)-diasterane
T7	C_{25} tricyclic terpane	S7	C_{27} 20R-13α(*H*),17β(*H*)-diasterane
T8	C_{26} tricyclic terpane	S8	C_{28} 20S-13β(*H*),17α(*H*)-diasterane
T9	C_{27} tetracyclic terpane	S9	C_{27} 20S-5α(*H*),14α(*H*),17α(*H*)-cholestane
T10	C_{27} tetracyclic terpane	S10	C_{27} 20R-5α(*H*),14β(*H*),17β(*H*)-cholestane
T11	C_{28} tetracyclic terpane	S11	C_{27} 20S-5α(*H*),14β(*H*),17β(*H*)-cholestane
T12	C_{28} tetracyclic terpane	S12	C_{27} 20R-5α(*H*),14α(*H*),17α(*H*)-cholestane (SS1)
T13	18α(*H*),21β(*H*)-22,29,30-trisnorhopane (Ts)	S13	C_{29} 20S-13β(*H*),17α(*H*)-diasterane
T14	17α(*H*),18α(*H*),21α(H)-25,28,30-trisnorhopane	S14	C_{28} 20S-5α(*H*),14α(*H*),17α(*H*)-ergostane
T15	17α(*H*),21β(*H*)-22,29,30-trisnorhopane (Tm)	S15	C_{28} 20R-5α(*H*),14β(*H*),17β(*H*)-ergostane
T16	17α(*H*),18α(*H*),21β(H)-28,30-bisnorhopane	S16	C_{28} 20S-5α(*H*),14β(*H*),17β(*H*)-ergostane
T17	17β(*H*),21α(*H*)-30-norhopane	S17	C_{29} 20R-13α(*H*),17β(*H*)-diasterane
T18	18α(*H*),21β(*H*)-30-norneohopane	S18	C_{28} 20R-5α(*H*),14α(*H*),17α(*H*)-ergostane
T19	17α(*H*),21β(*H*)-30-norhopane (Normoretane)	S19	C_{29} 20S-5α(*H*),14α(*H*),17α(*H*)-stigmastane
T20	17α(*H*),21β(*H*)-hopane	S20	C_{29} 20R-5α(*H*),14β(*H*),17β(*H*)-stigmastane
T21	17β(*H*),21α(*H*)-hopane (Moretane)	S21	C_{29} 20S-5α(*H*),14β(*H*),17β(*H*)-stigmastane
T22	22S-17α(*H*),21β(*H*)-30-homohopane	S22	C_{29} 20R-5α(*H*),14α(*H*),17α(*H*)-stigmastane

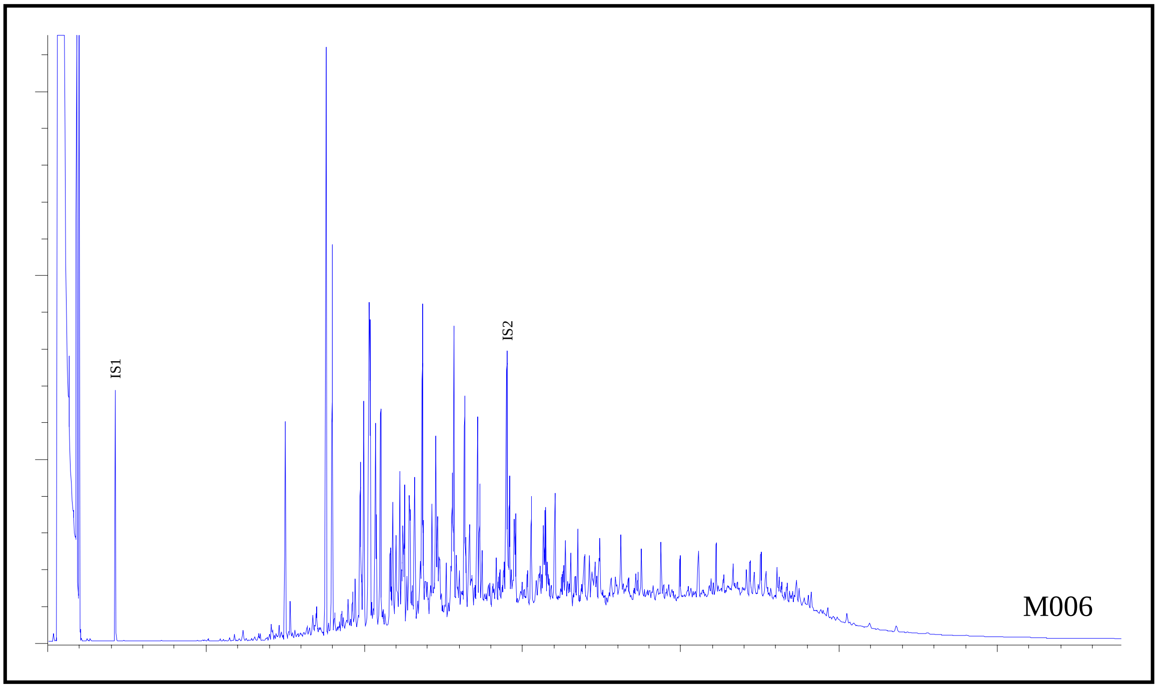
B

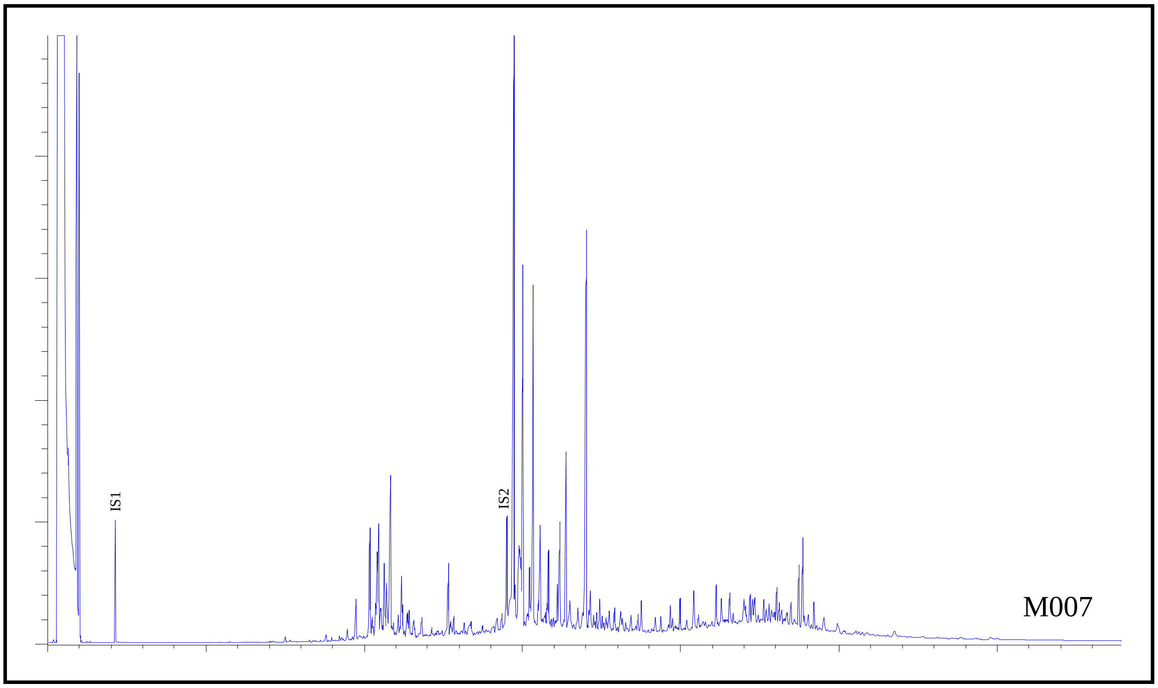
GC/FID CHROMATOGRAMS

Table B-1
Identification of Peak Numbers in GC/FID Chromatograms

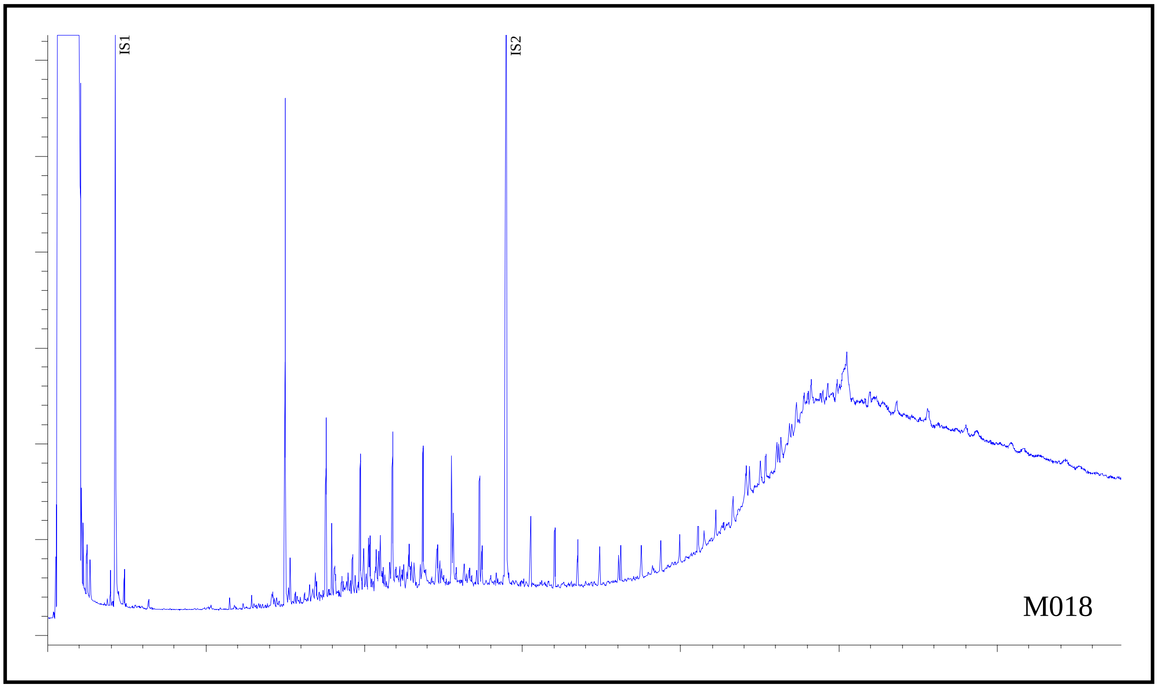
Peak Number	Compound	Peak Number	Compound
1	benzene	19	benz(a)anthracene
2	toluene	20	chrysene
3	ethylbenzene	21	benzo(b)fluoranthene
4	m/p-xylene	22	benzo(k)fluoranthene
5	styrene	23	benzo(a)pyrene
6	o-xylene	24	indeno(1,2,3-cd)pyrene
7	1,2,4-trimethylbenzene	25	dibenz(a,h)anthracene
8	naphthalene	26	benzo(g,h,i)perylene
9	2-methylnaphthalene		
10	1-methylnaphthalene	IS1	2,4-difluorotoluene
11	acenapthylene	IS2	o-terphenyl
12	acenaphthene		
13	dibenzofuran		
14	fluorene		
15	phenanthrene		
16	anthracene		
17	fluoranthene		
18	pyrene		

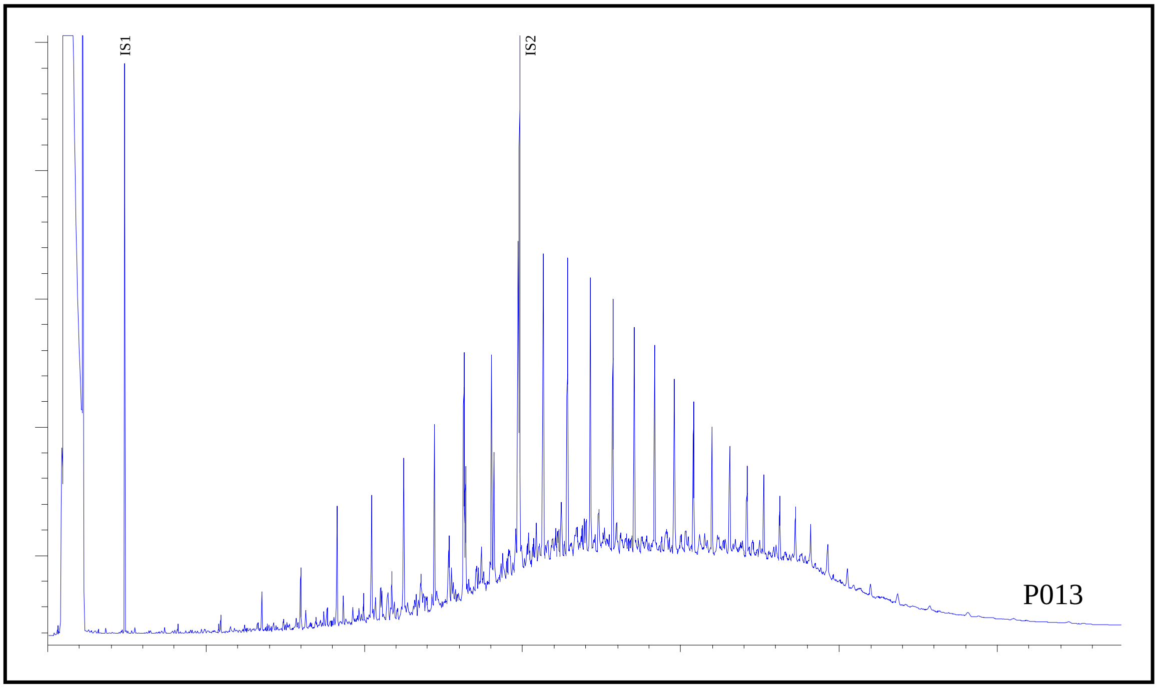
Whole Extracts





Whole Extracts





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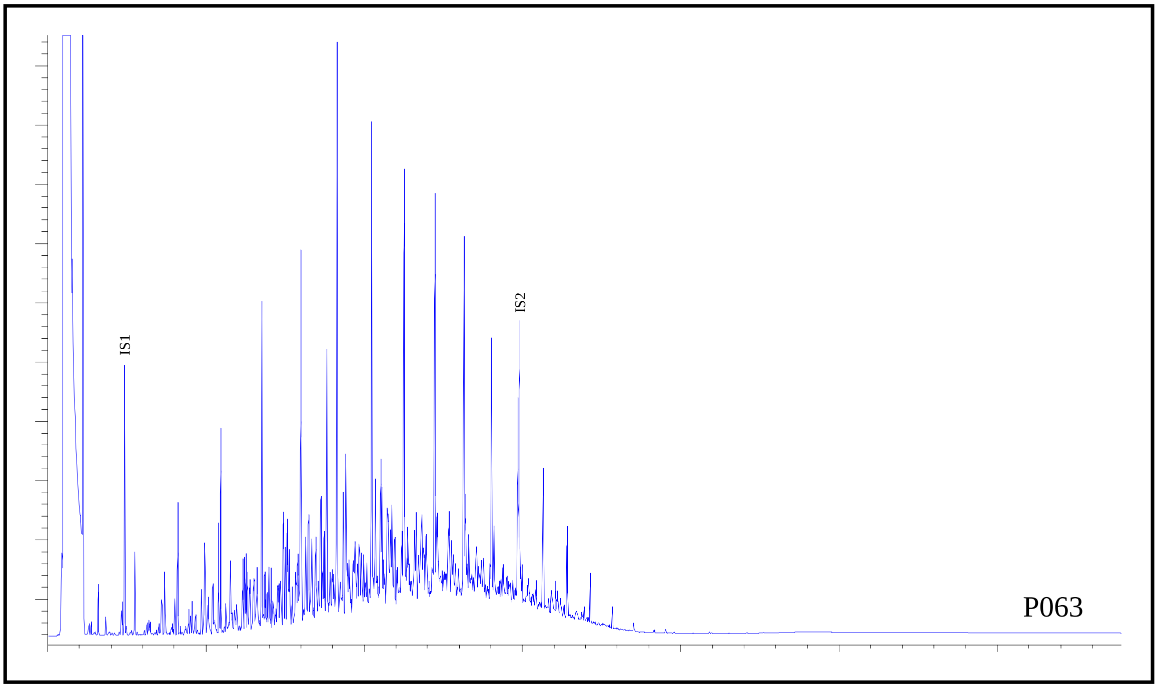

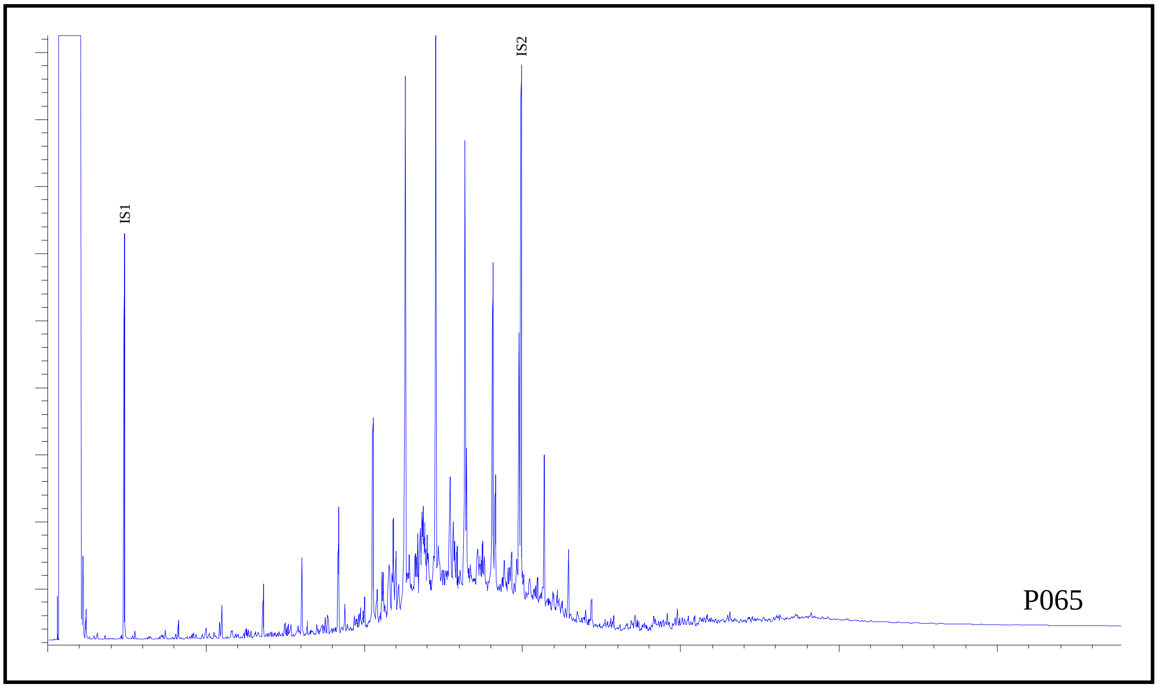

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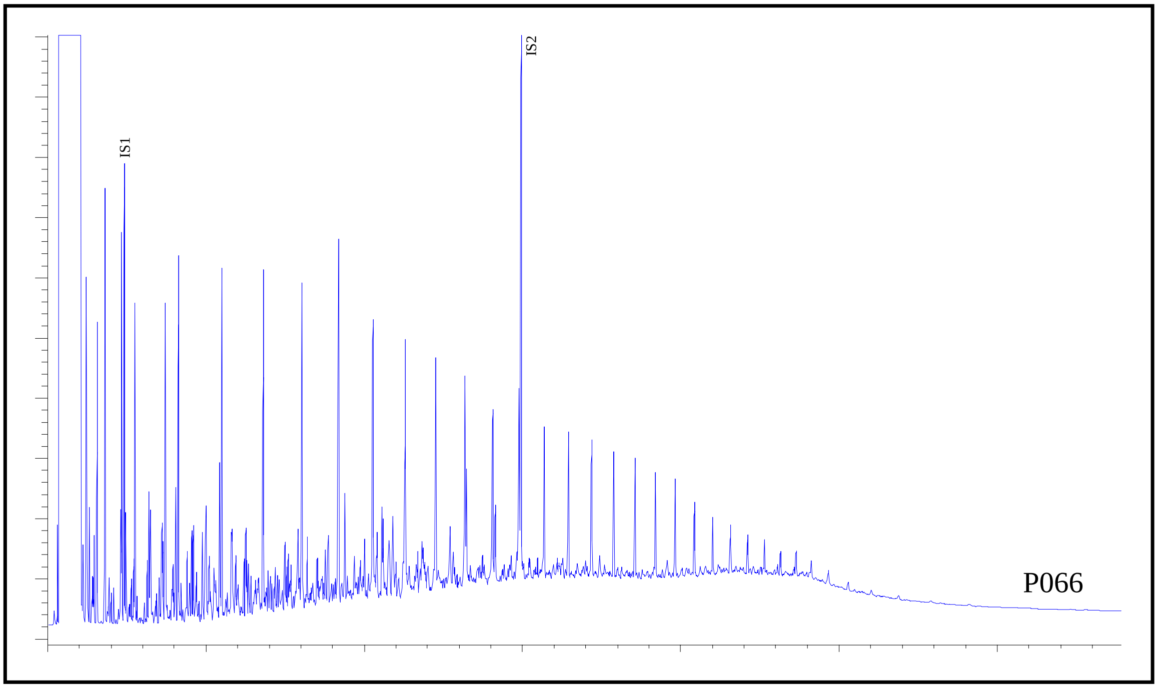

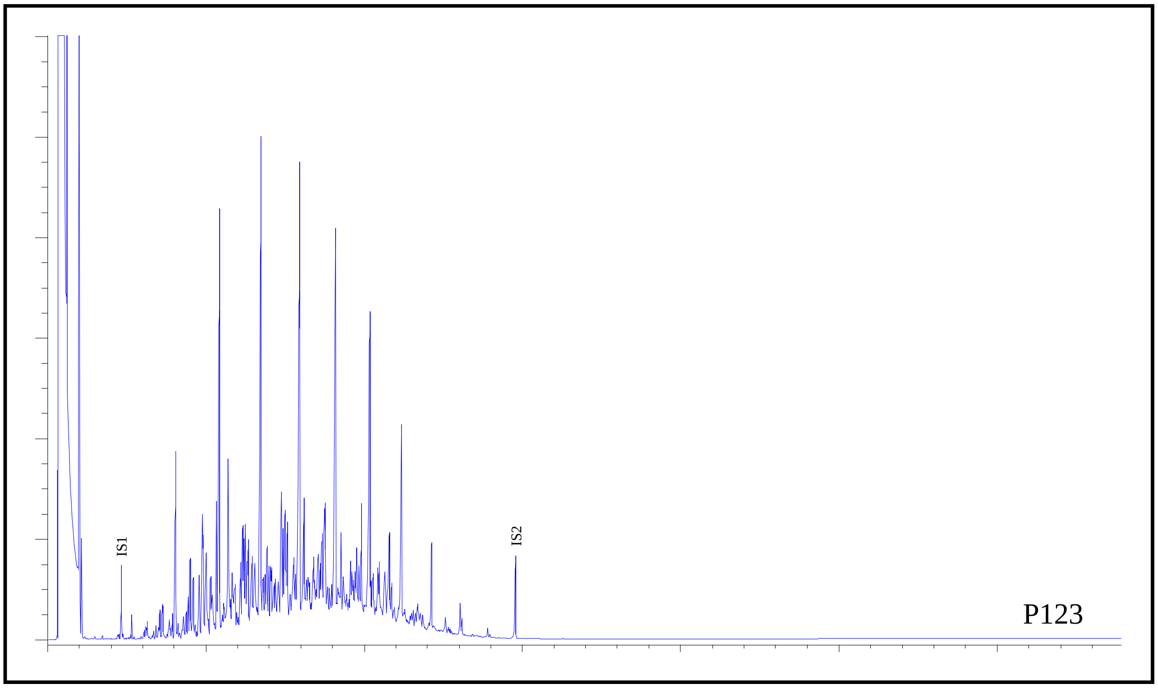

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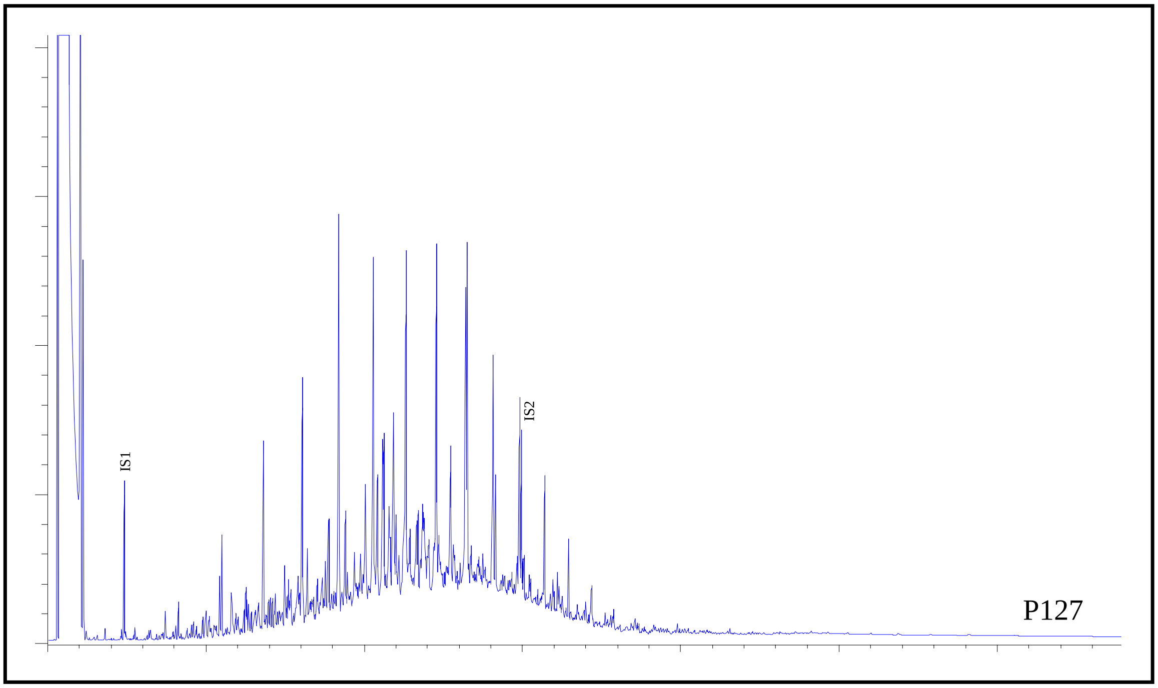

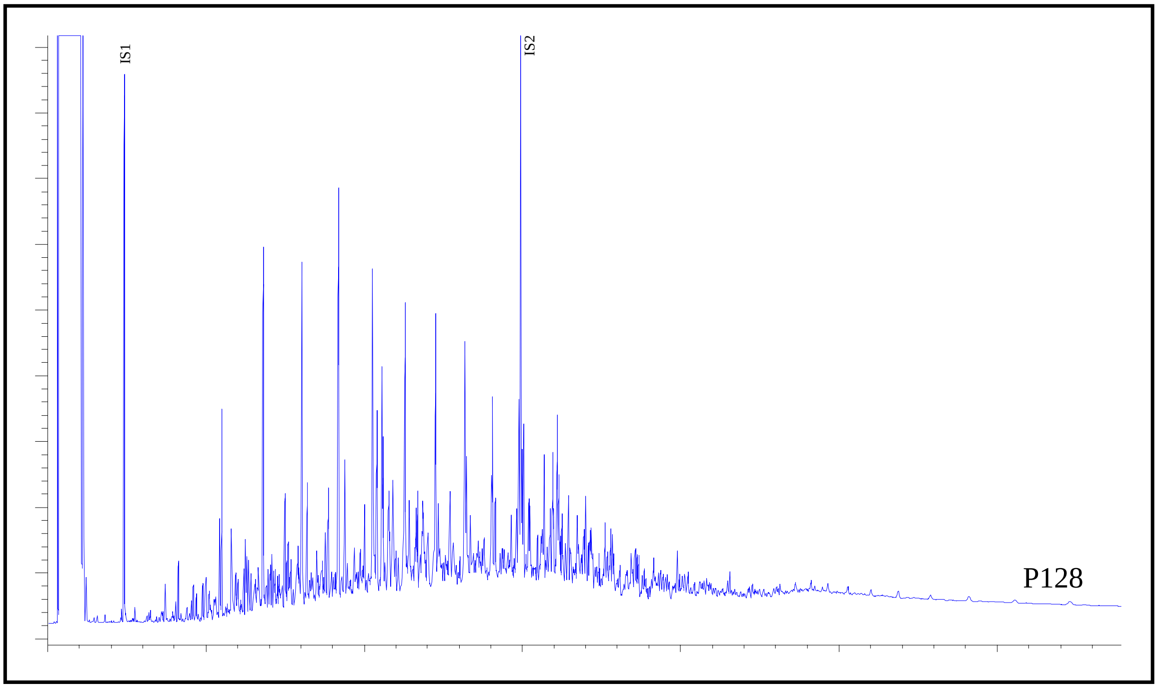

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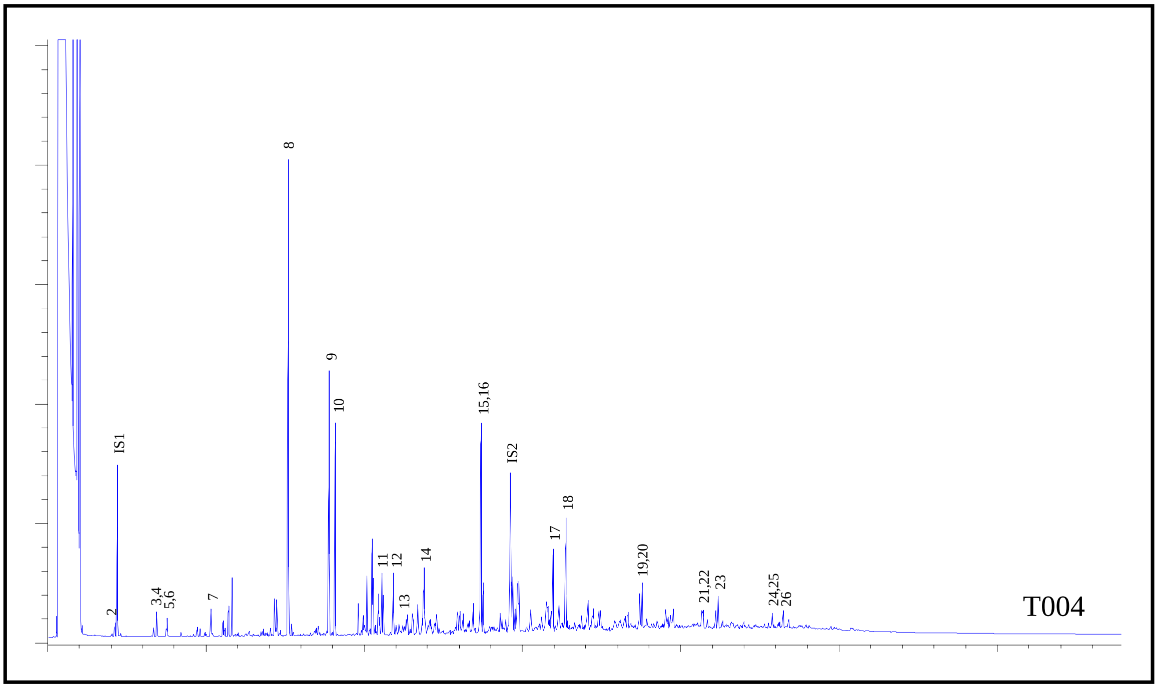

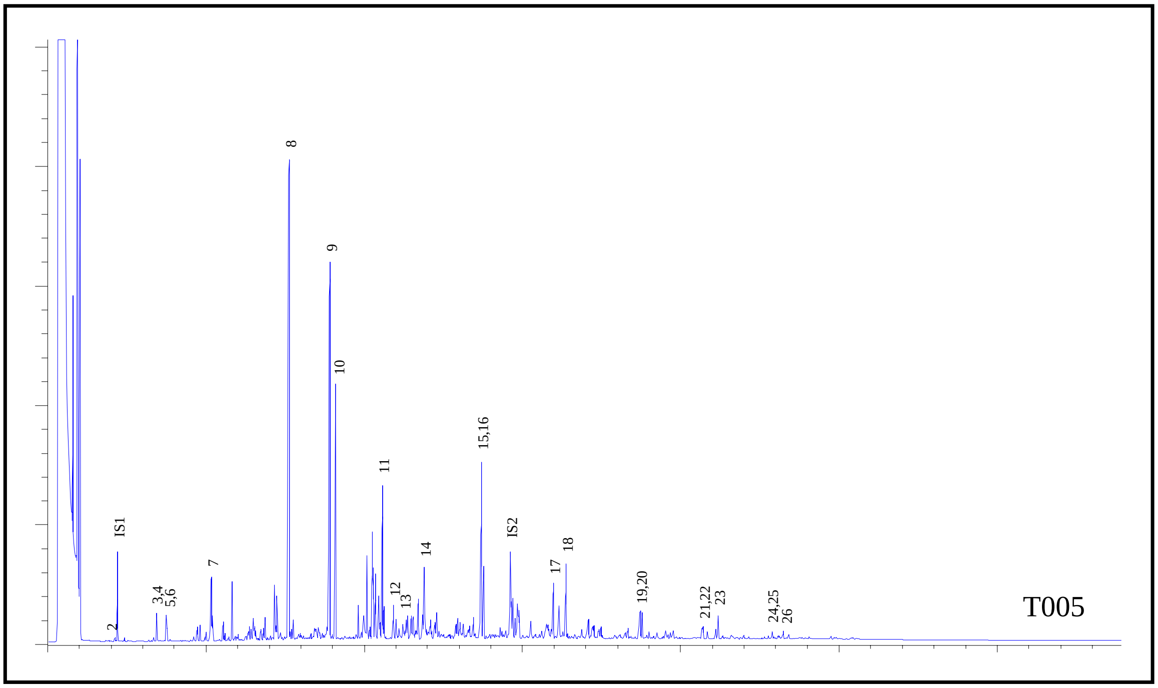

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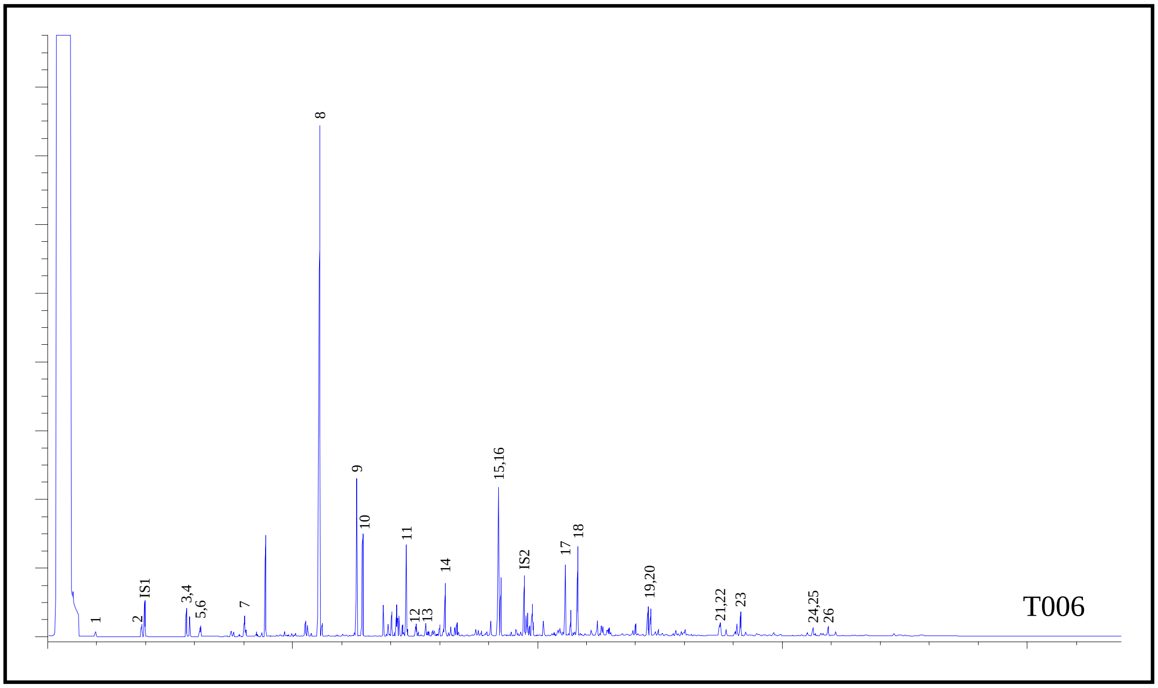

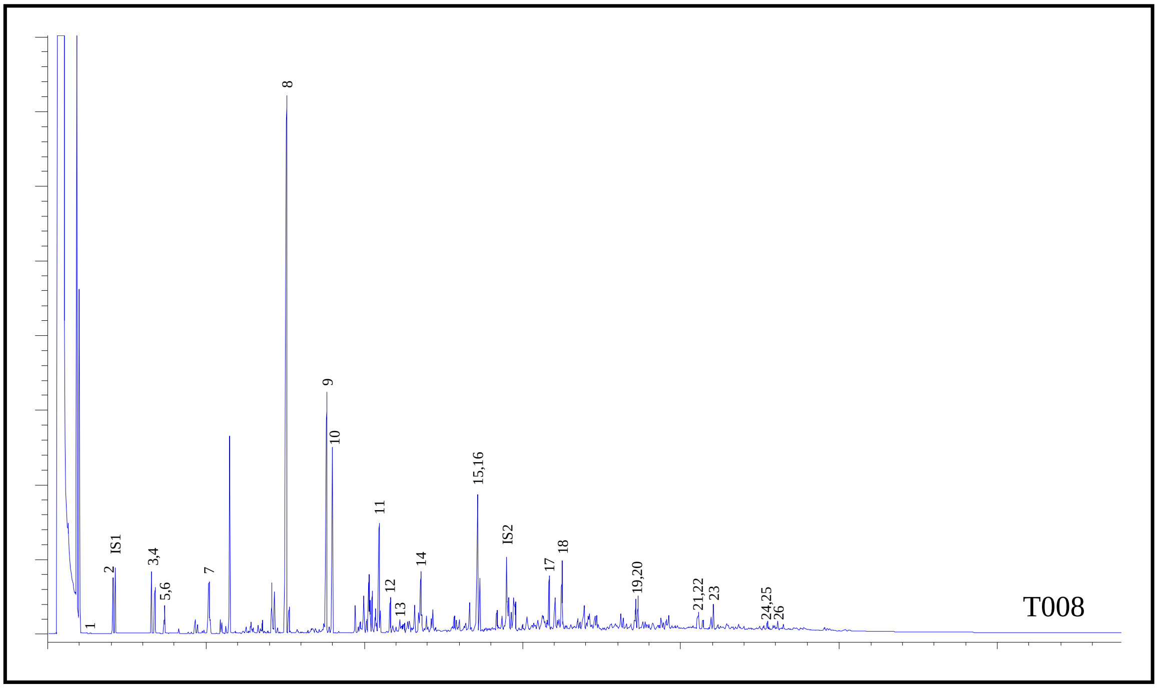

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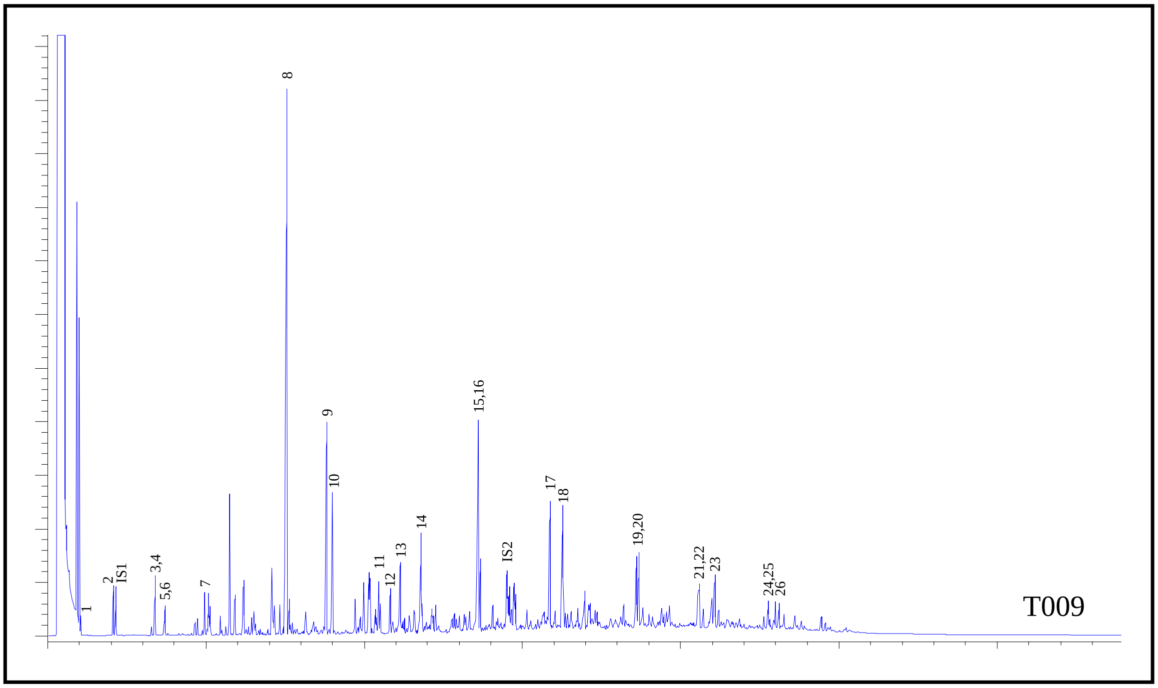

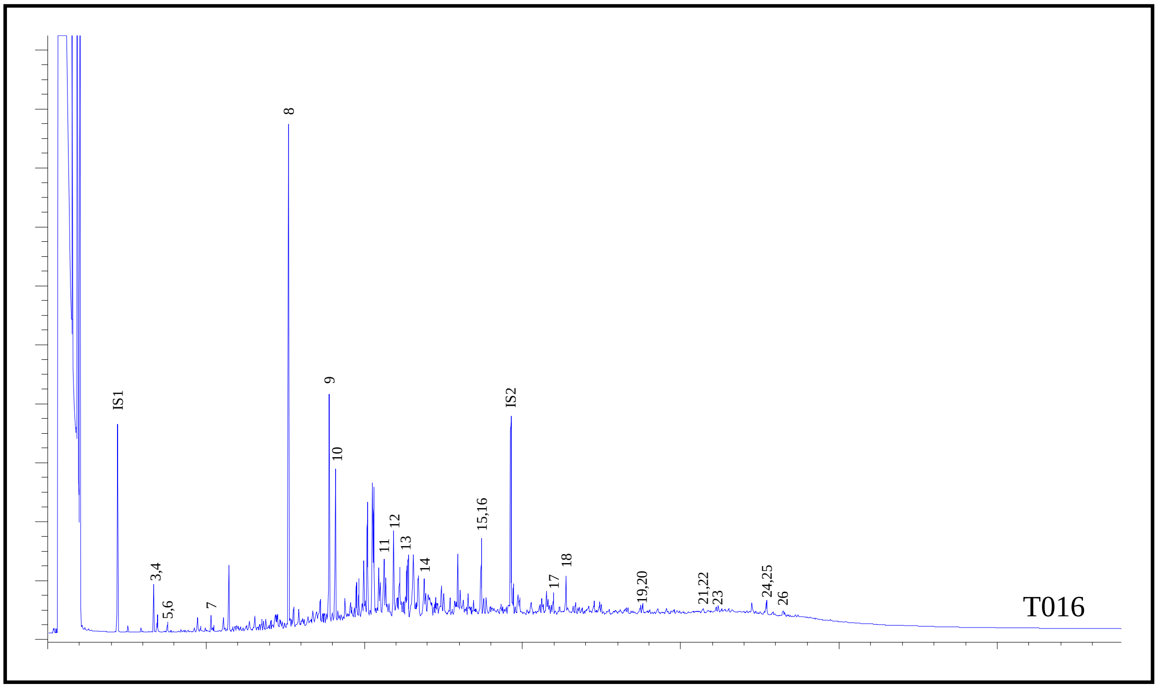

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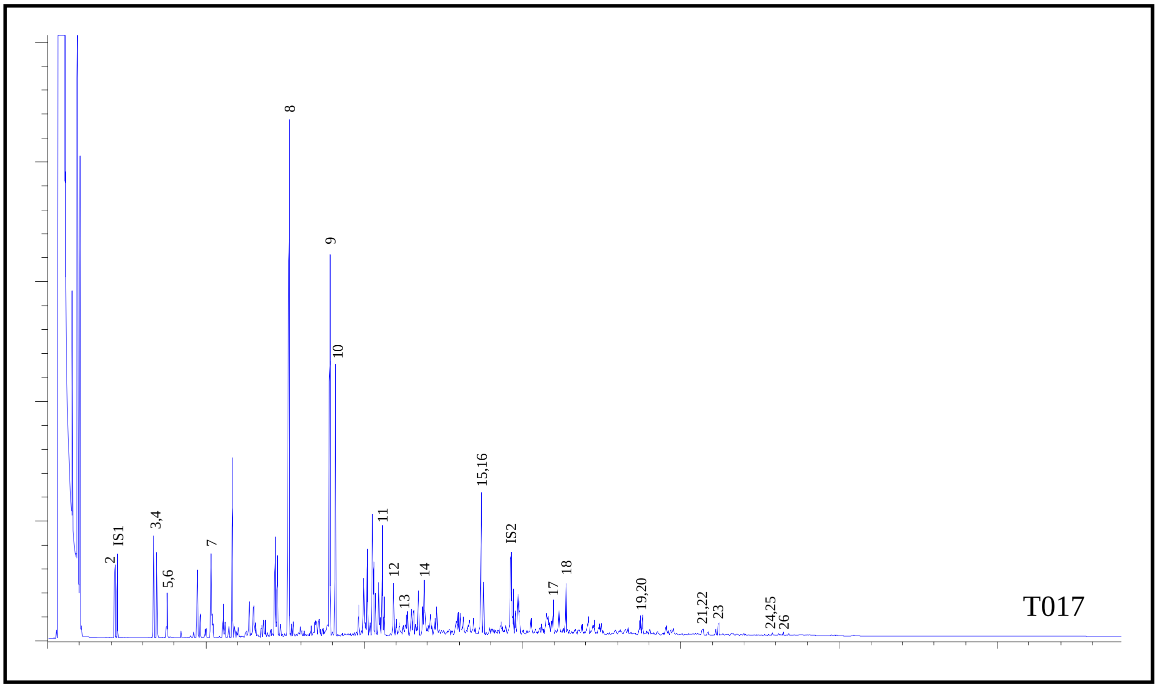

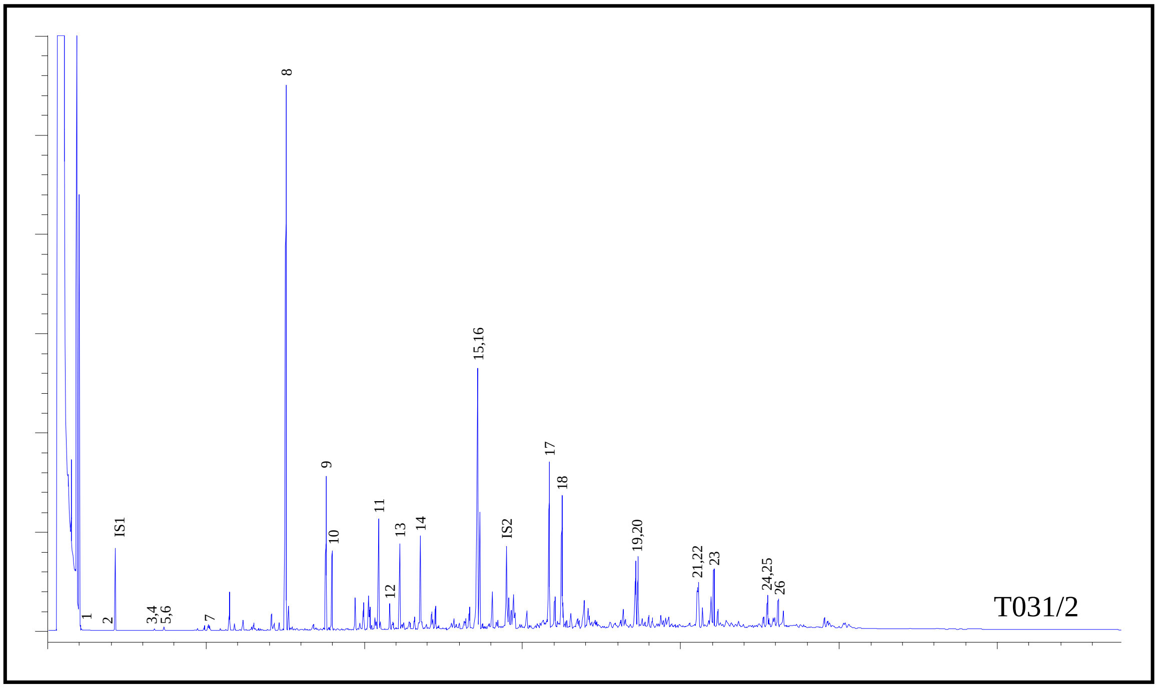

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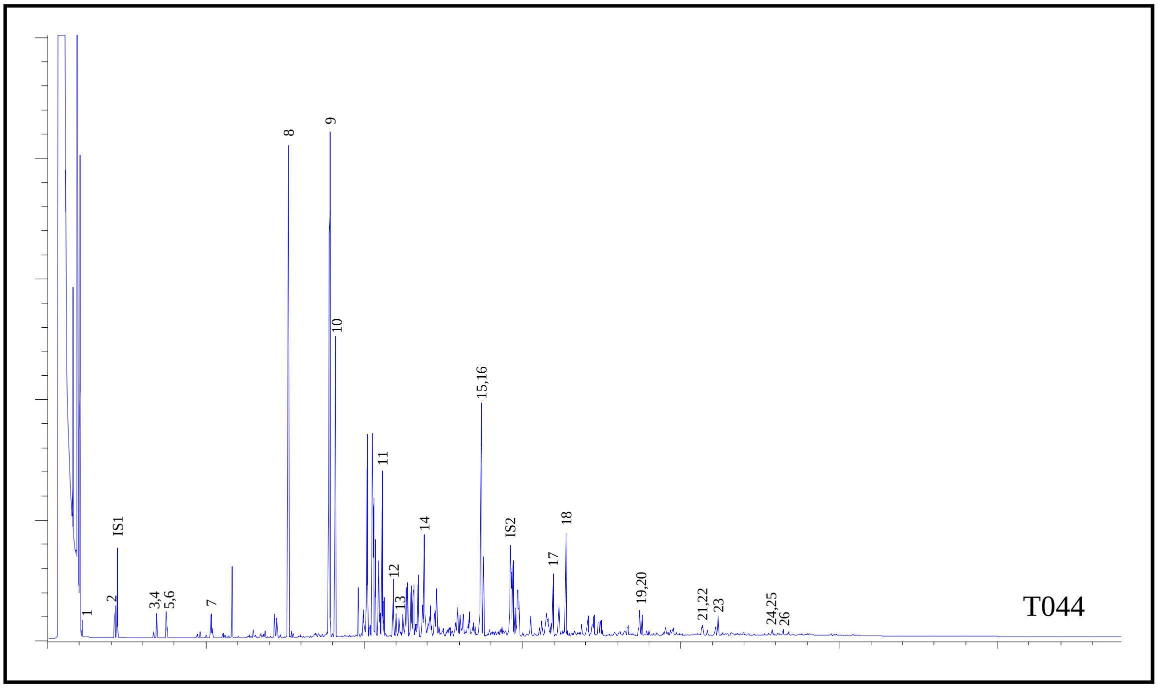

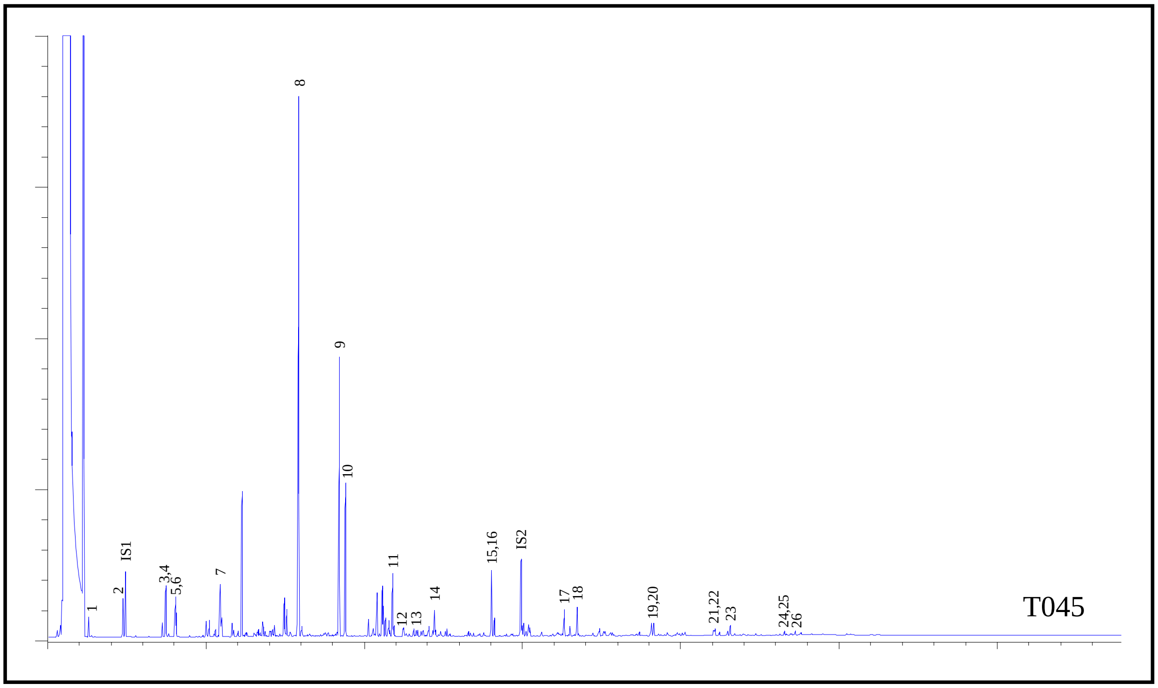

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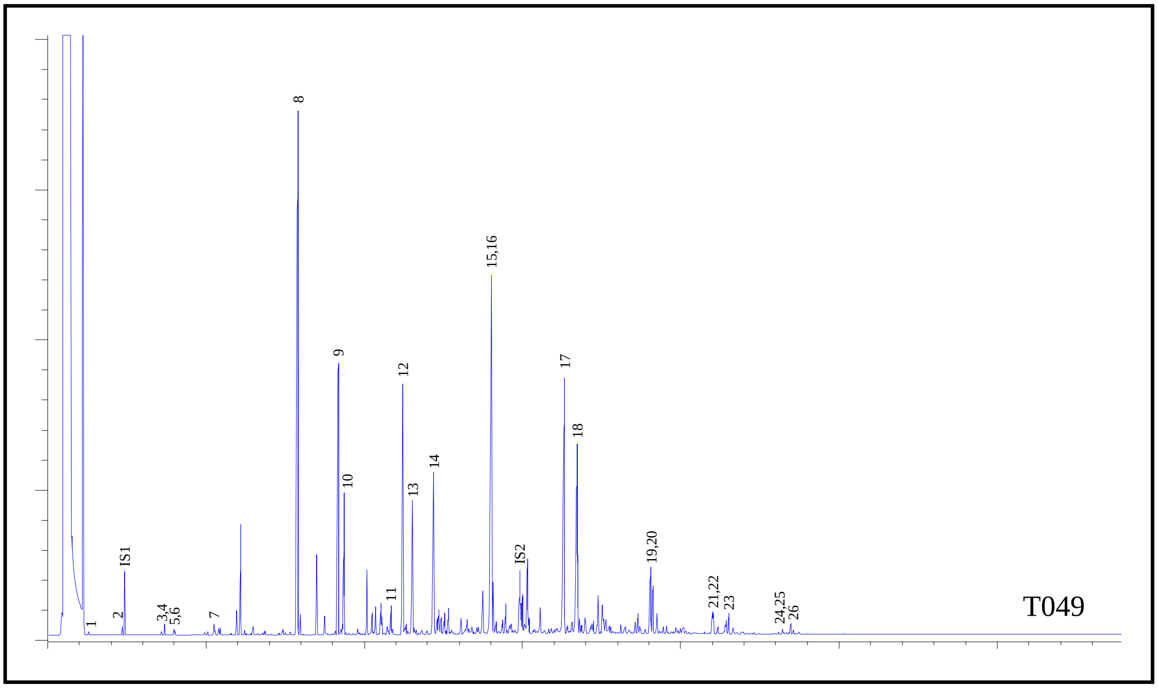

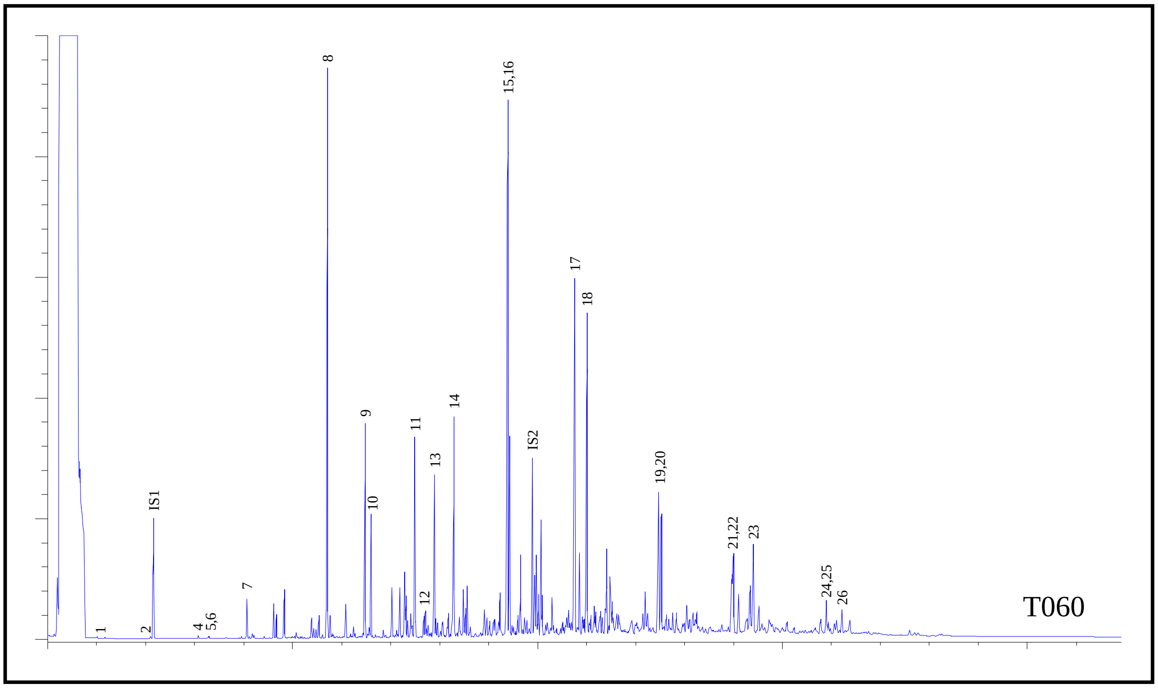

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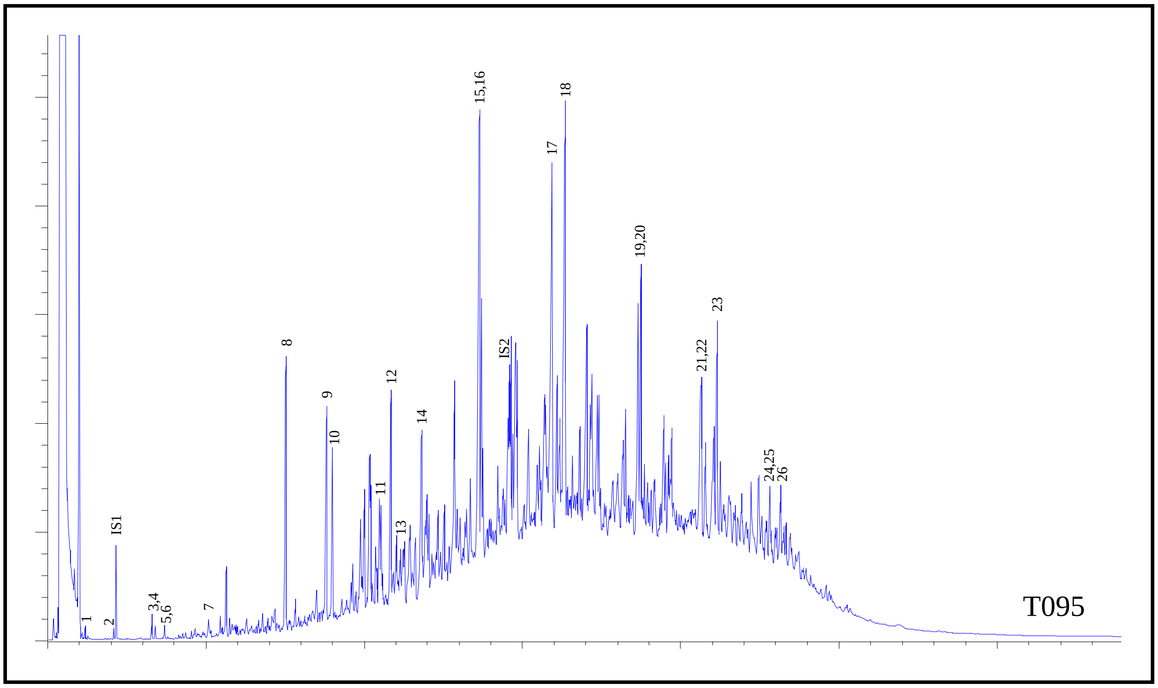

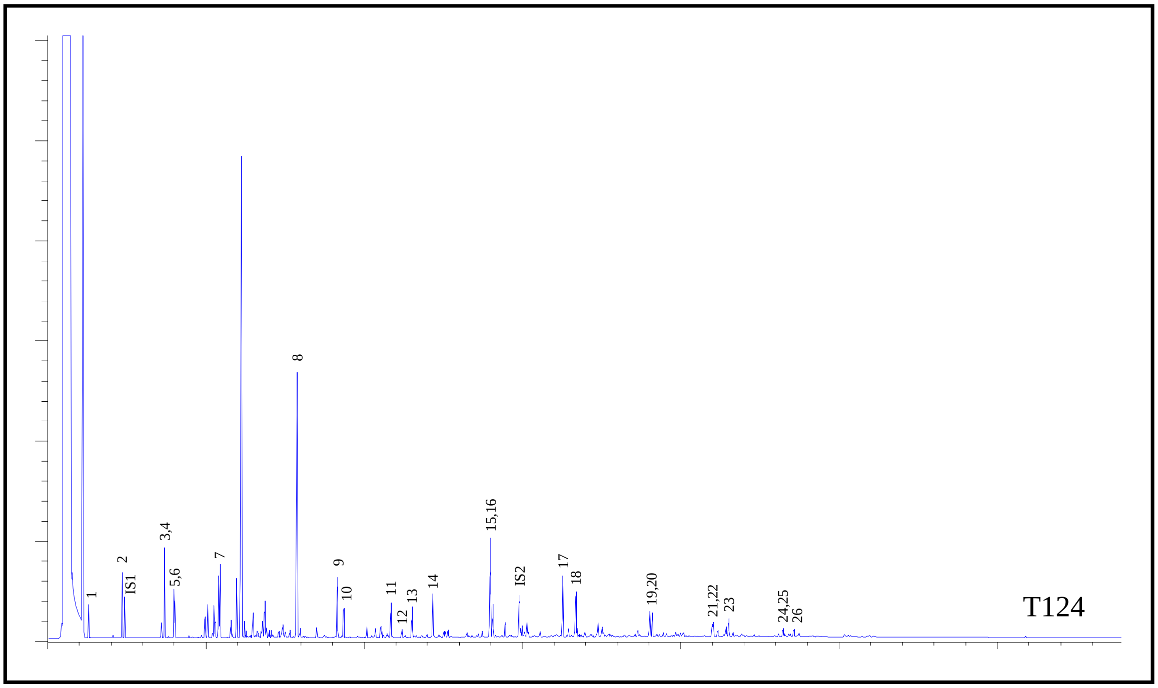

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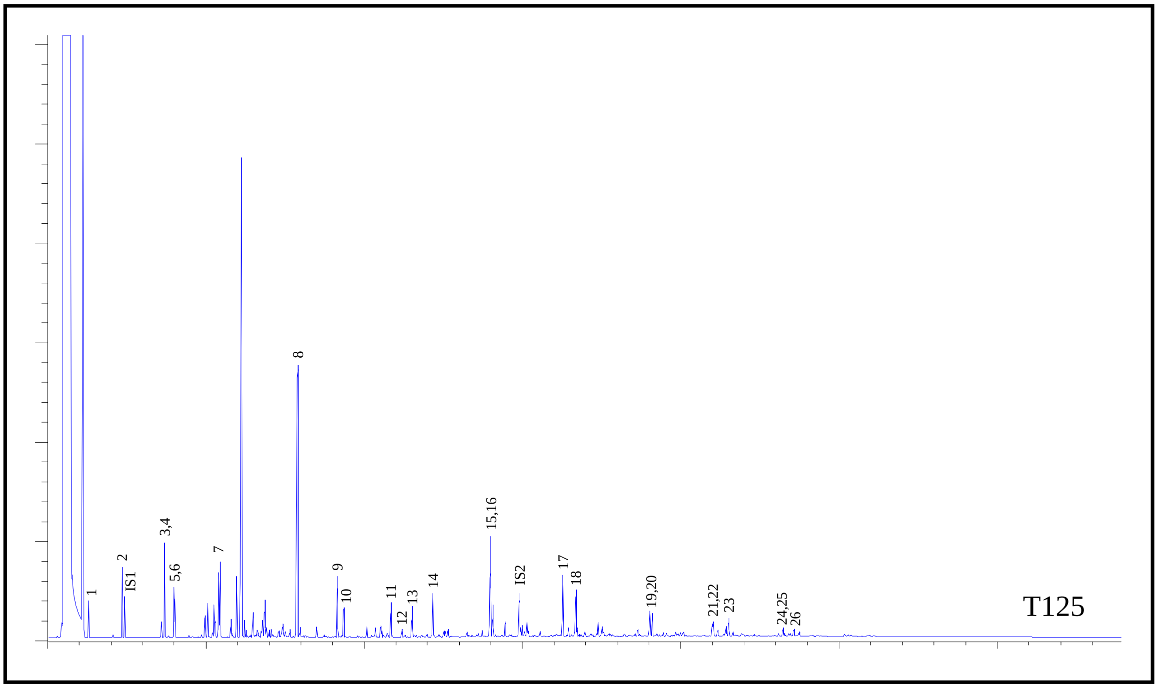

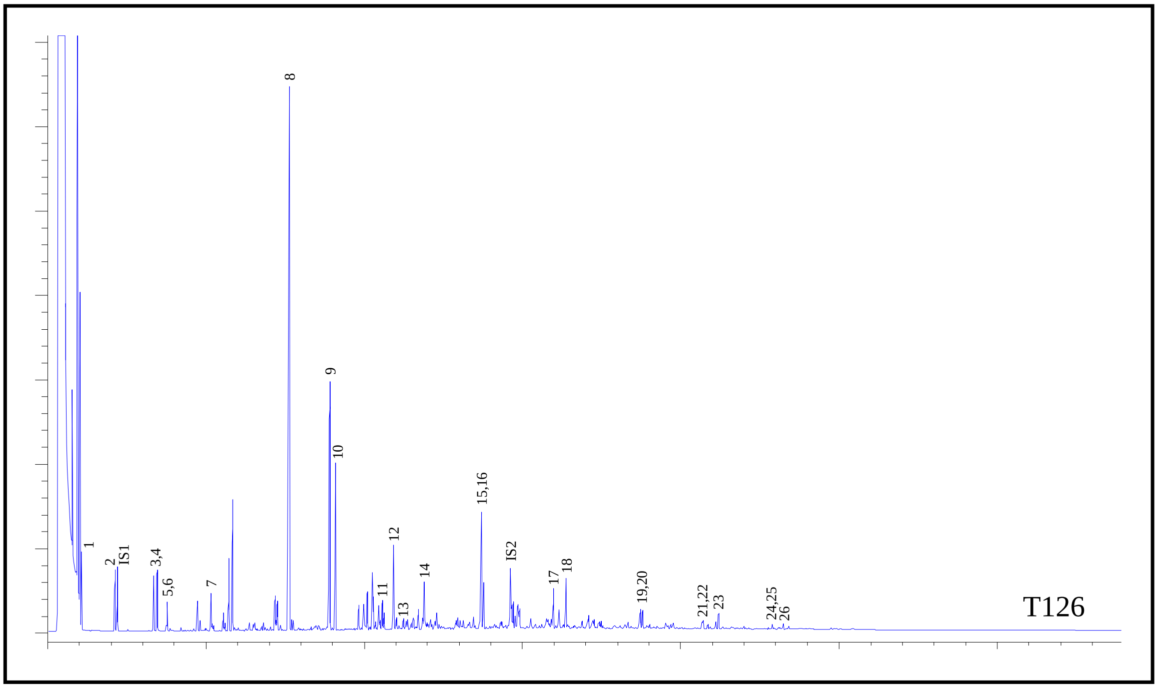

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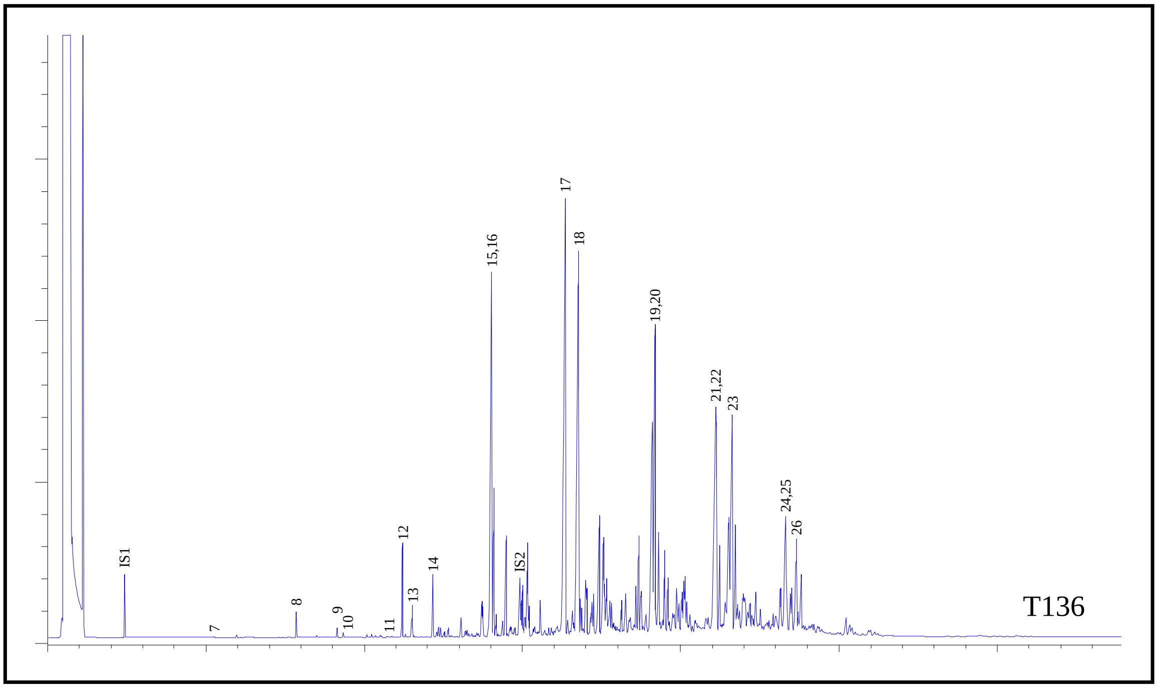

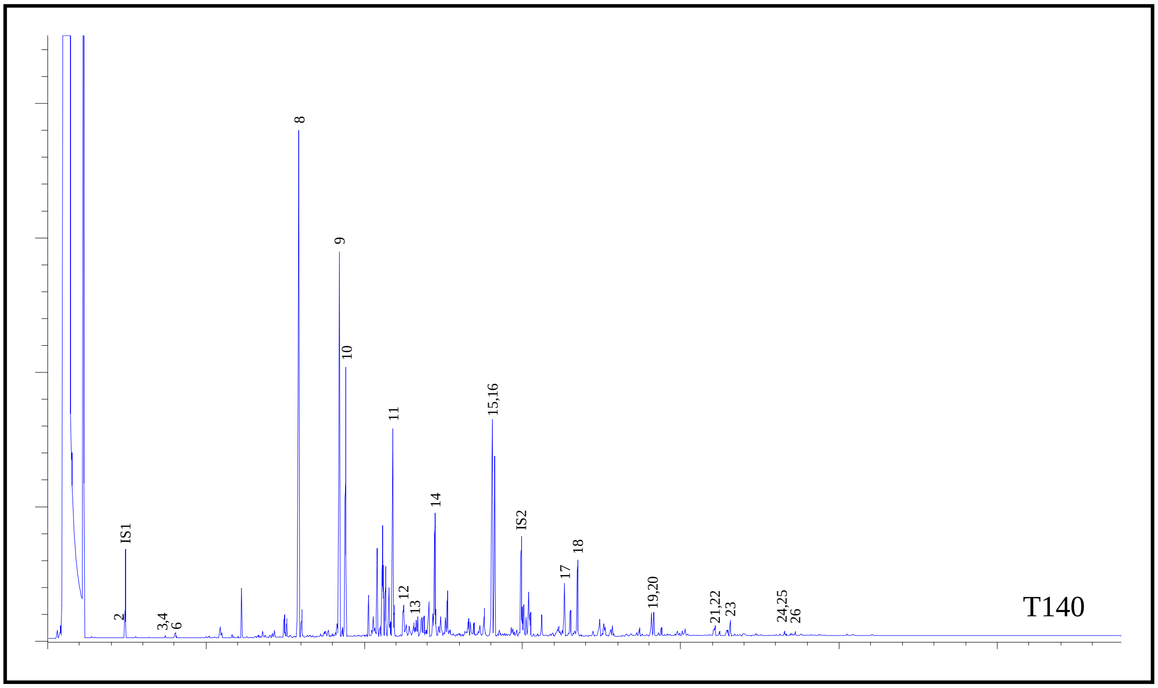

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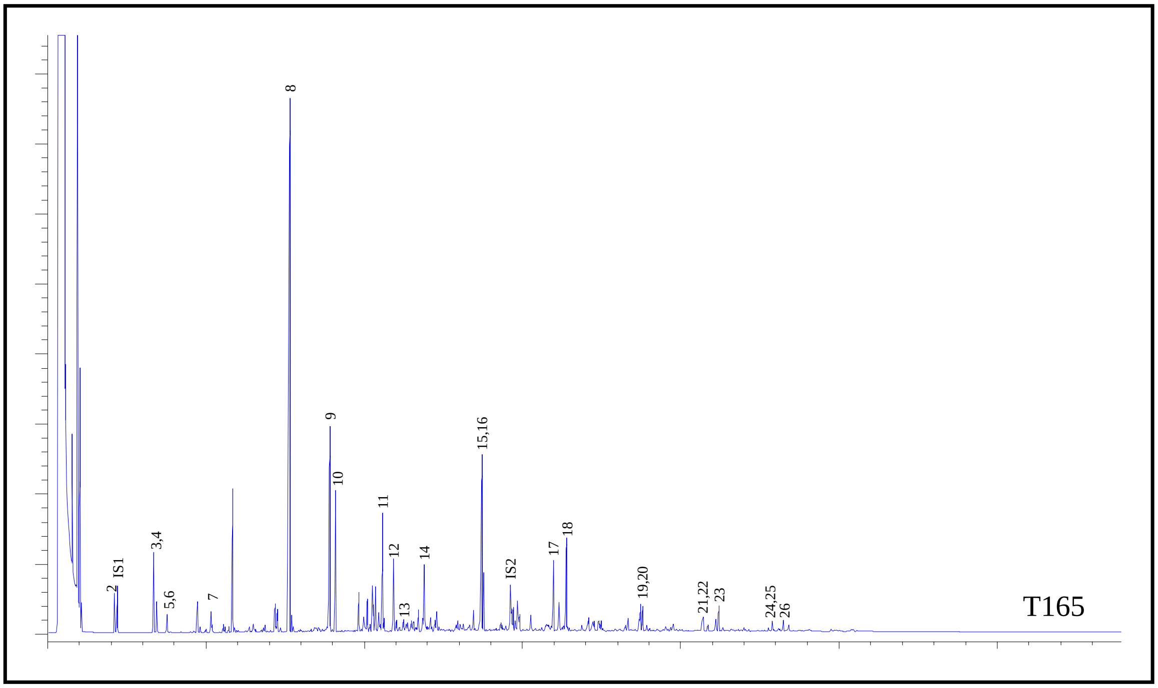

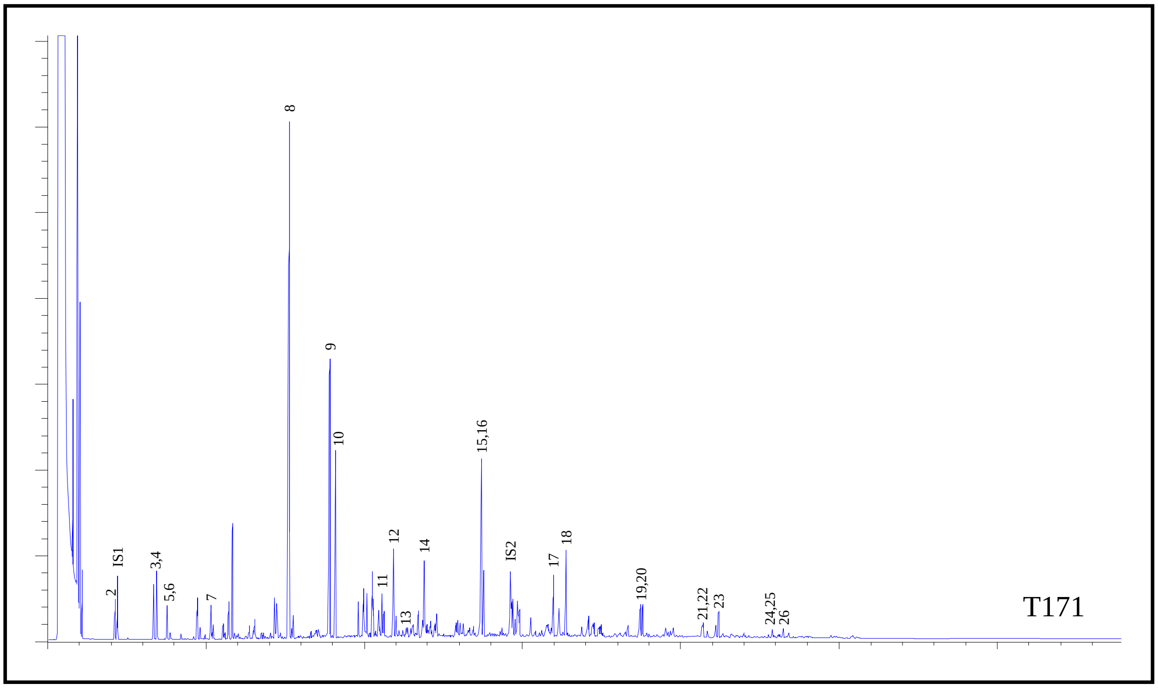

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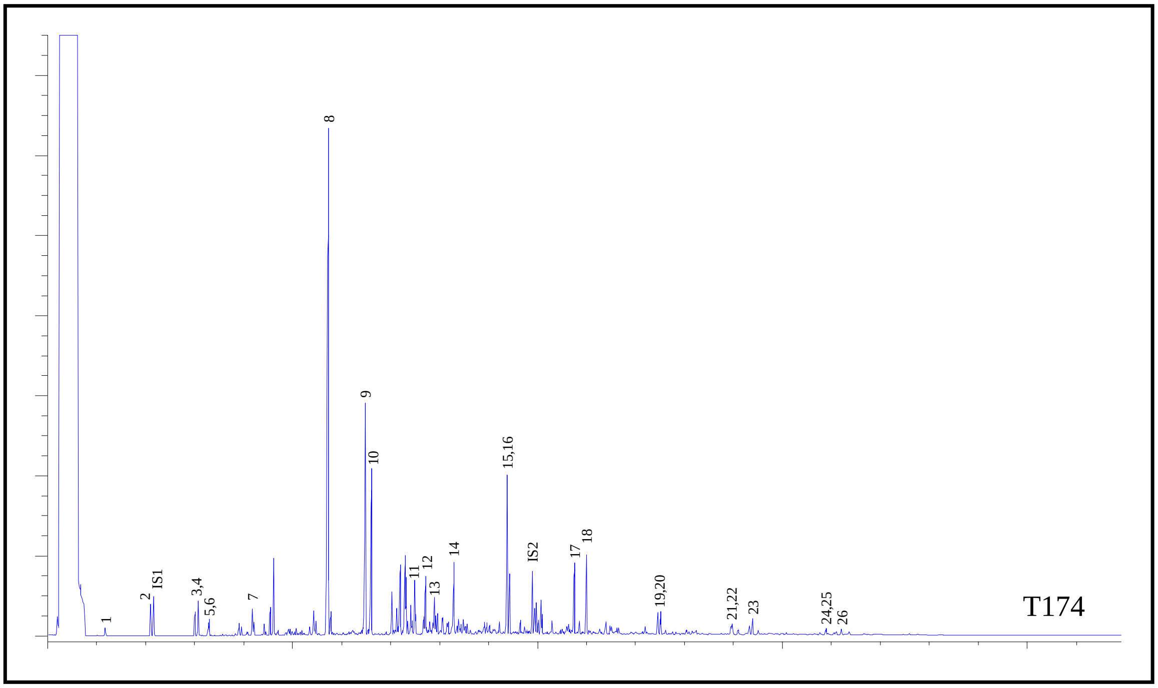

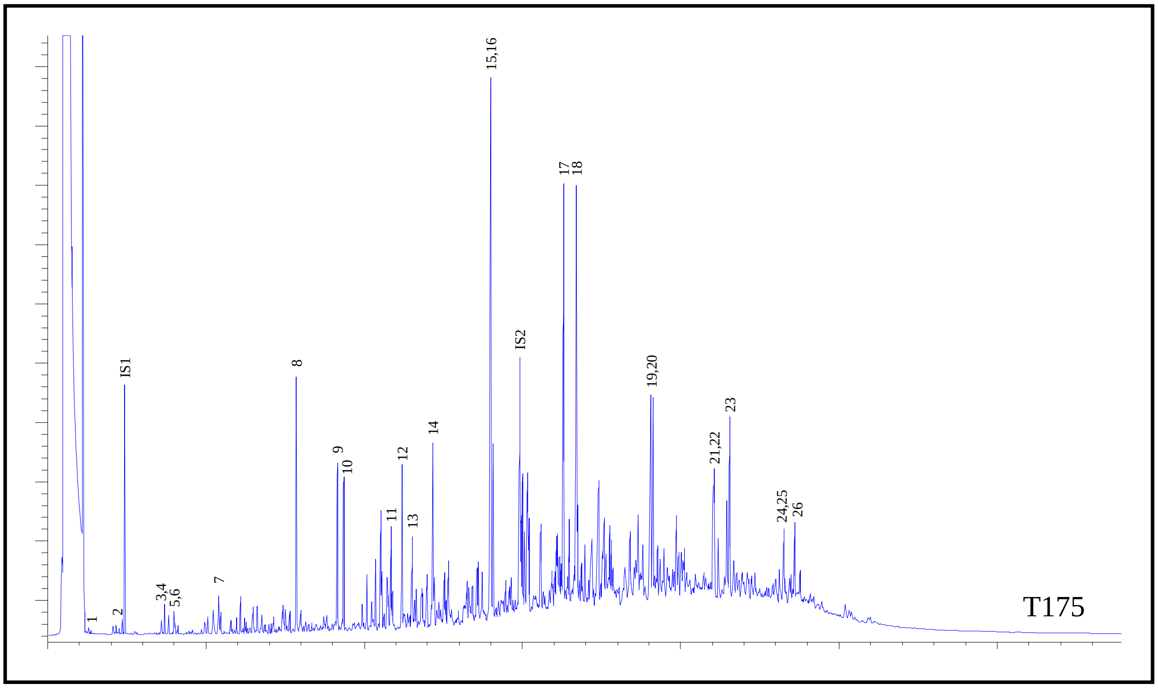

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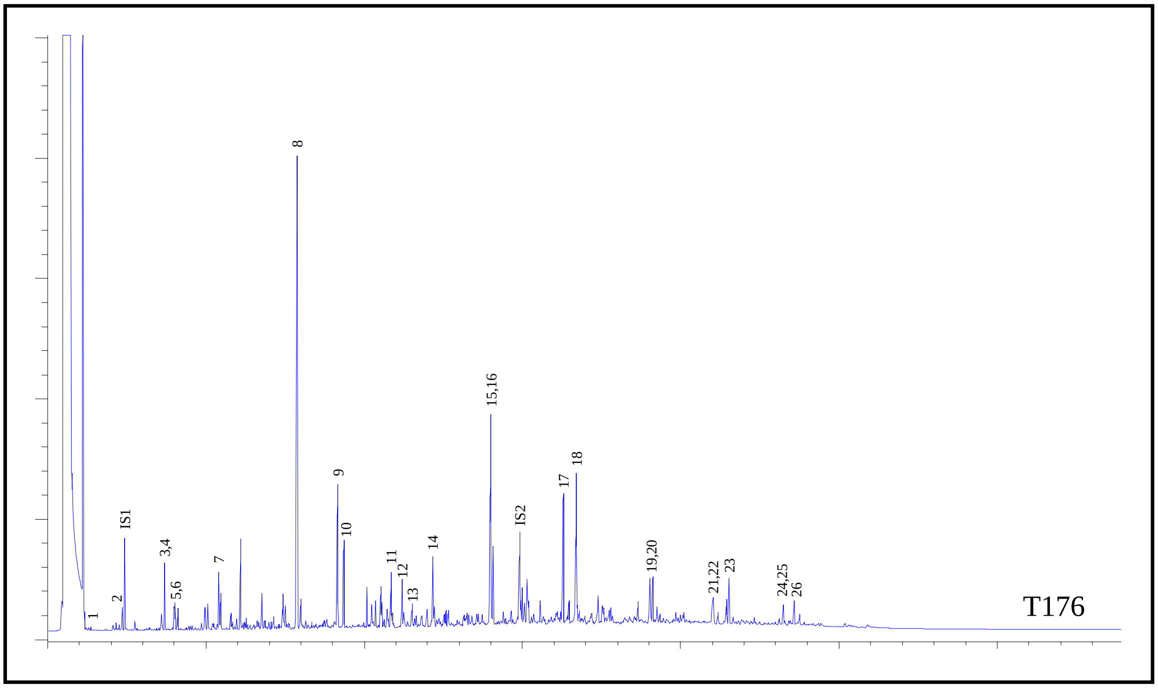

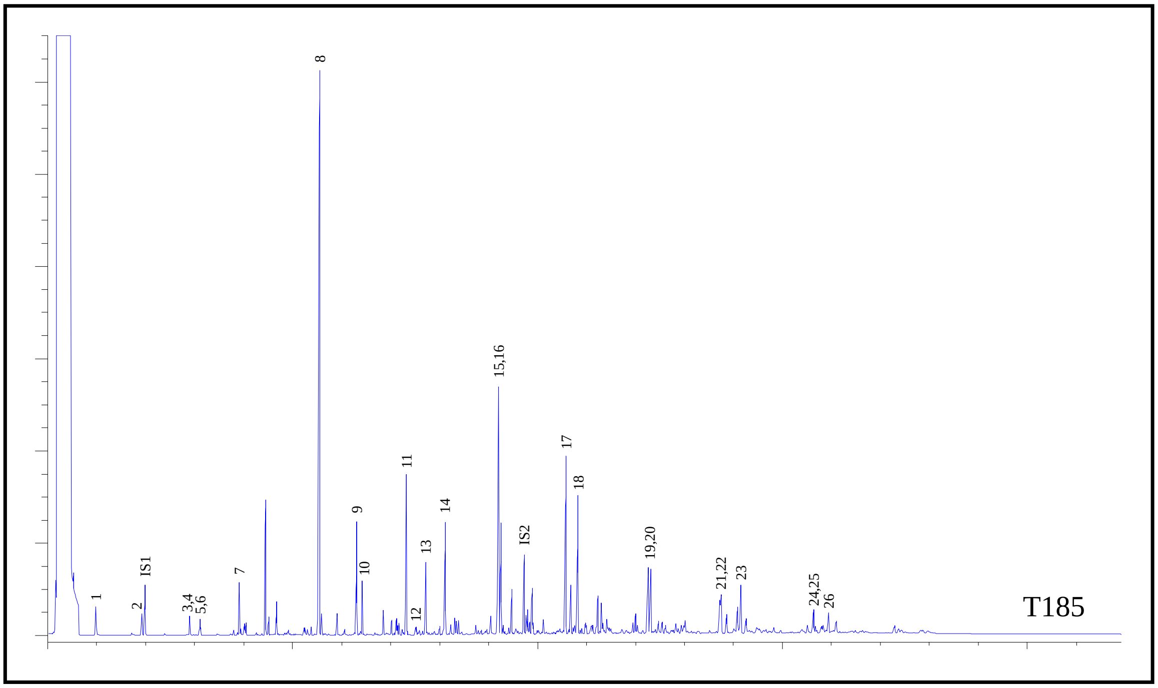

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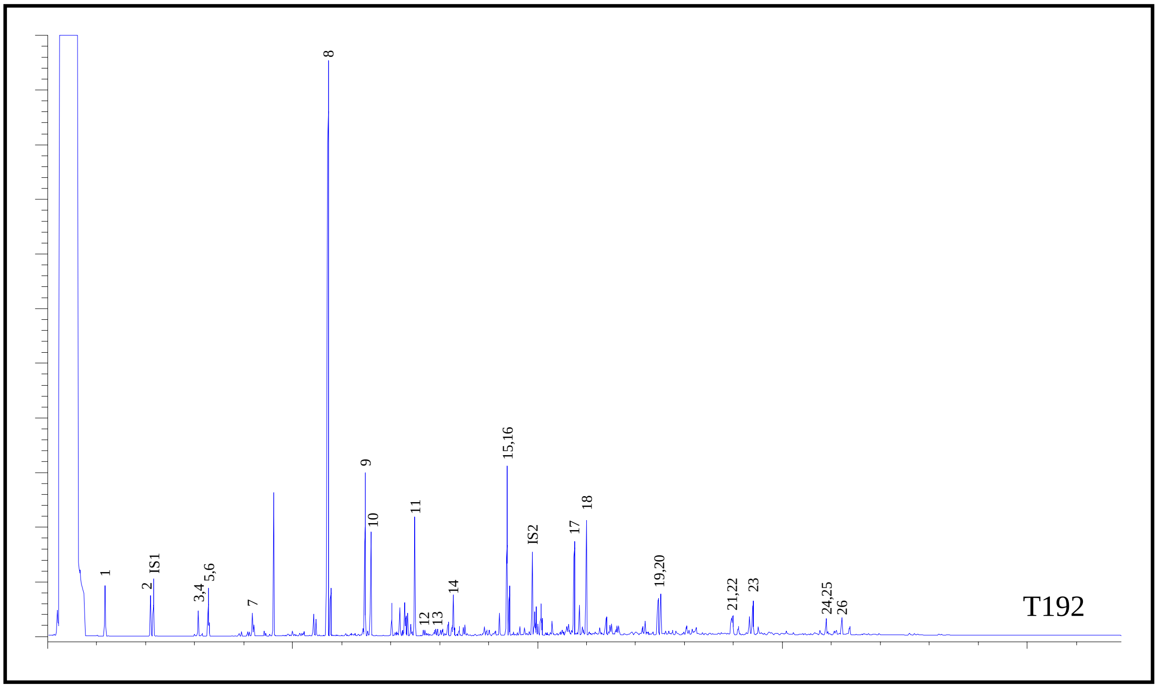

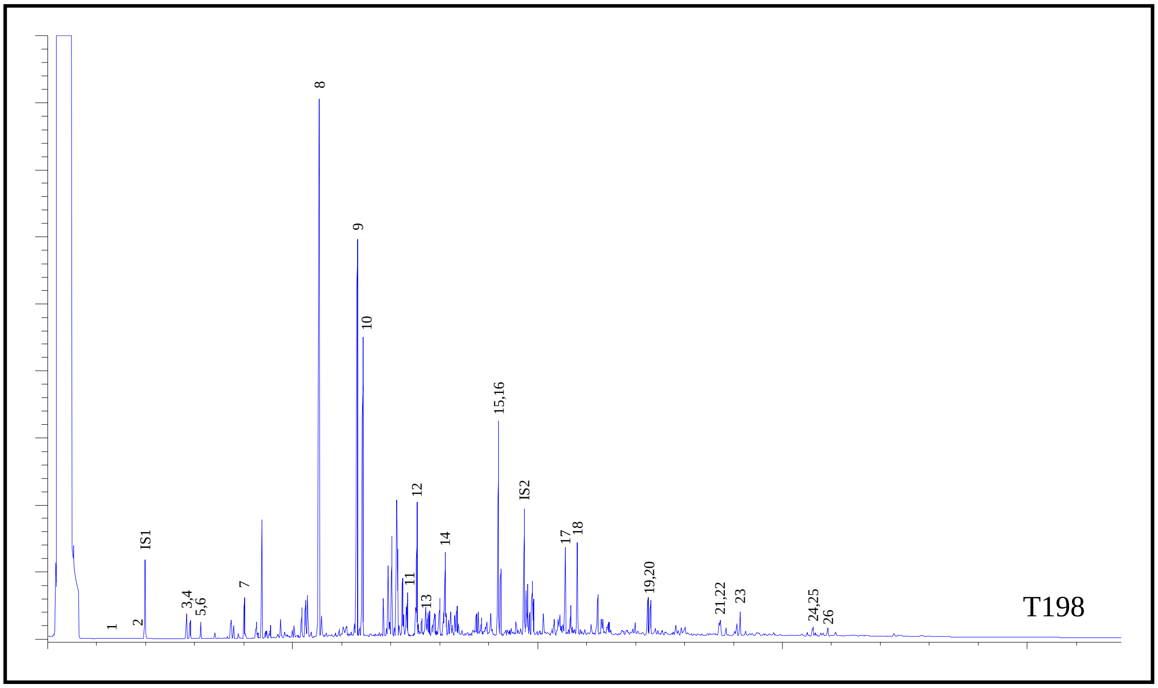

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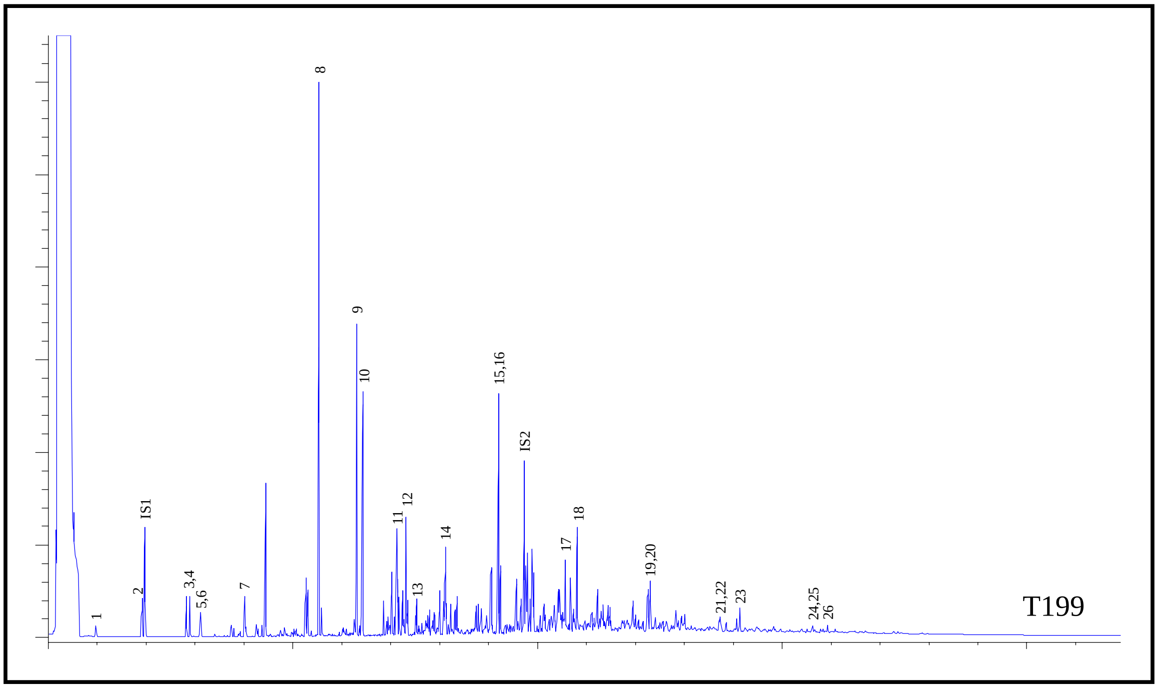

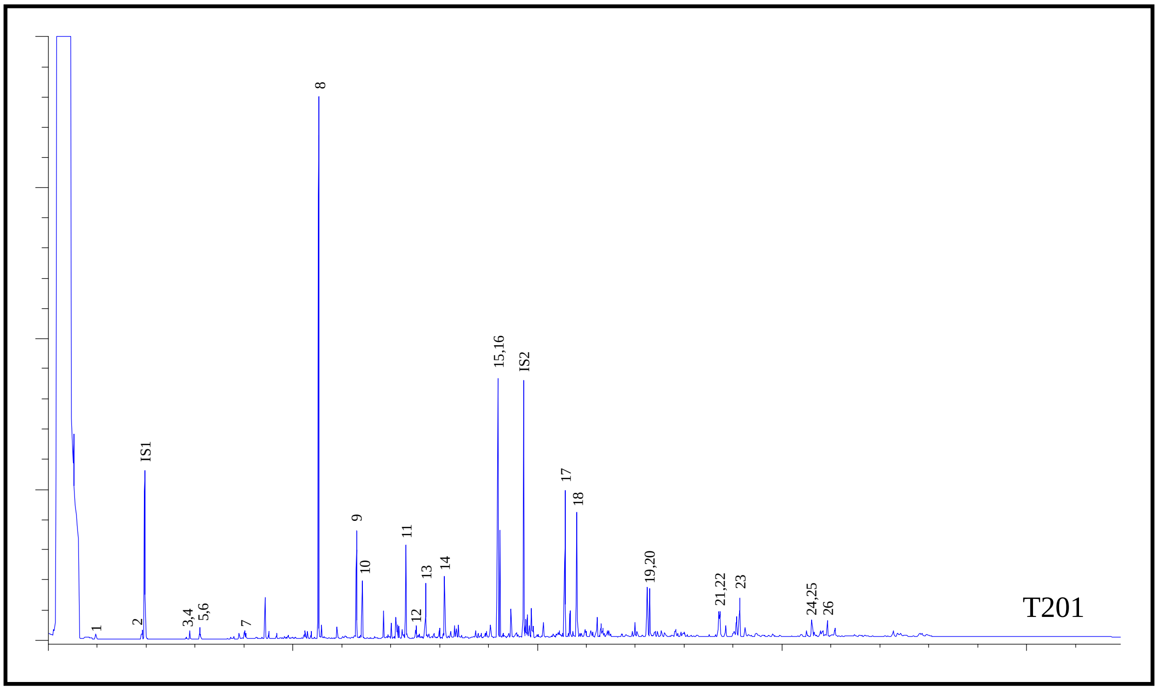

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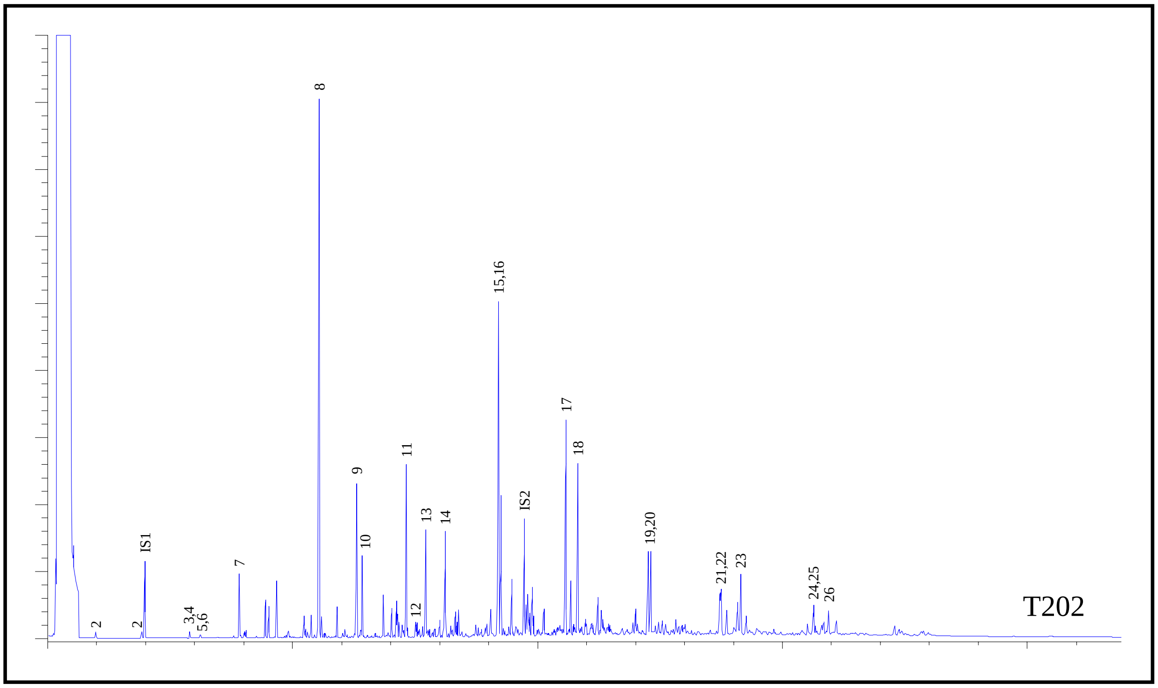

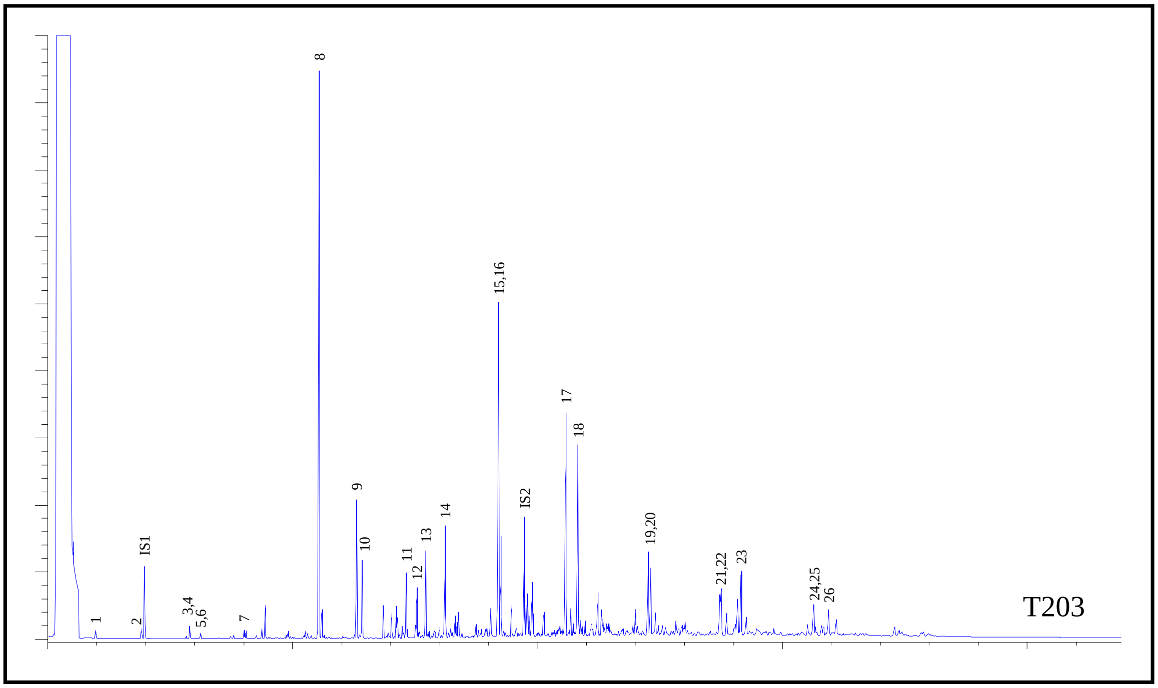

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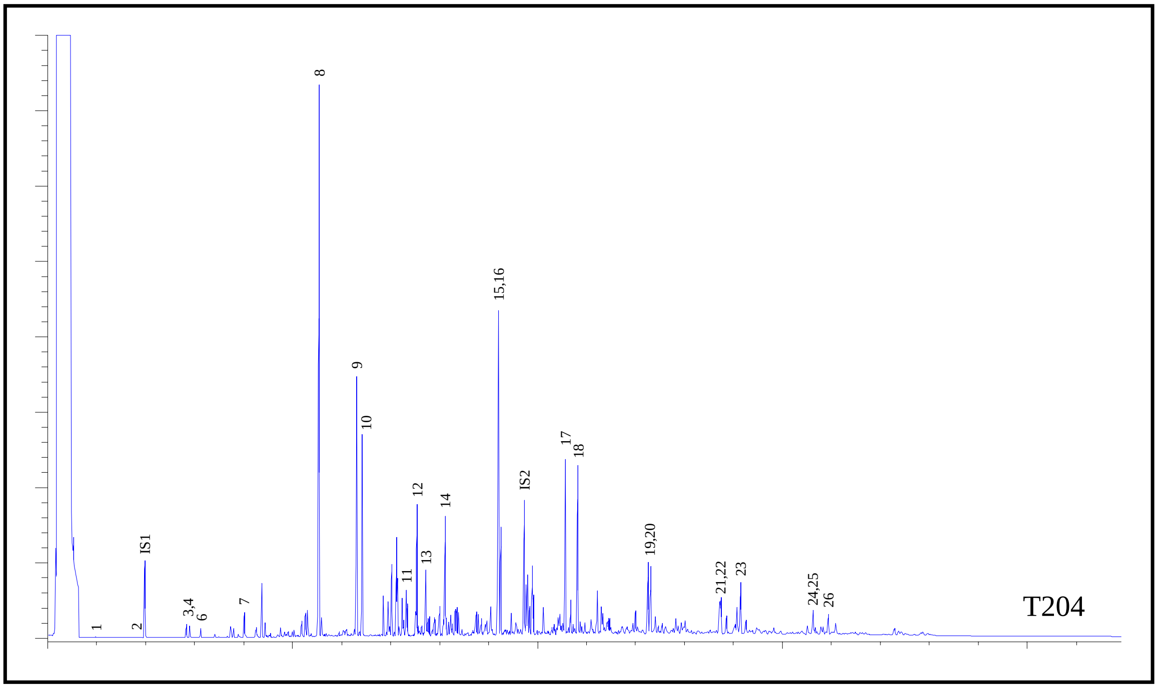

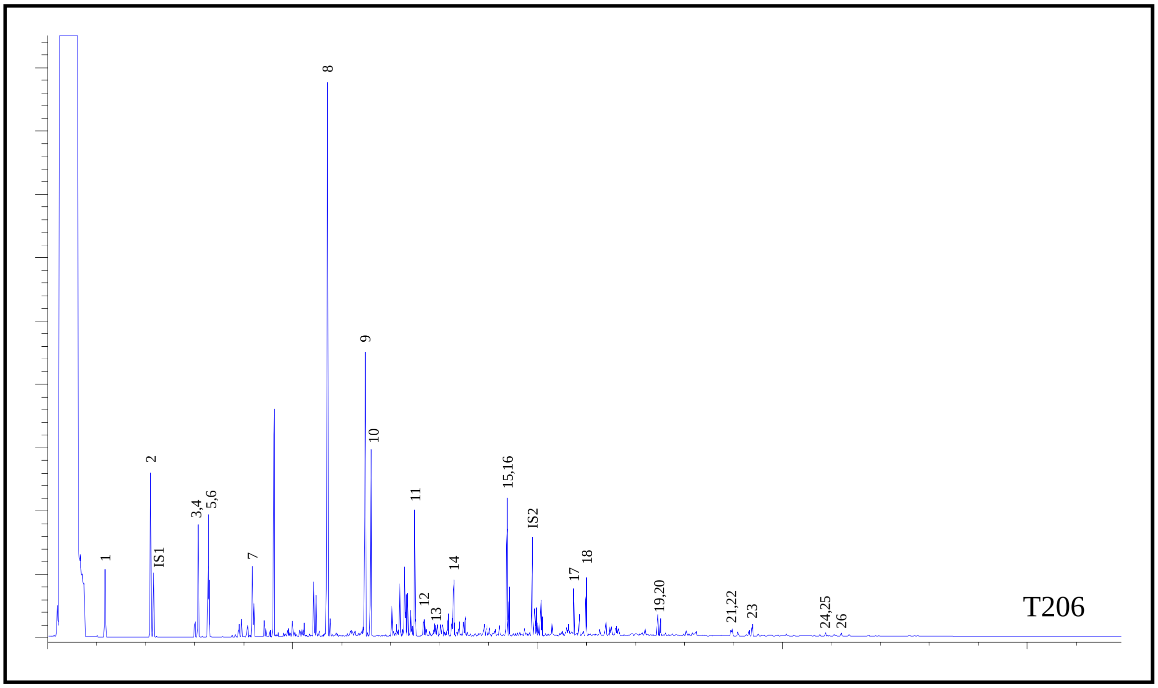

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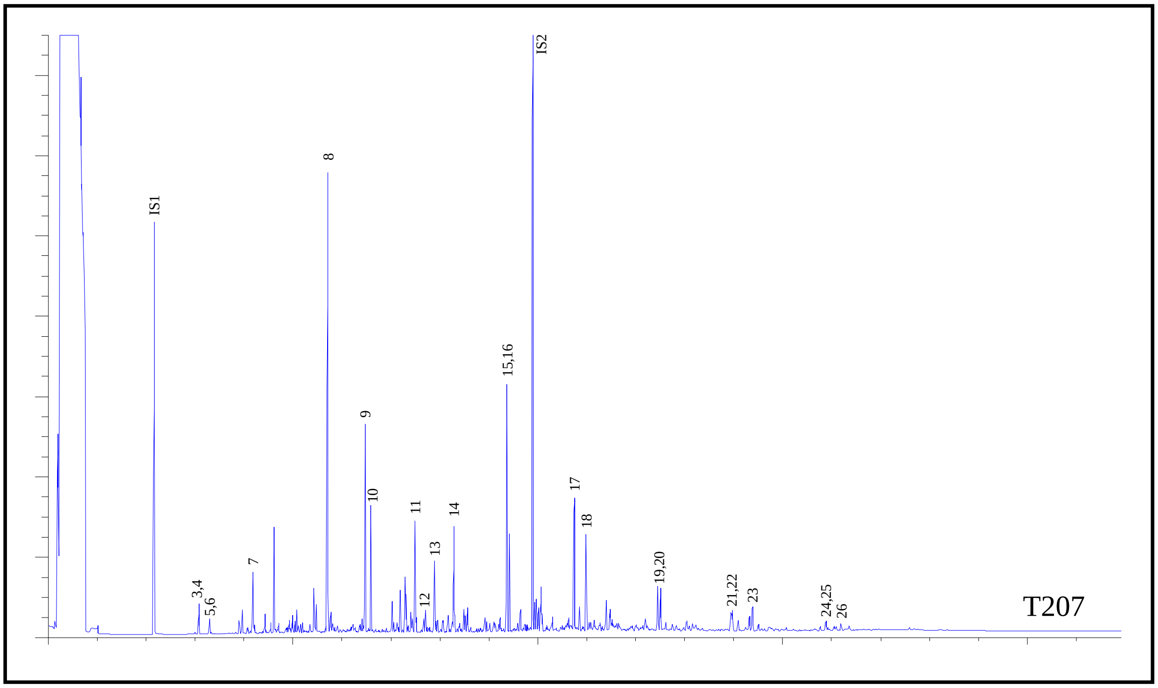

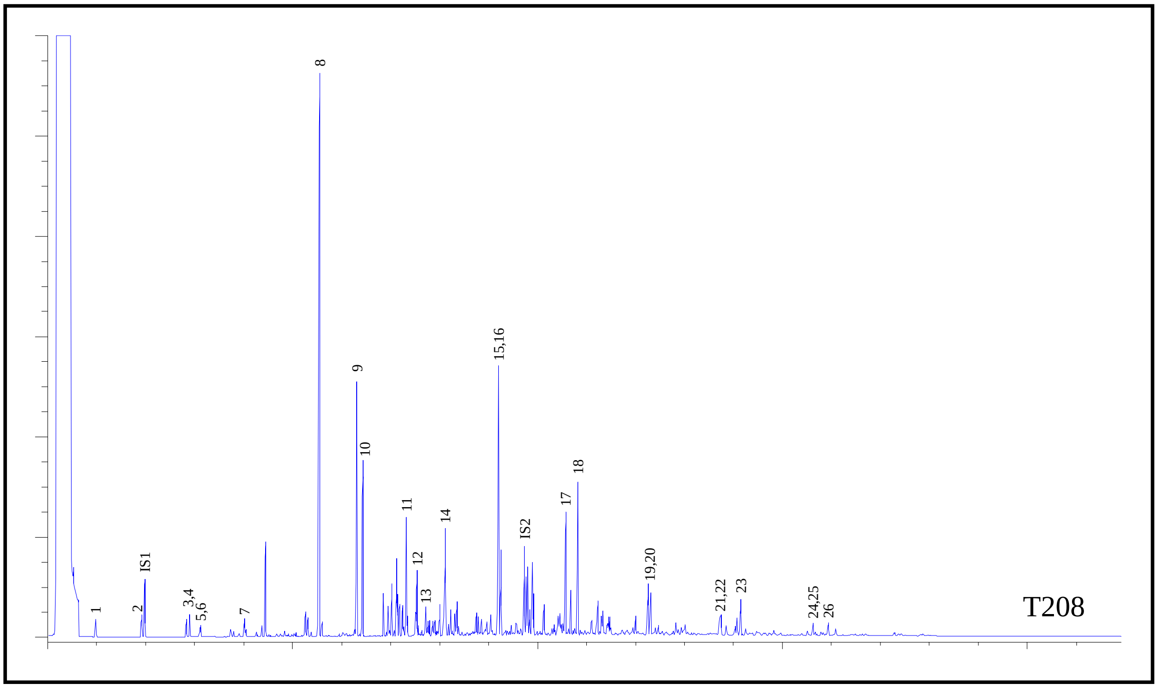

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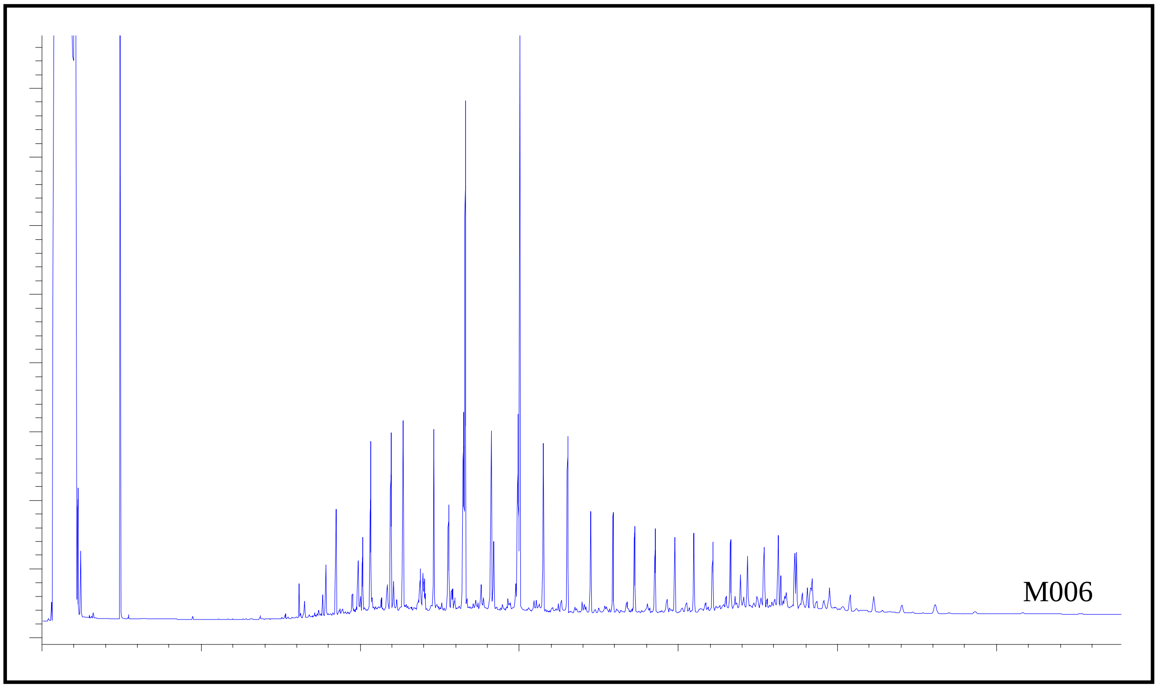

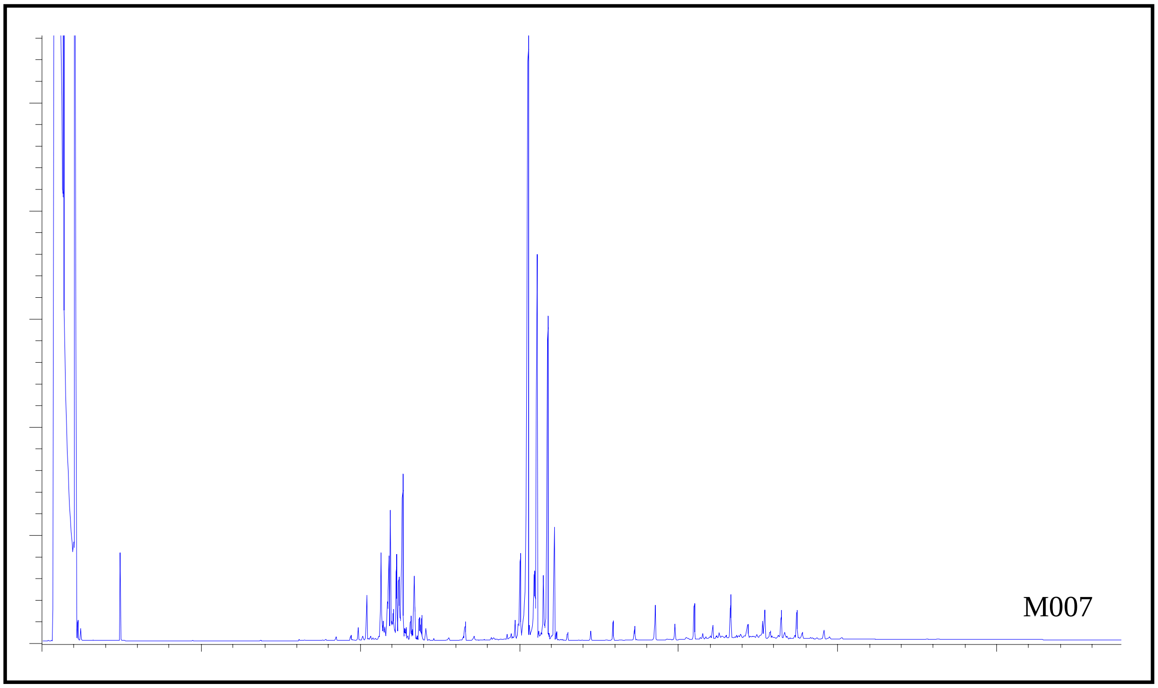

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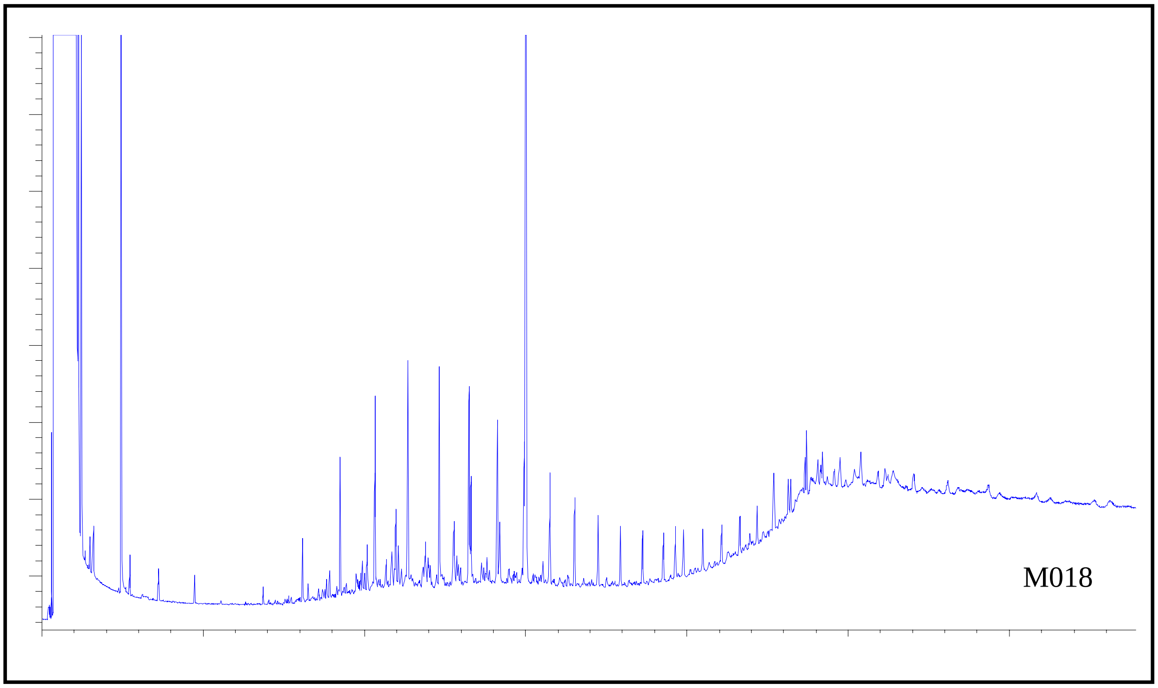

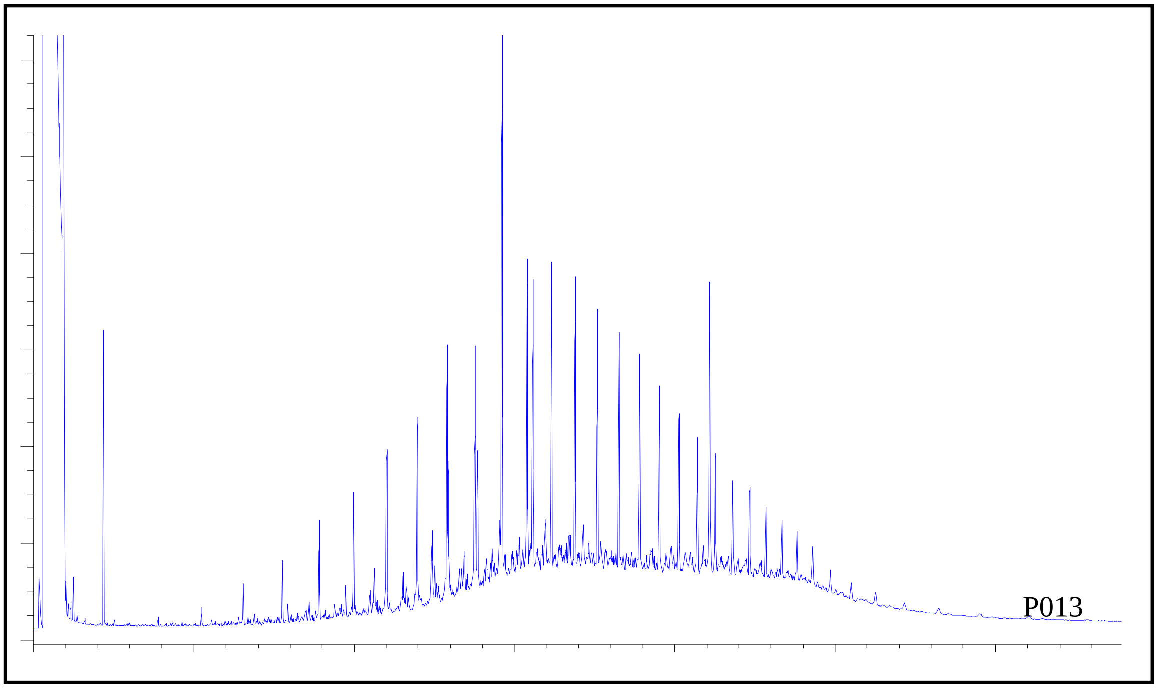

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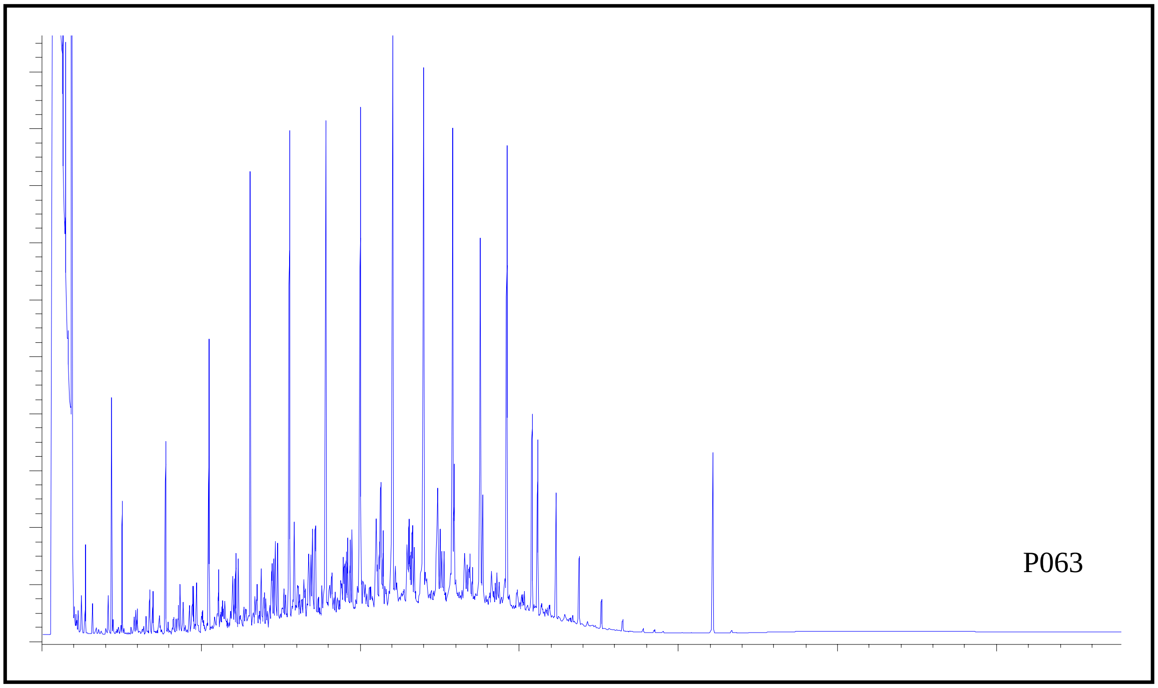

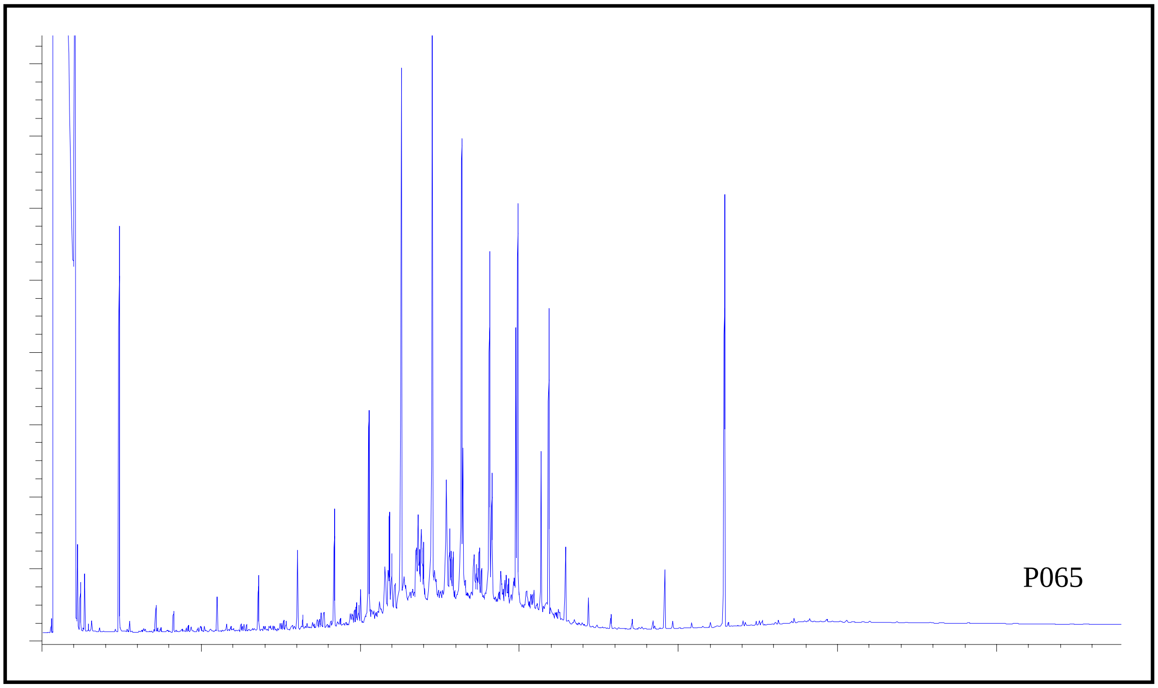

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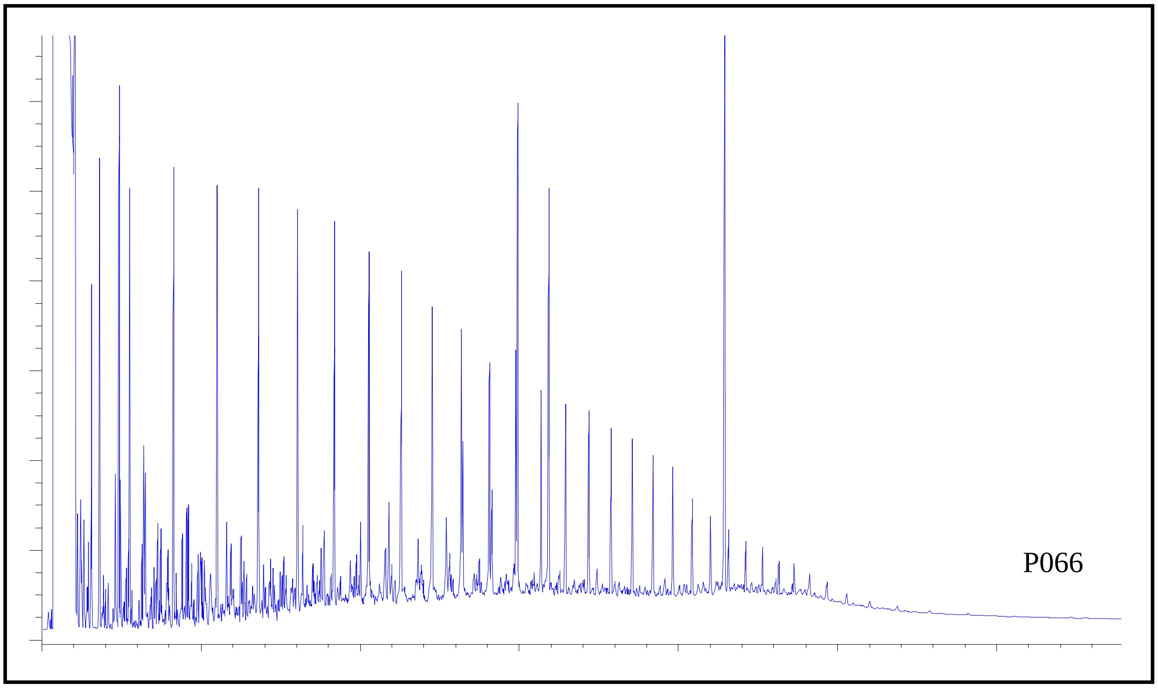

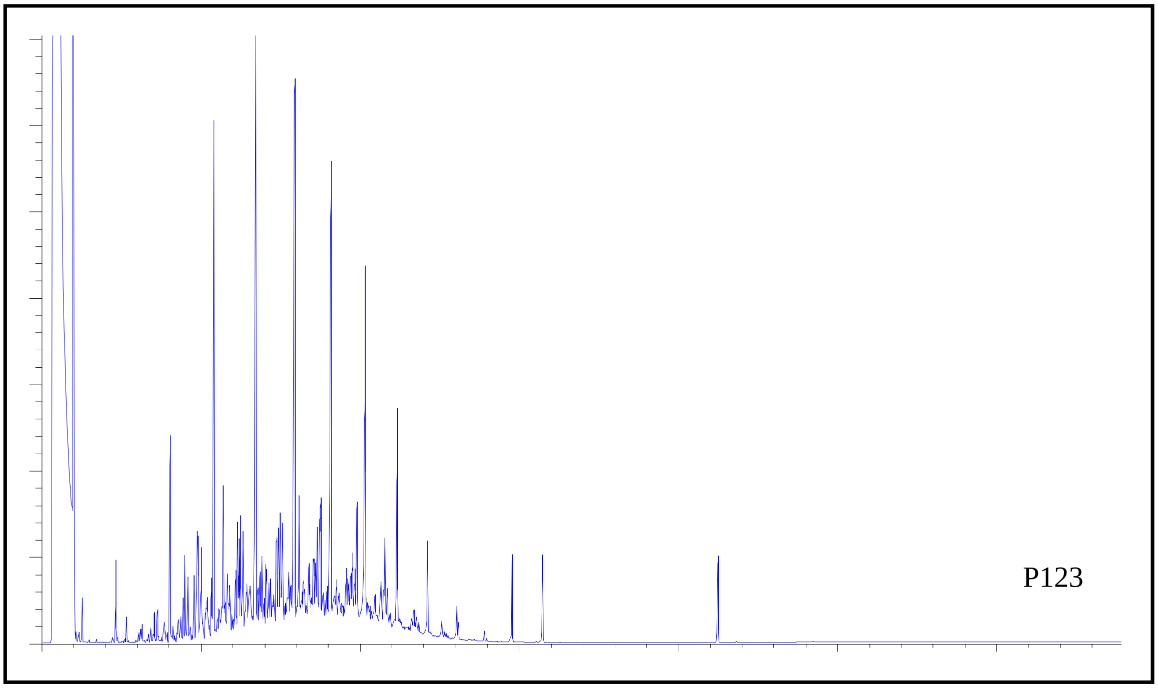

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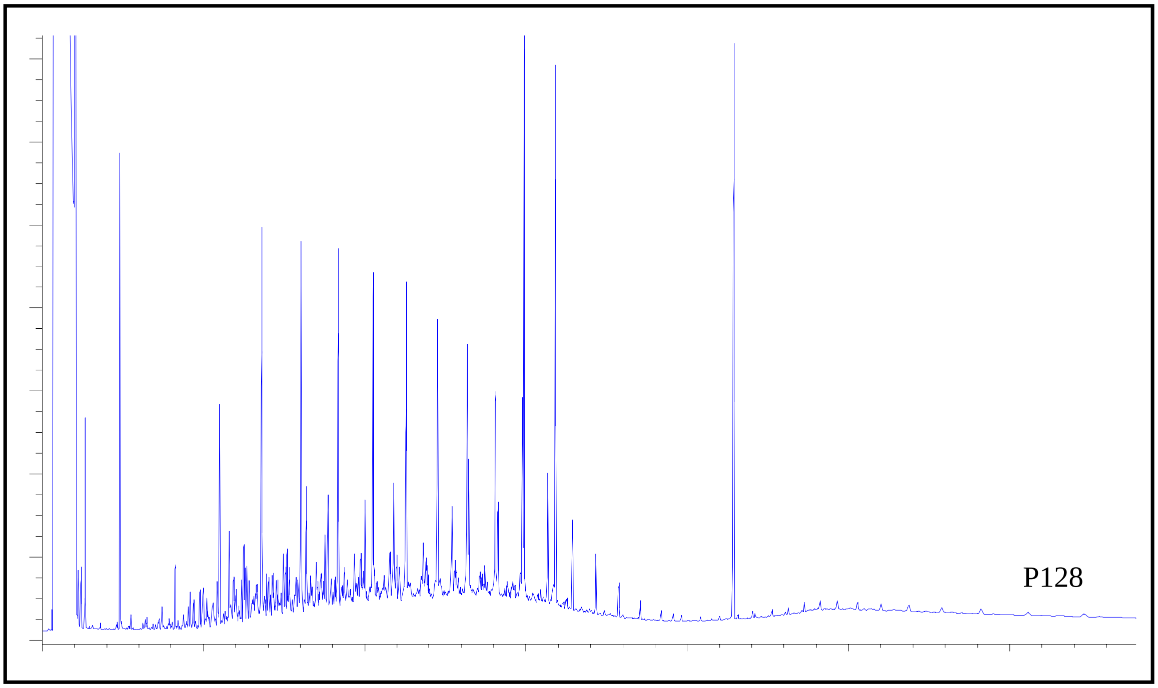

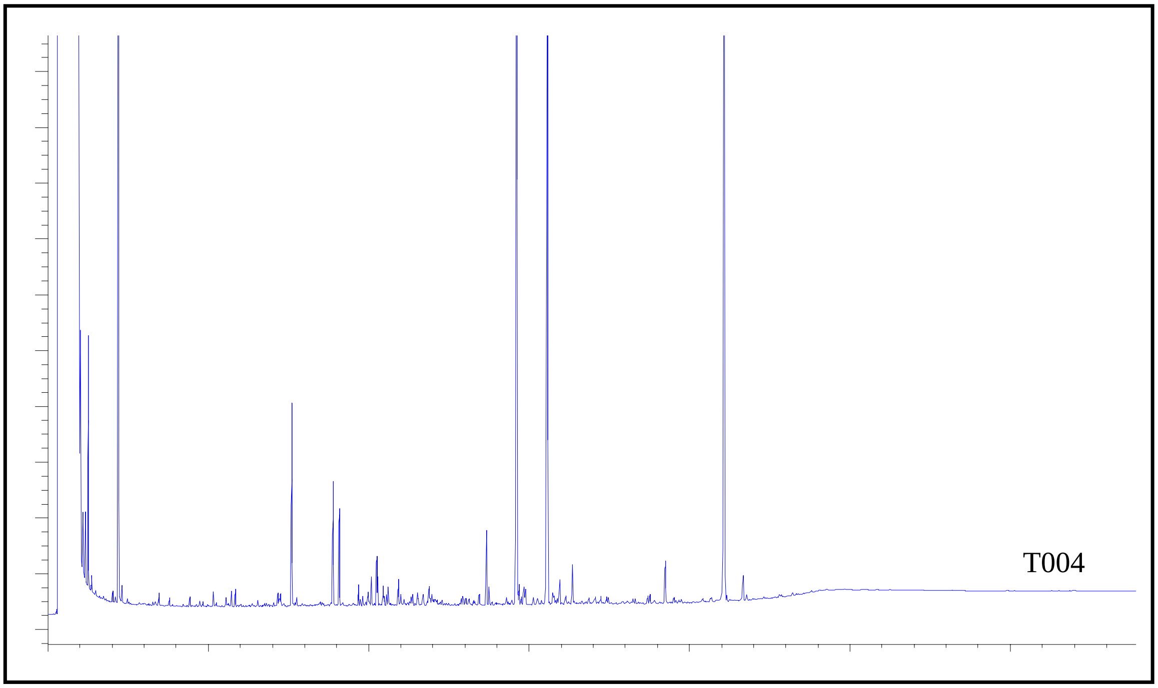

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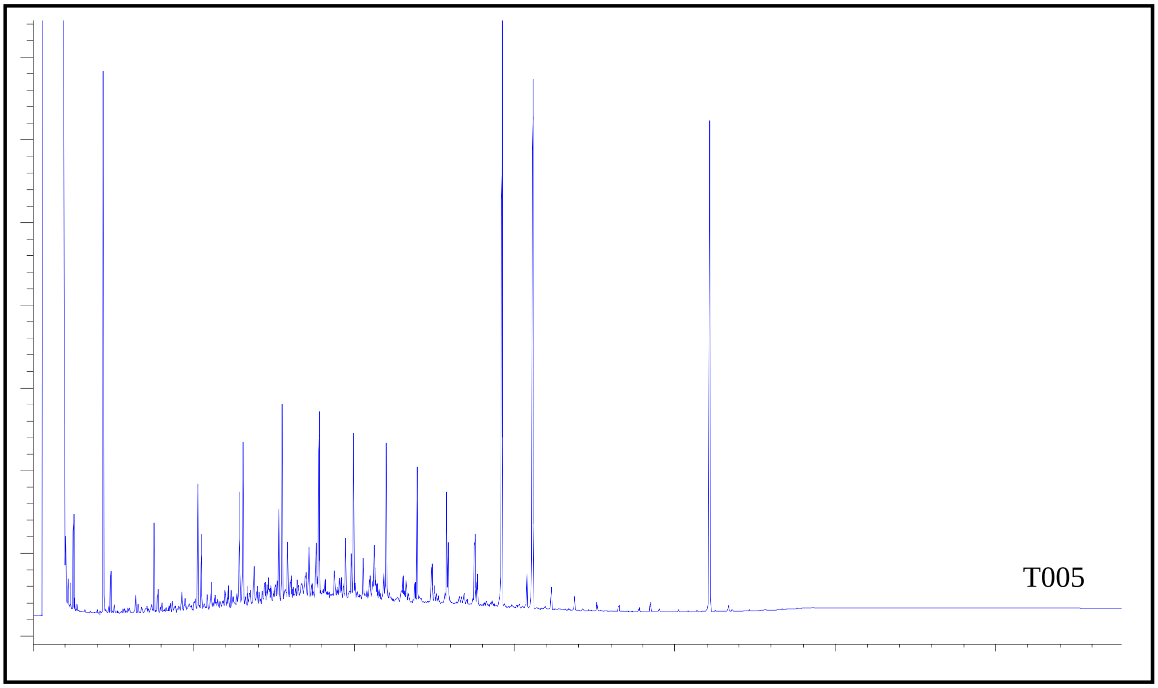

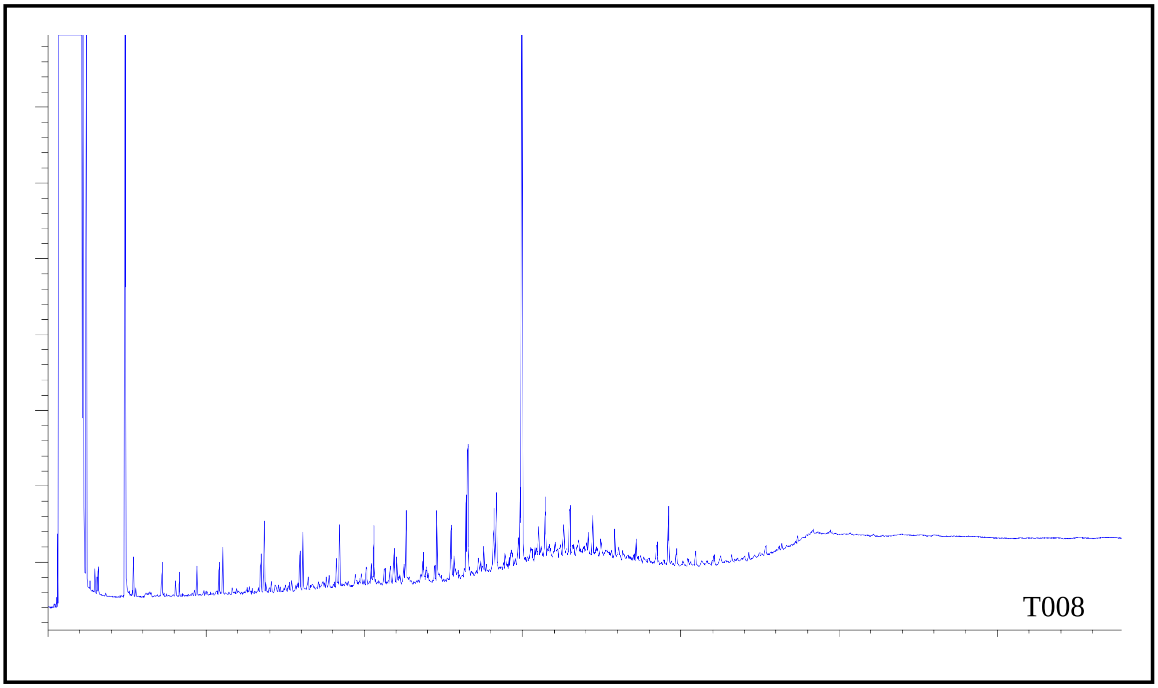

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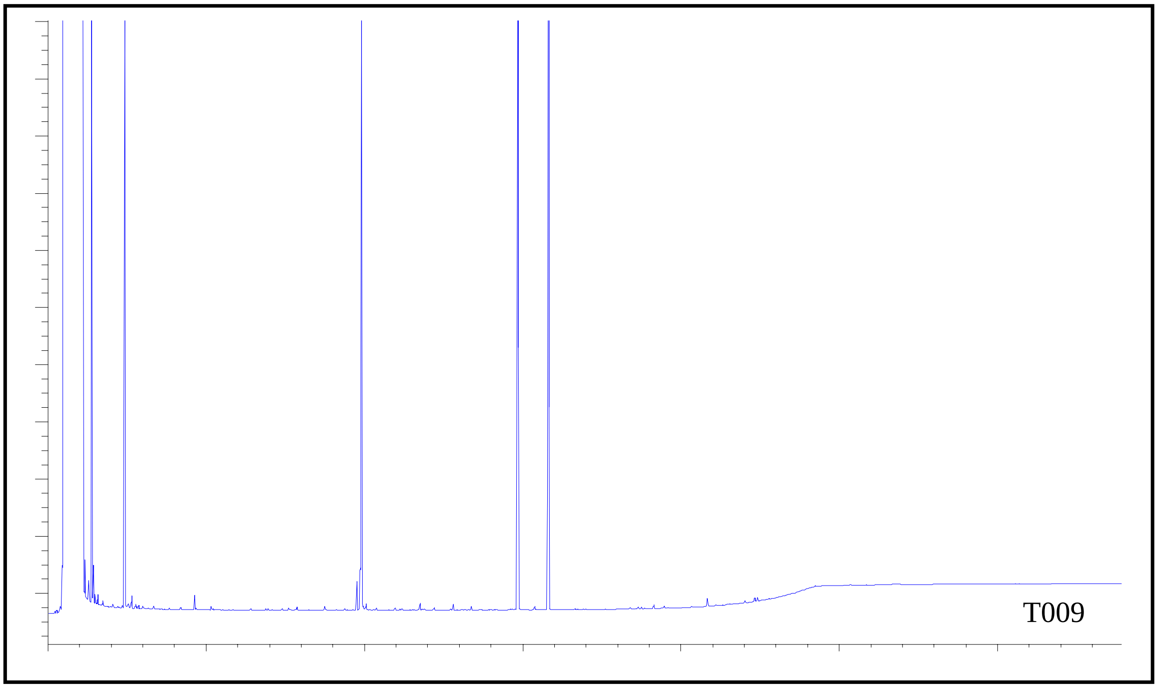

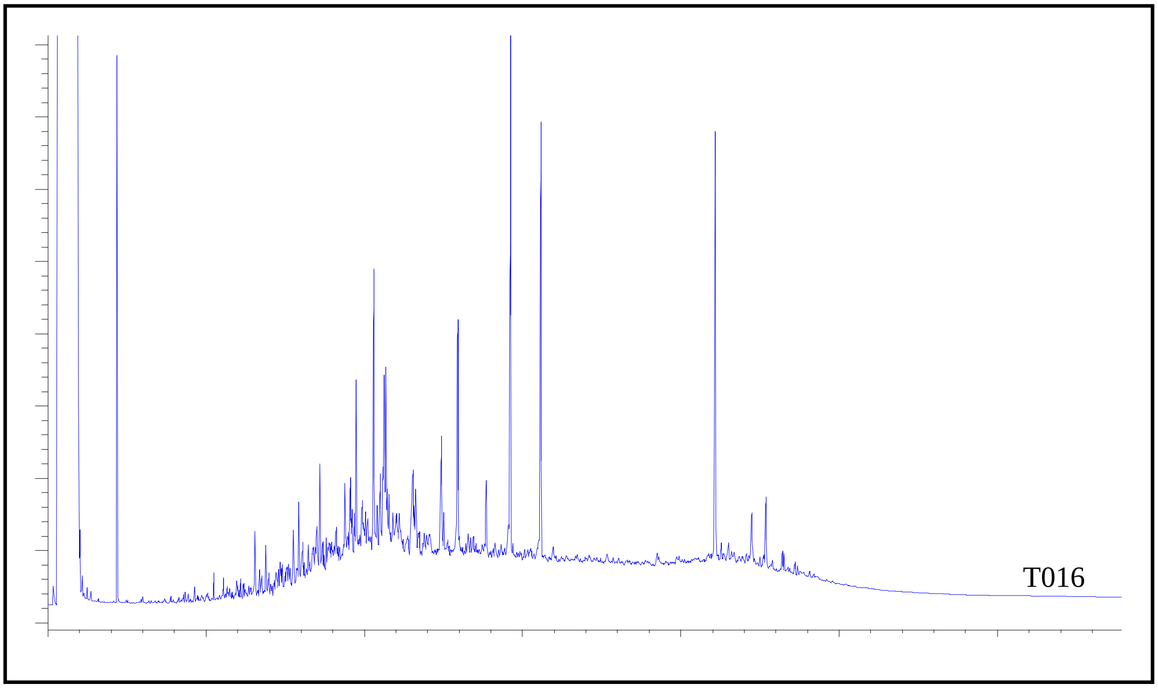

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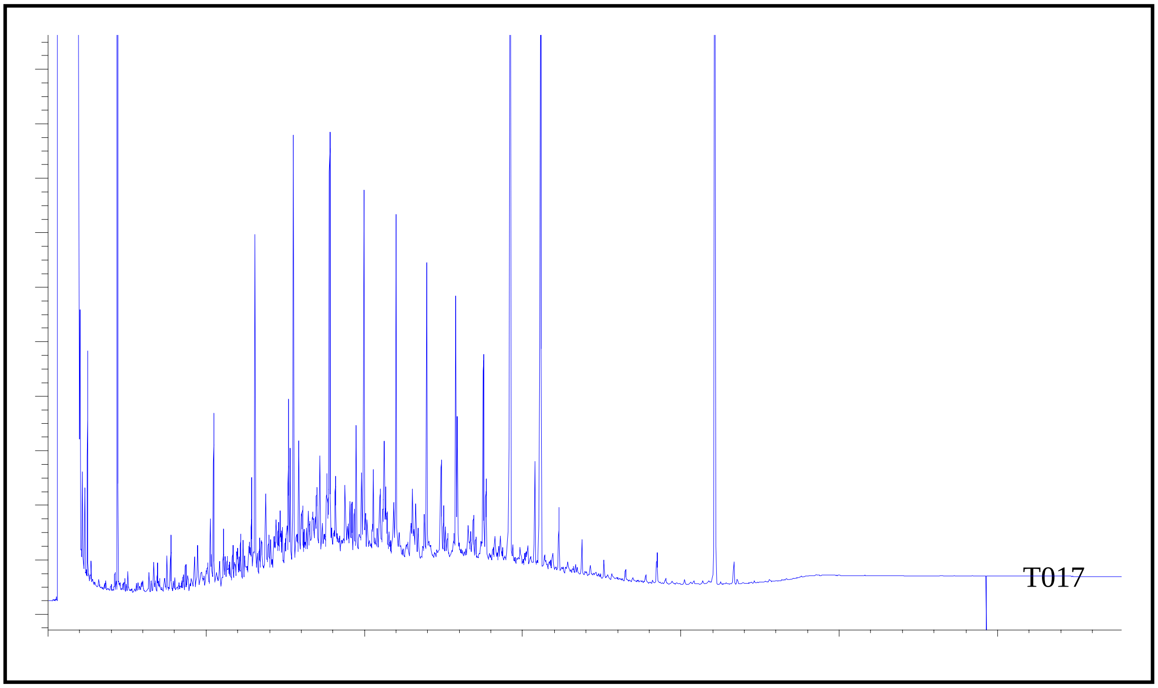

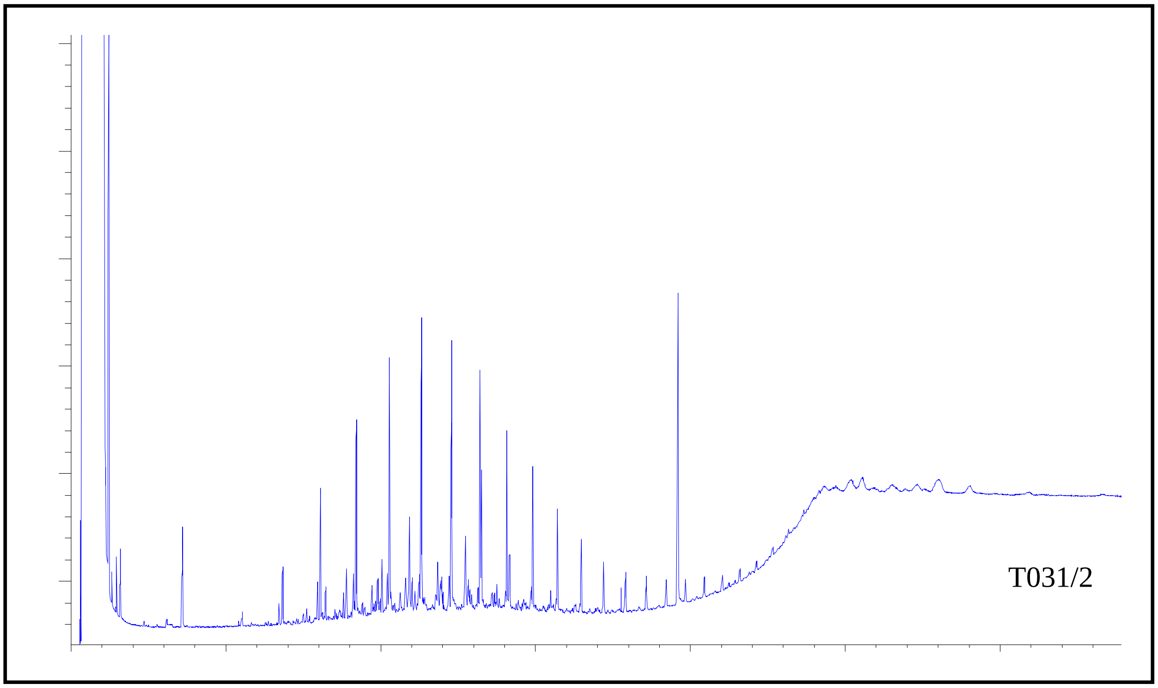

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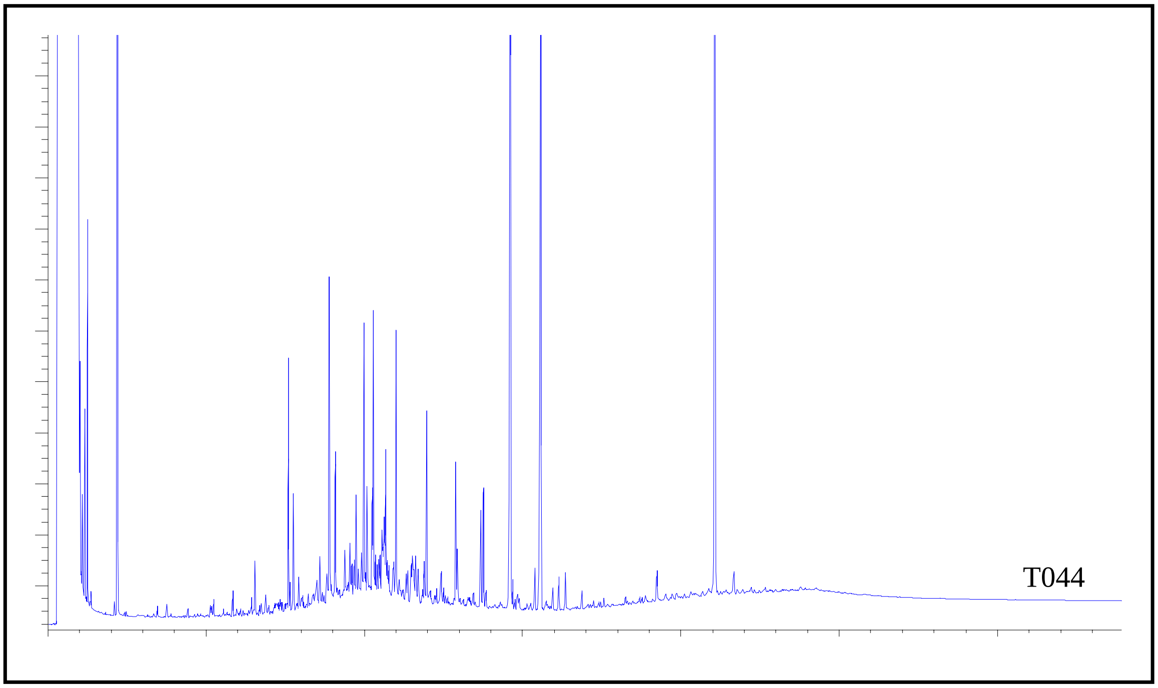

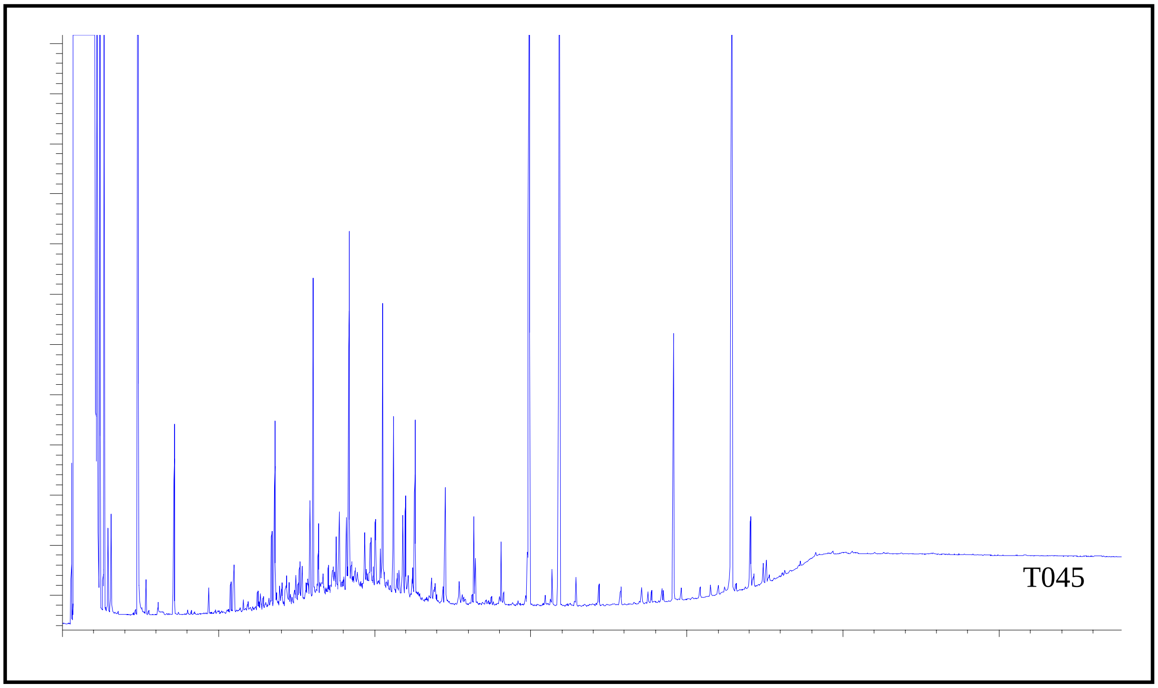

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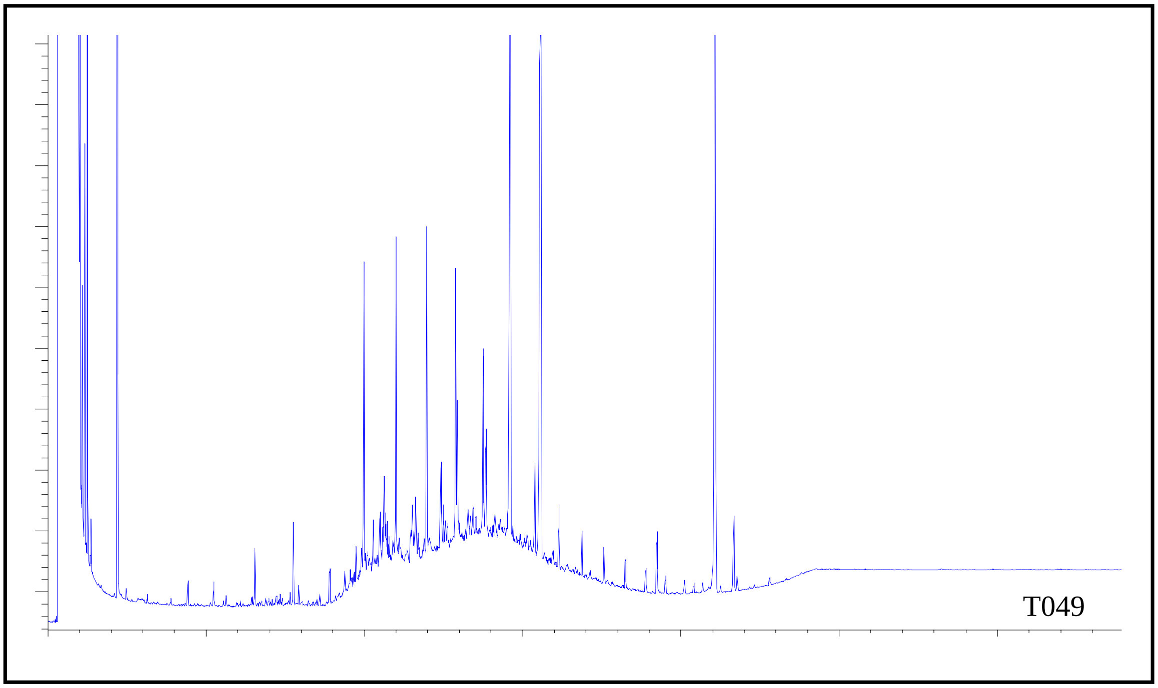

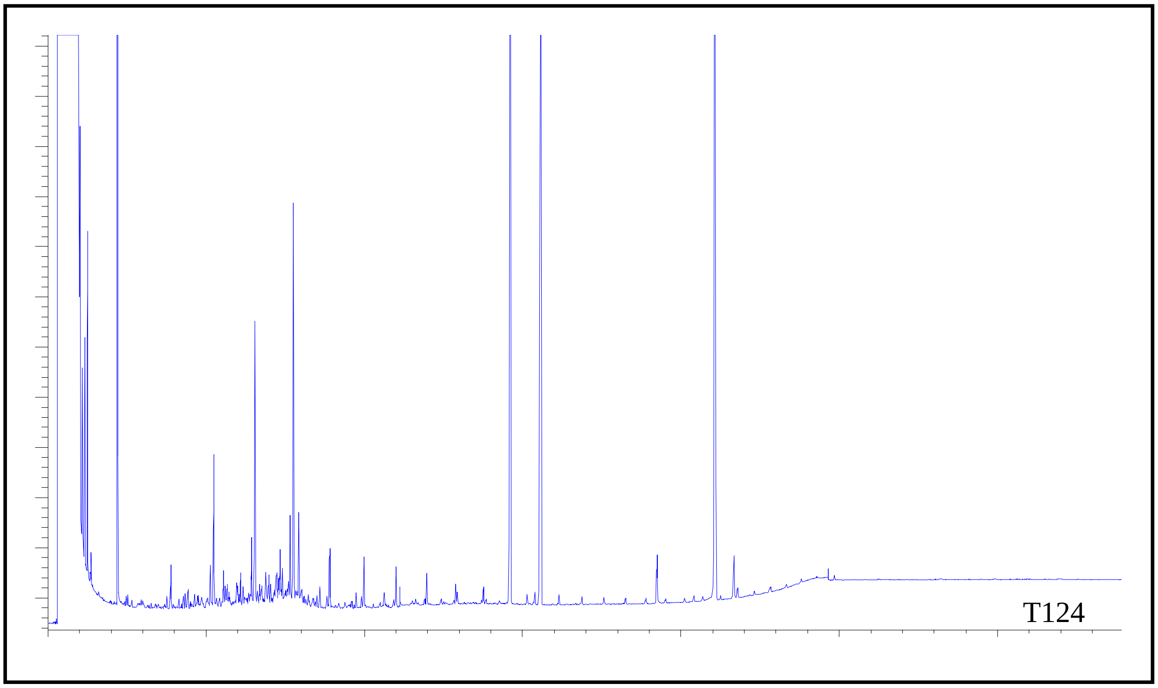

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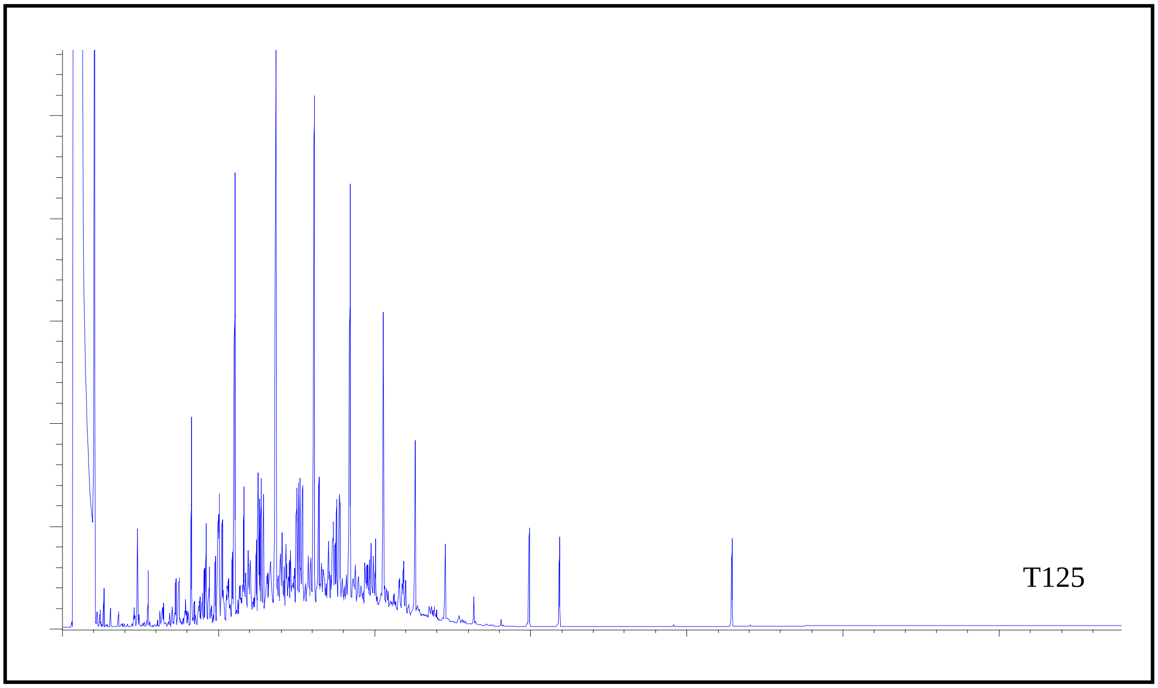

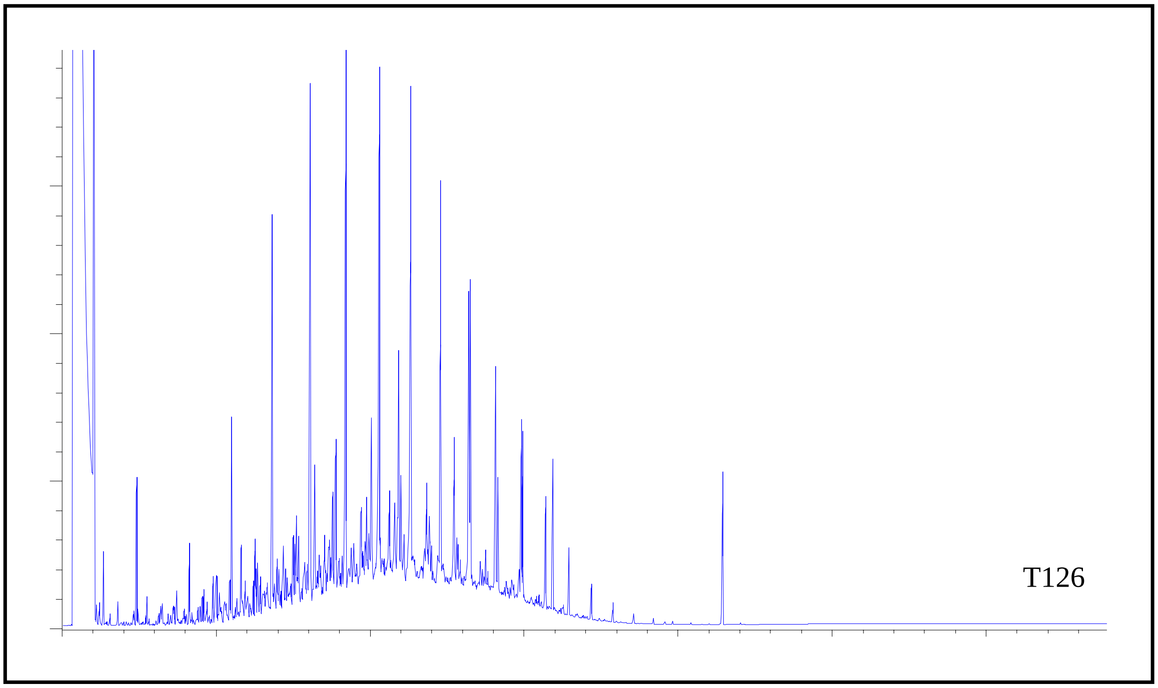

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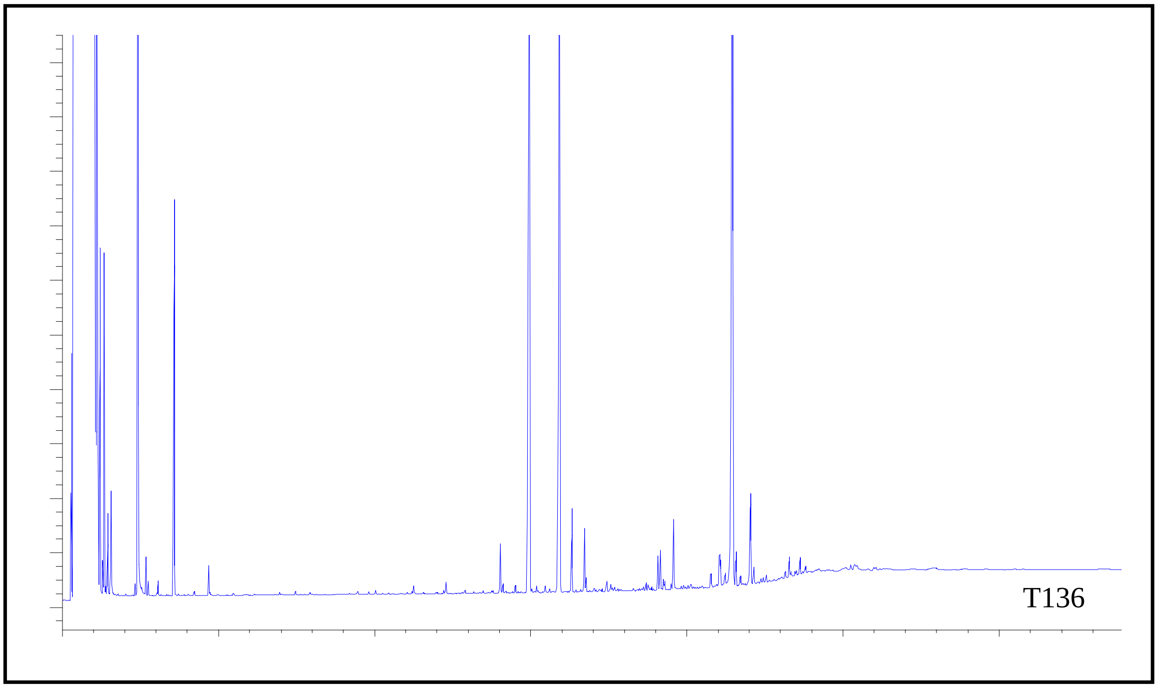

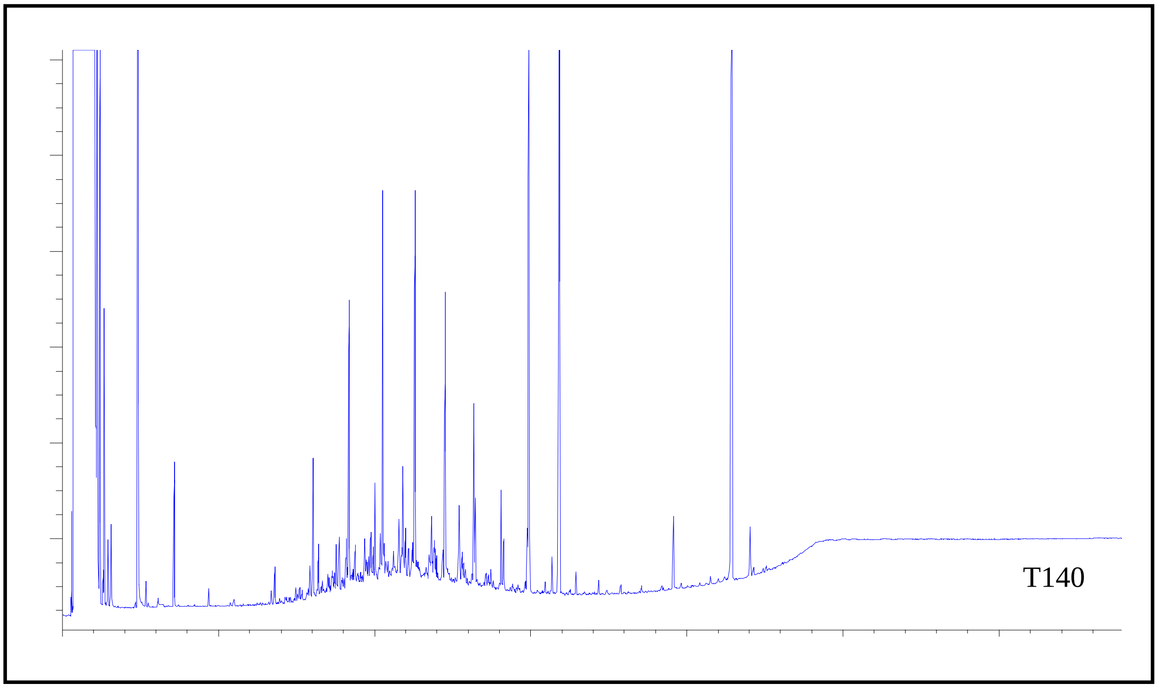

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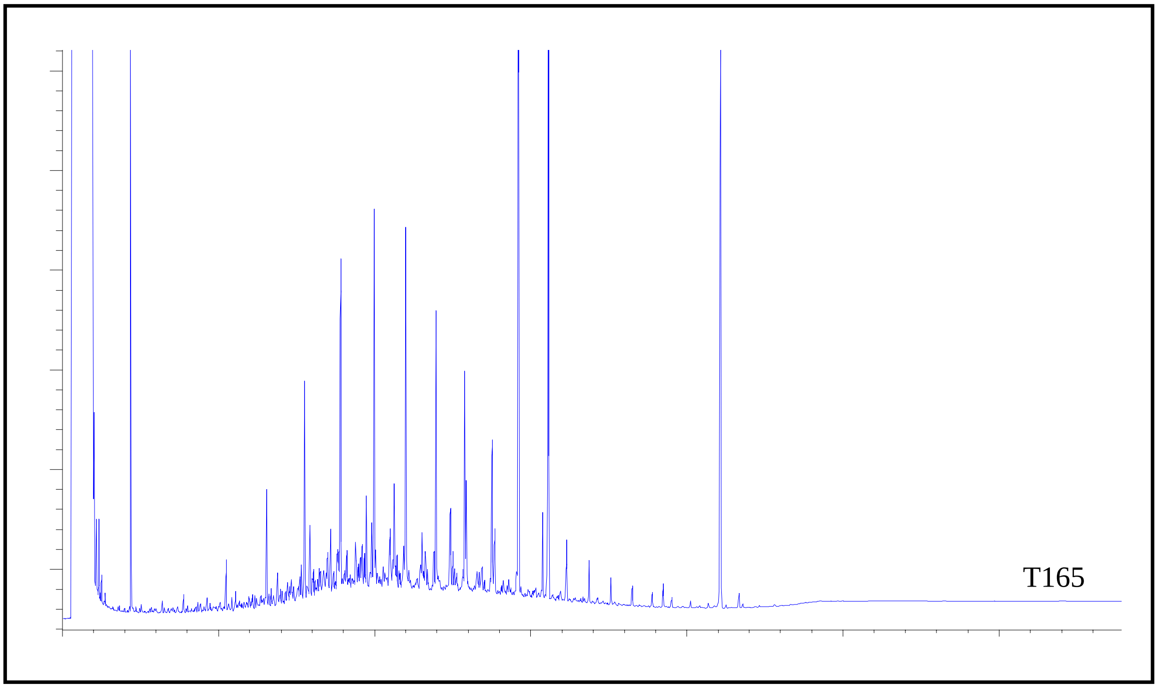

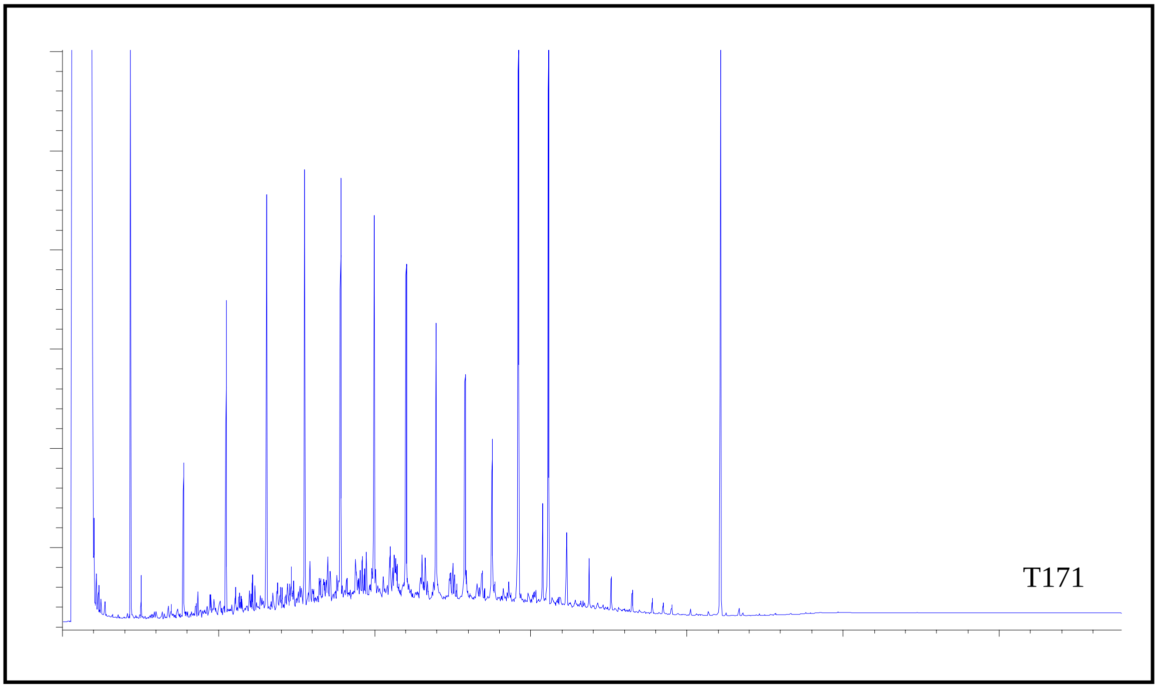

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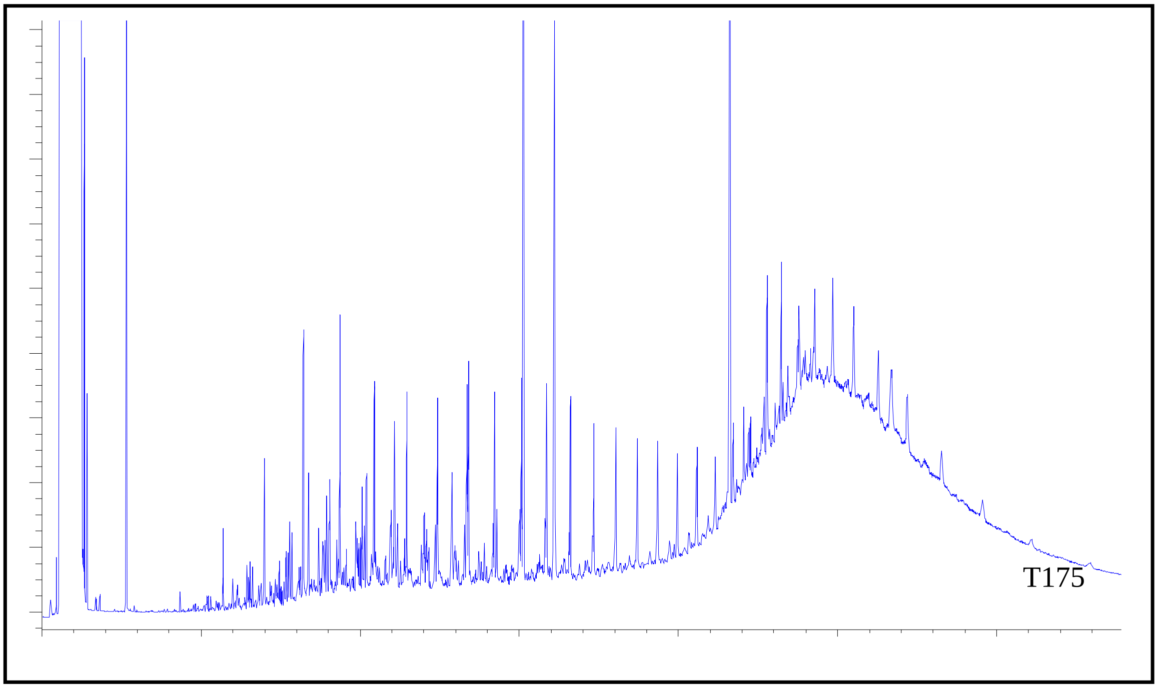
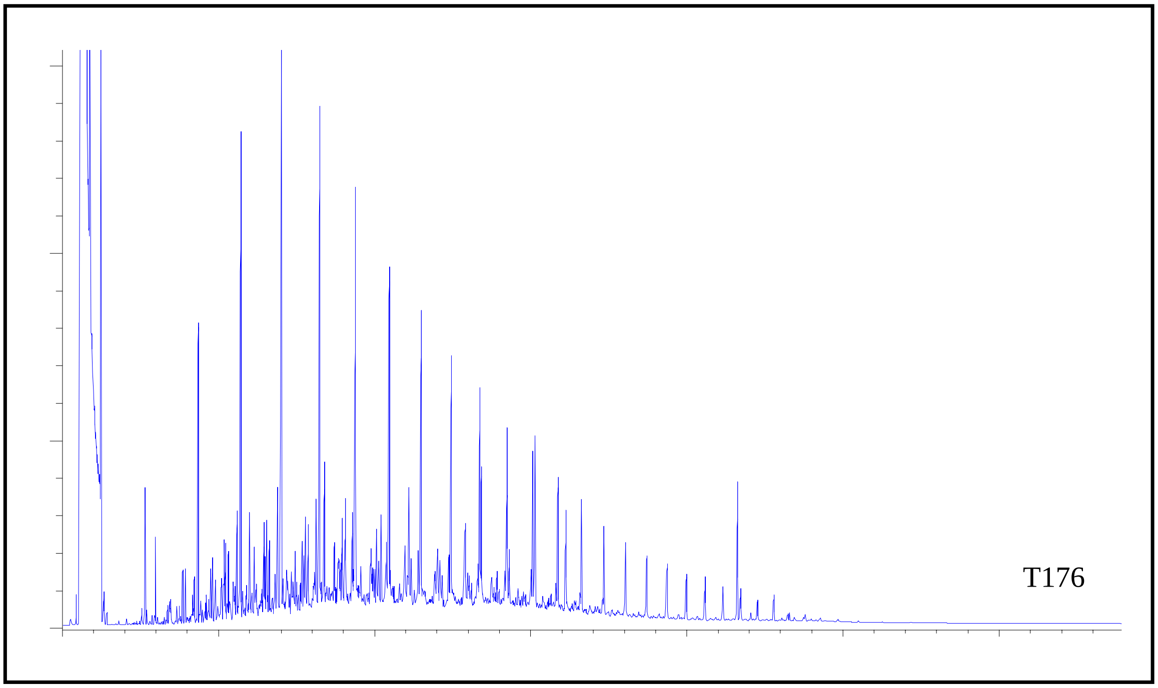
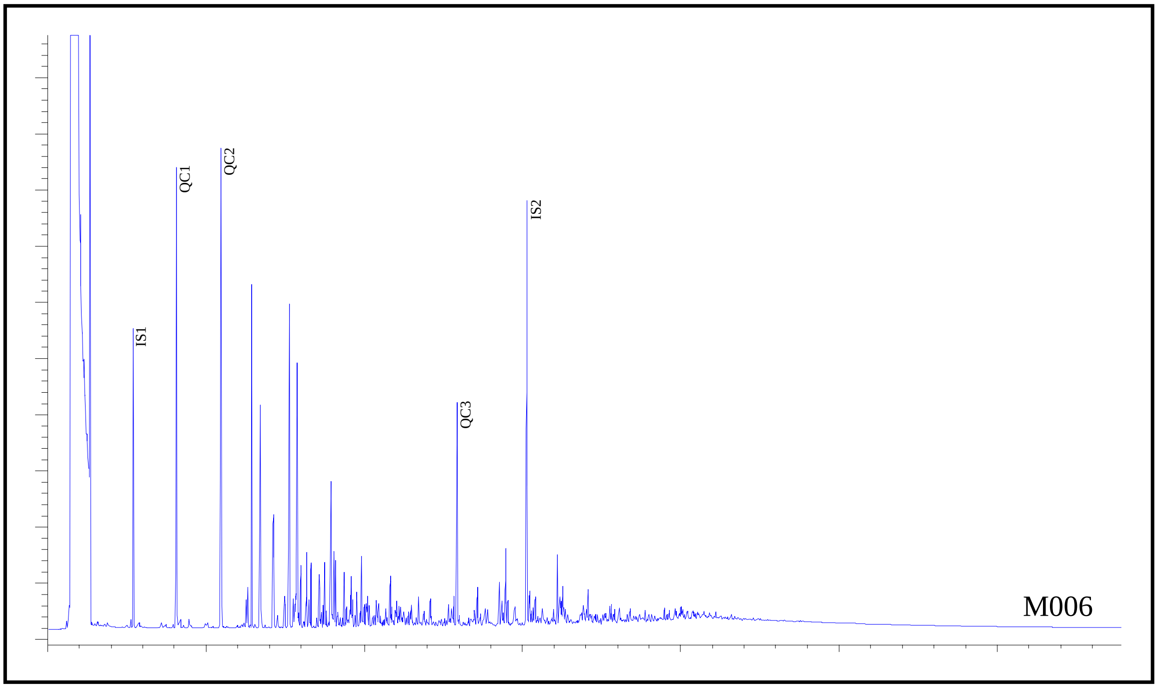
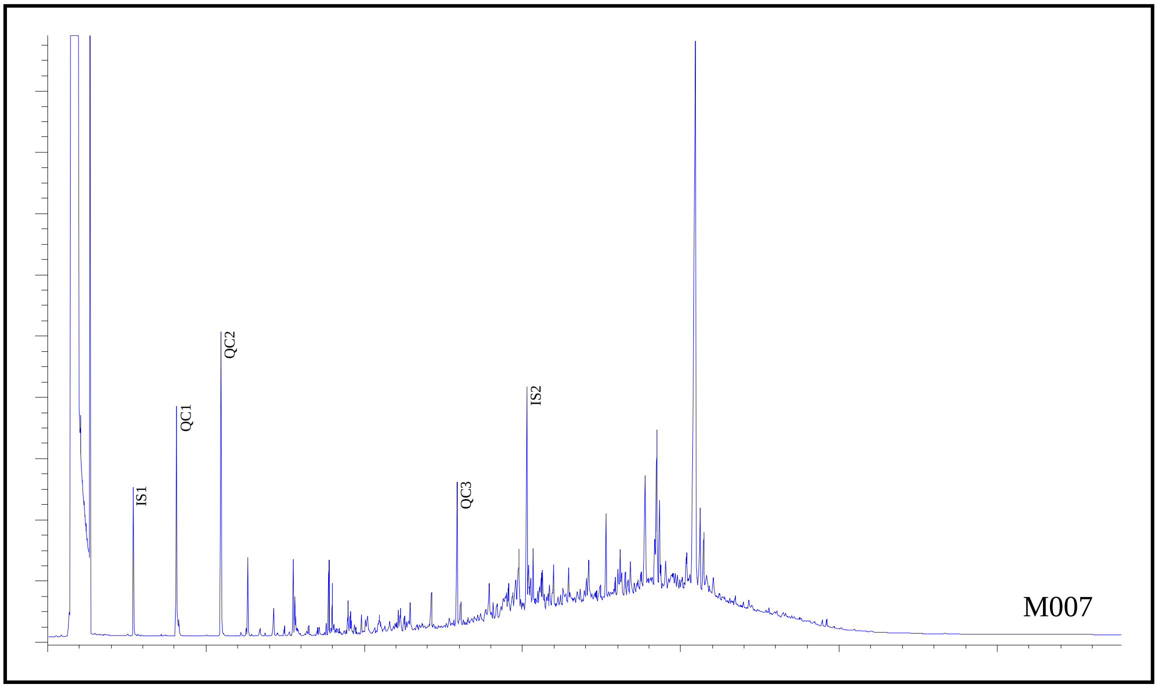




Organic Acids





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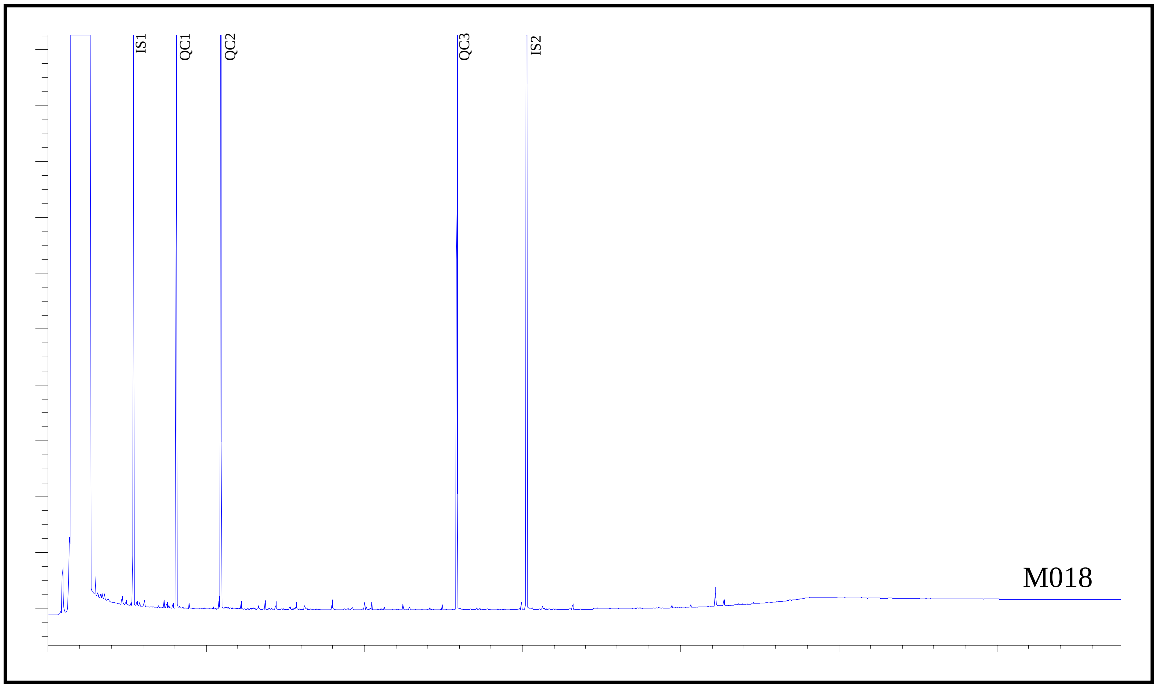
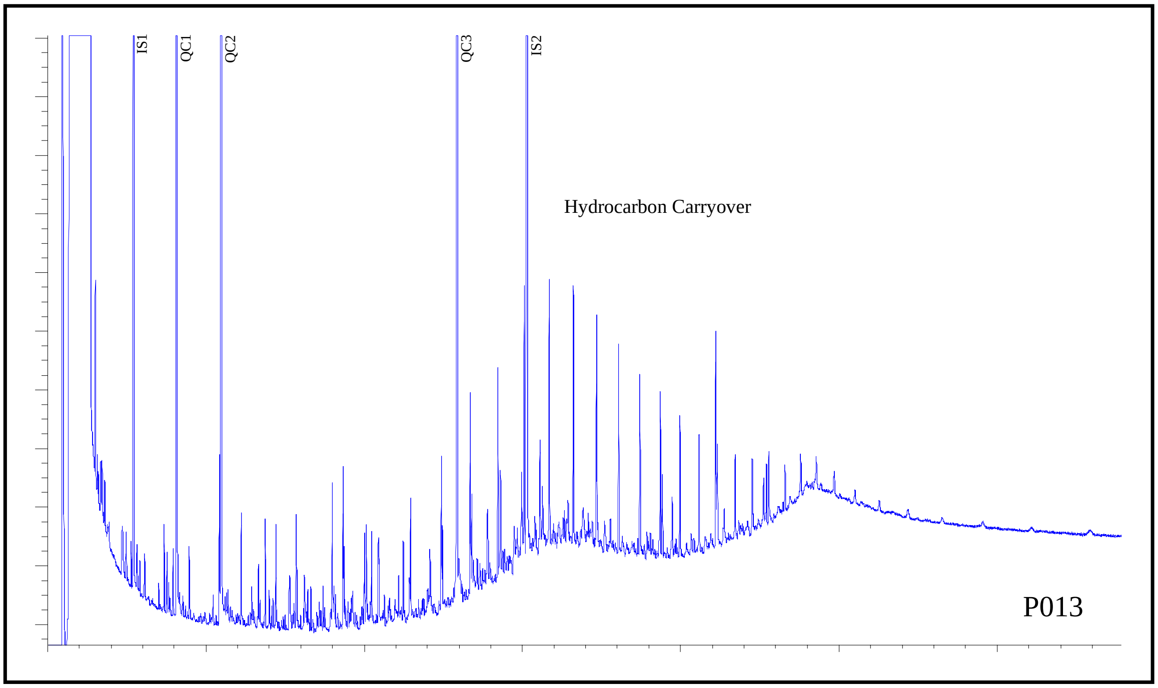
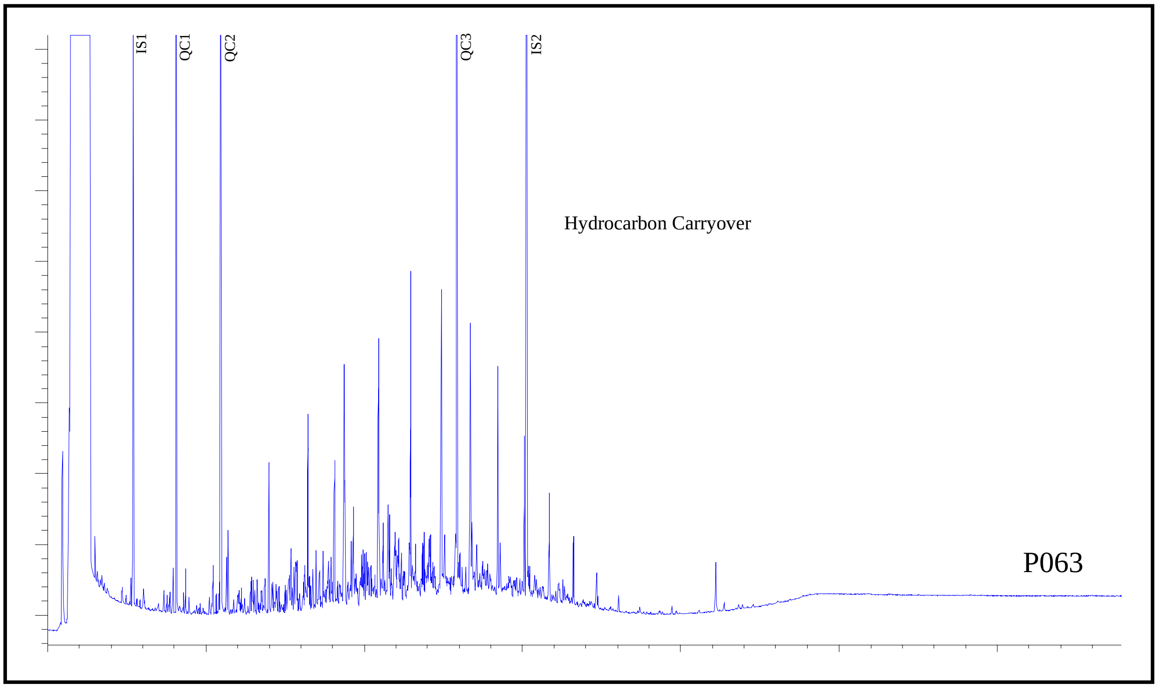
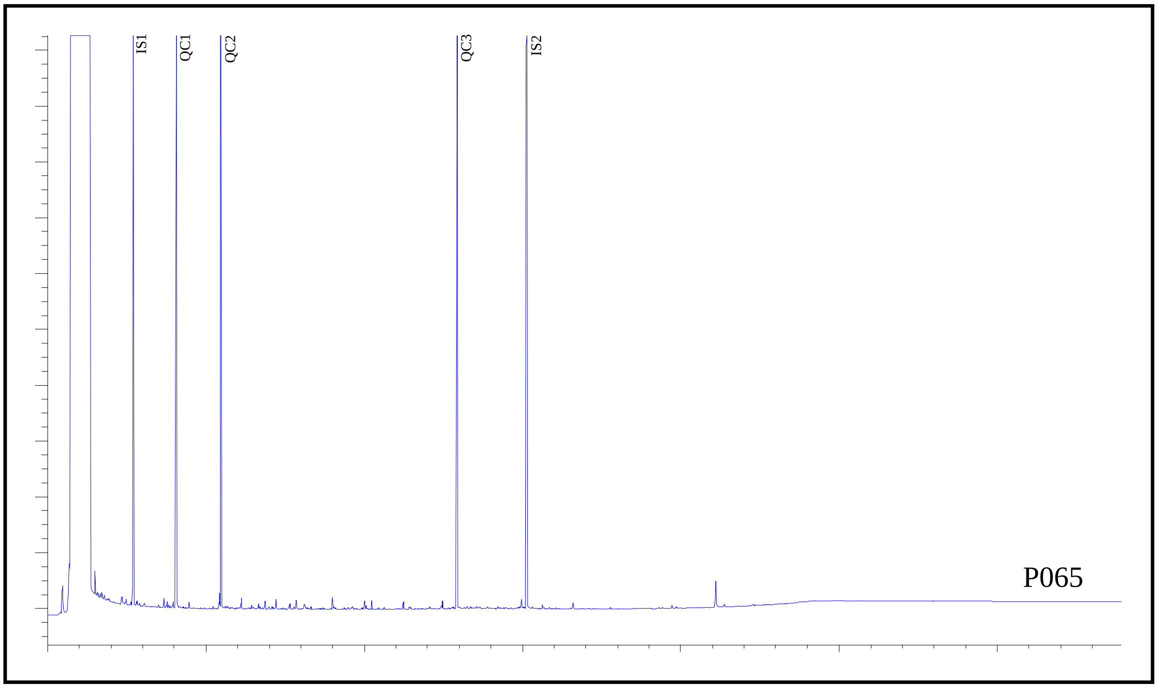




Organic Acids





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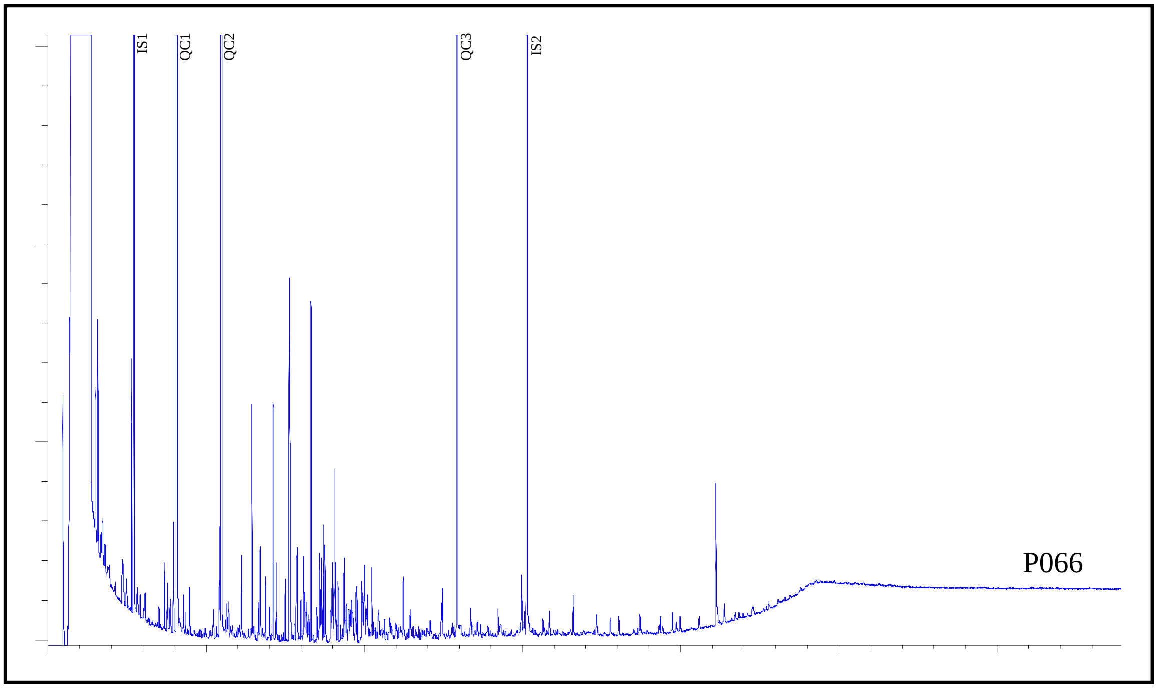

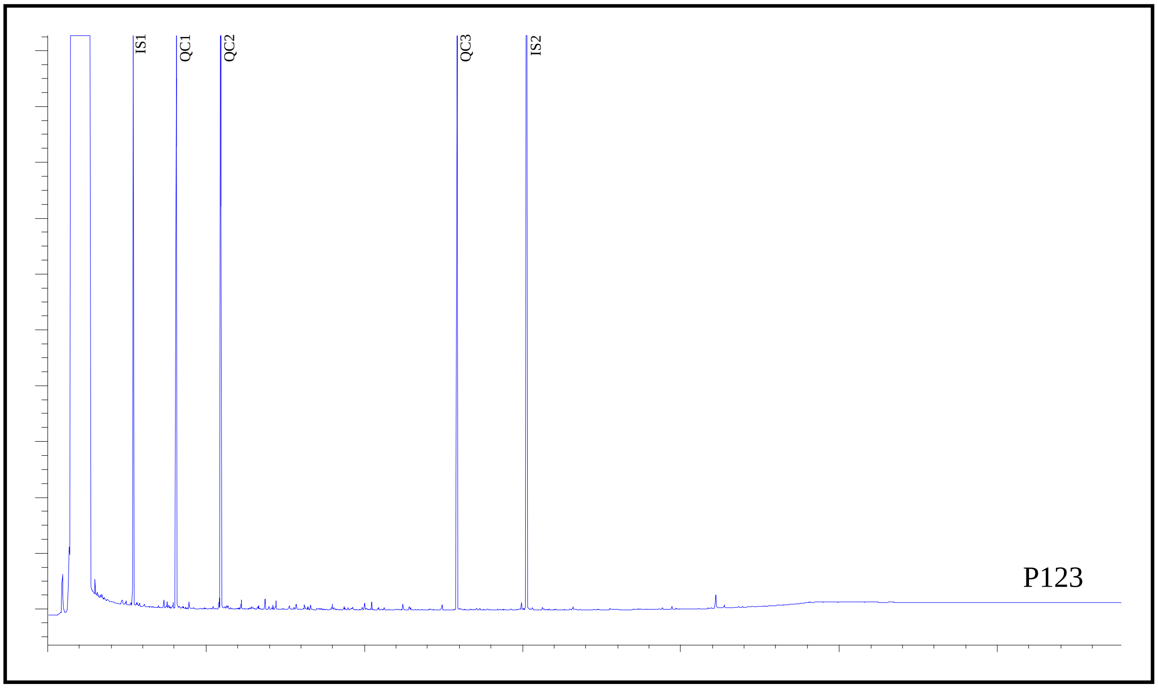

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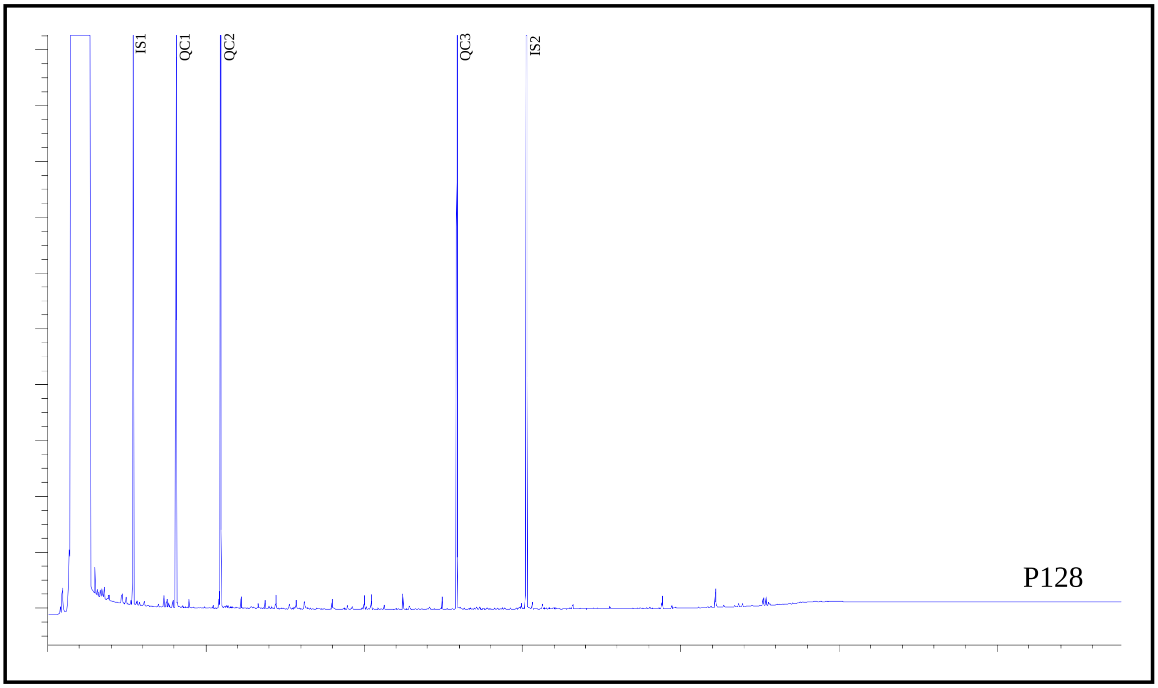

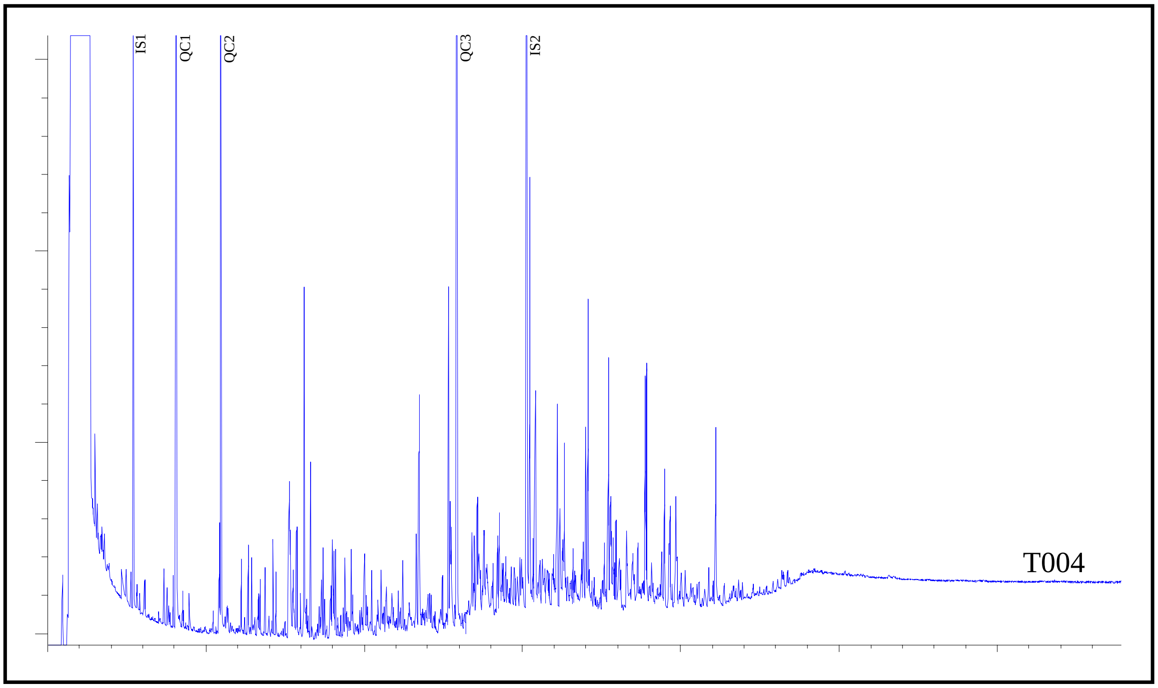

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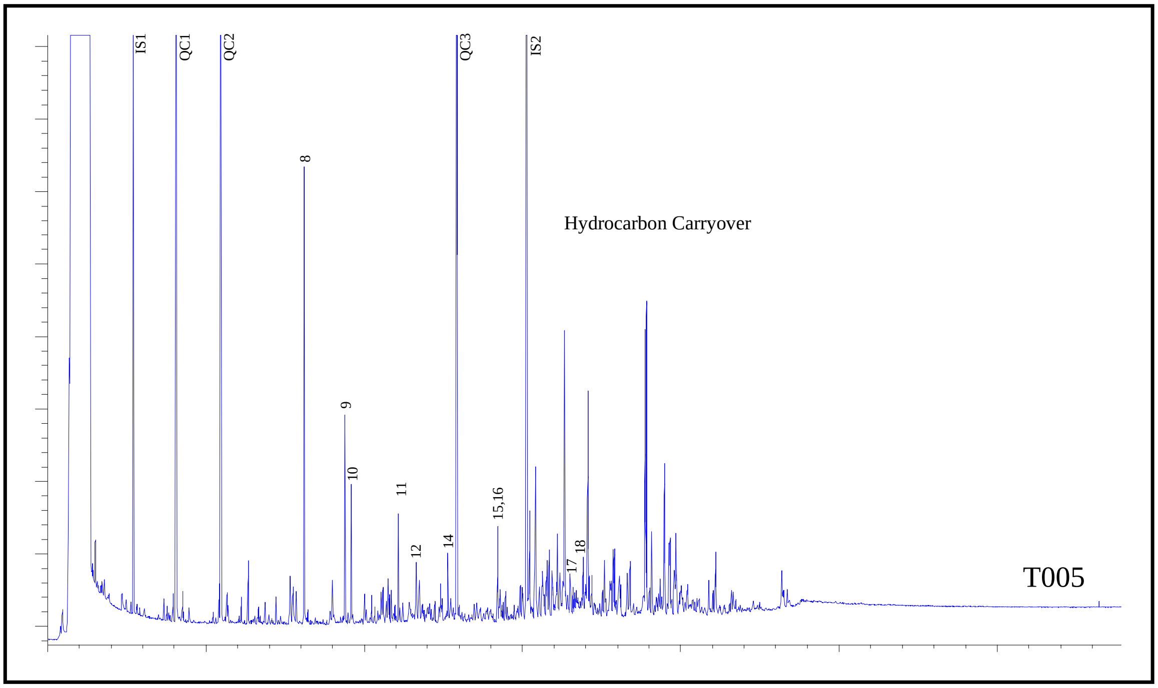

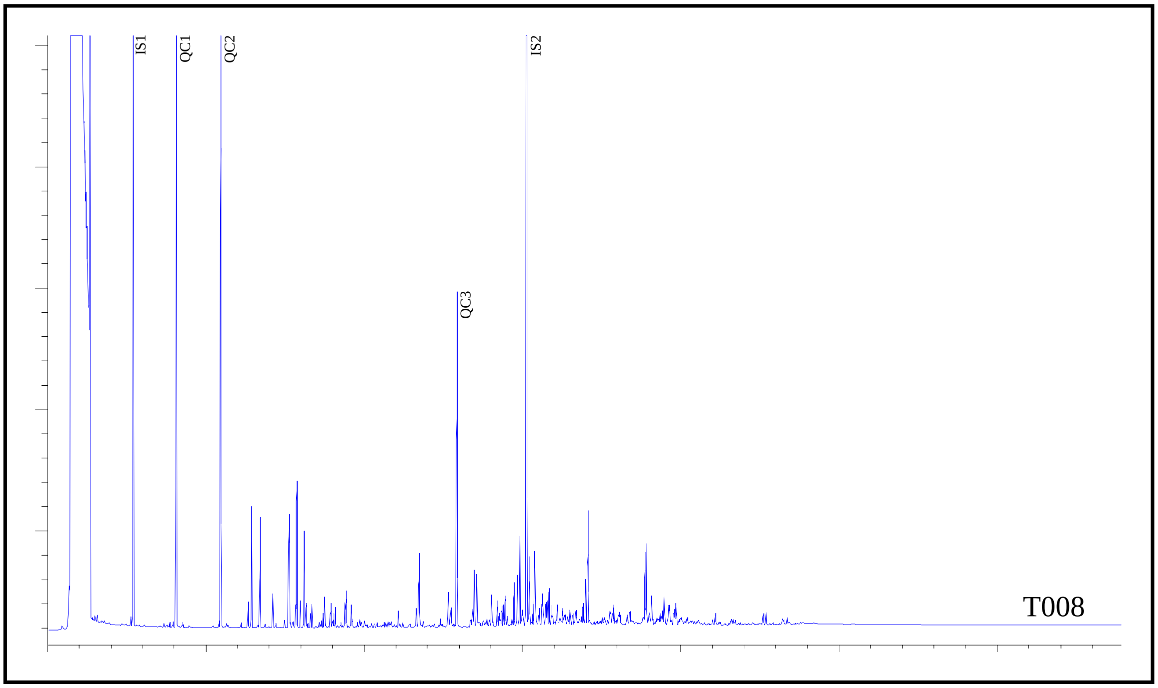

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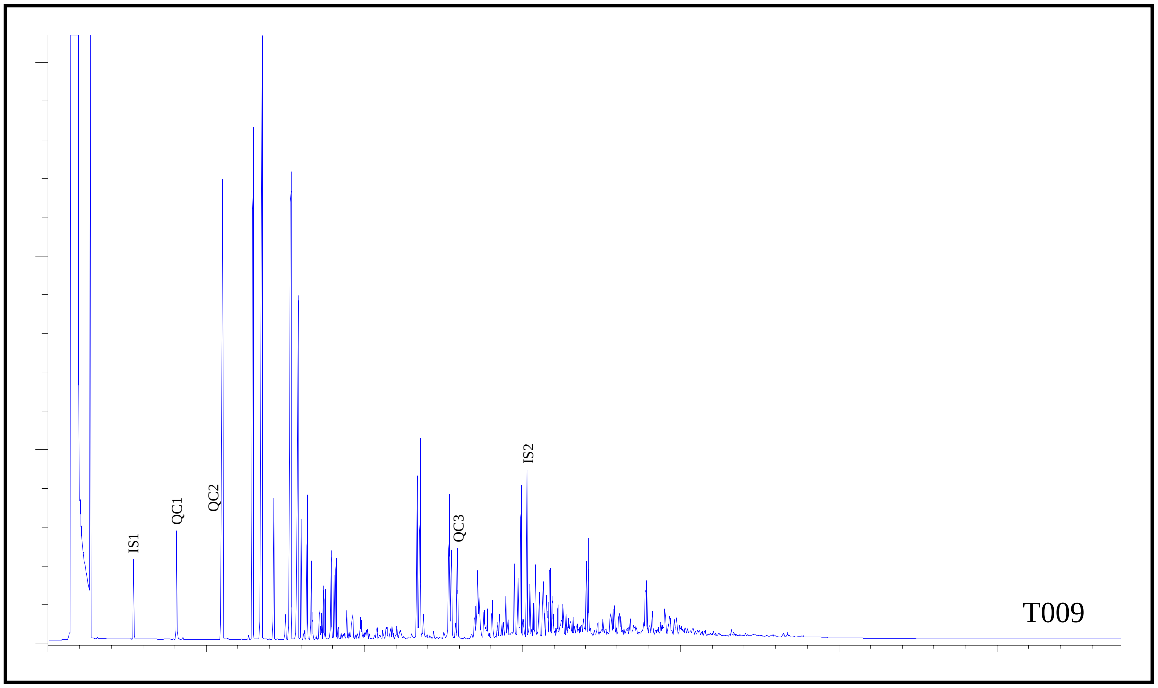

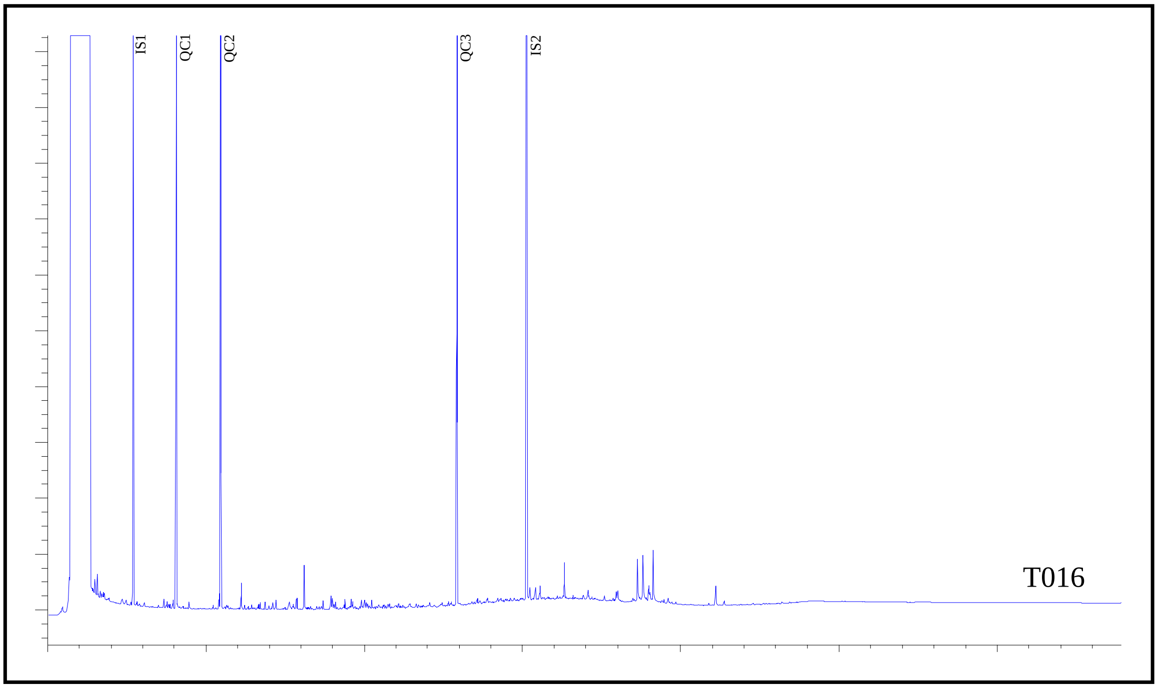

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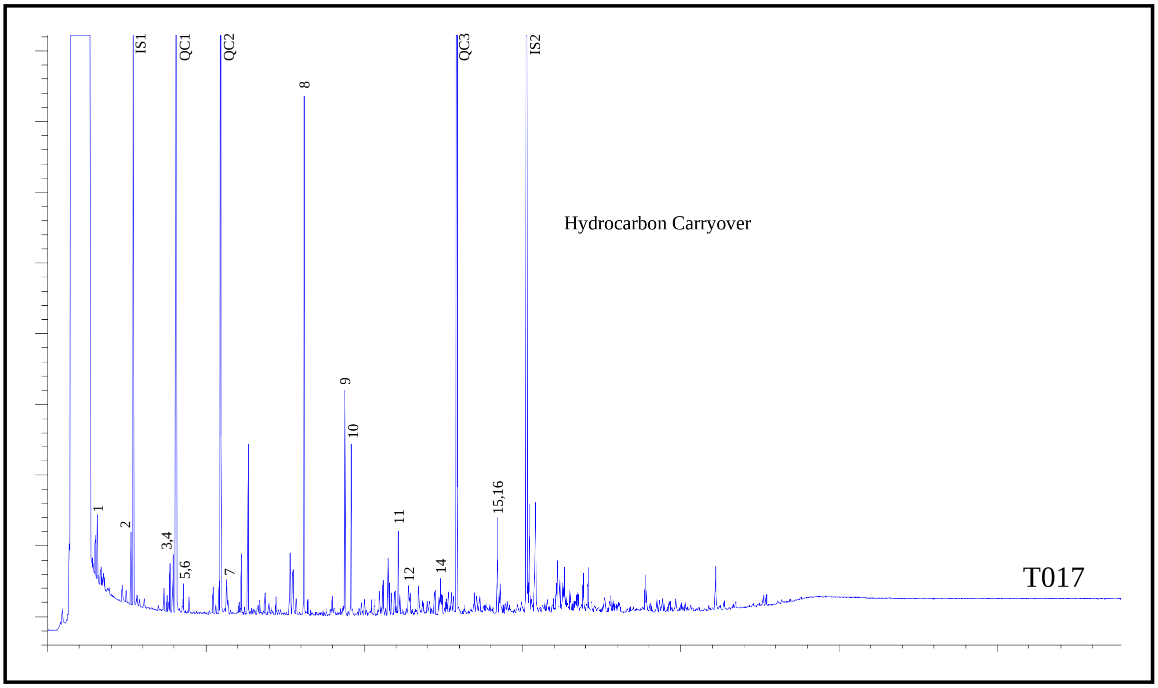

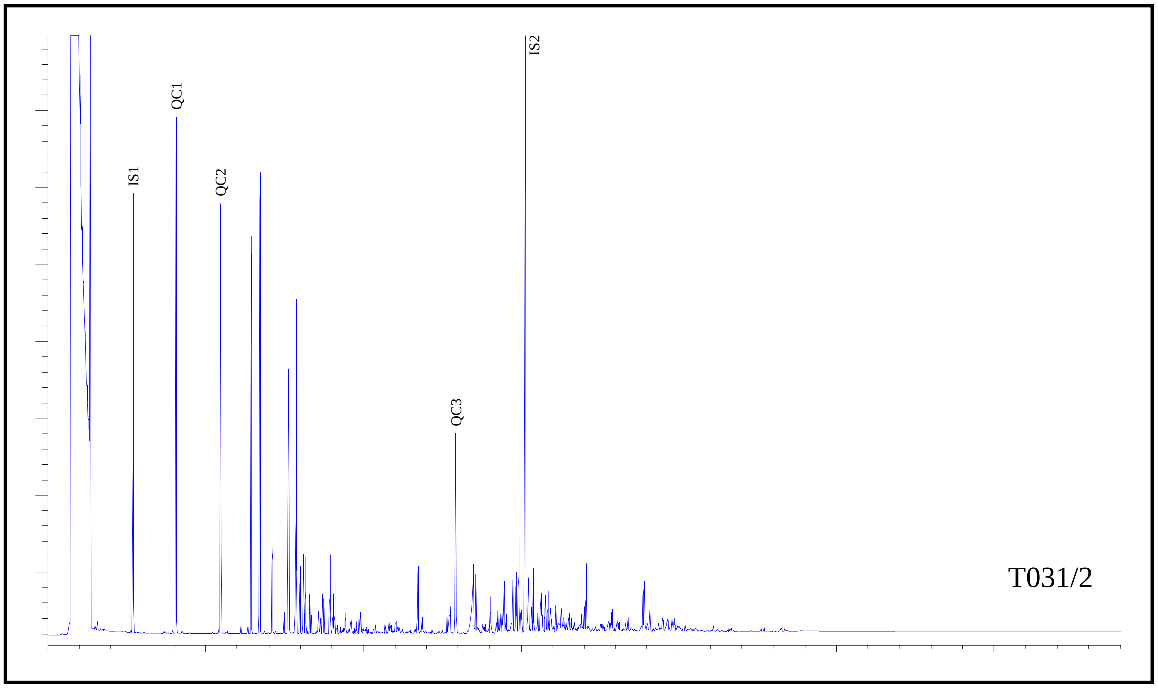

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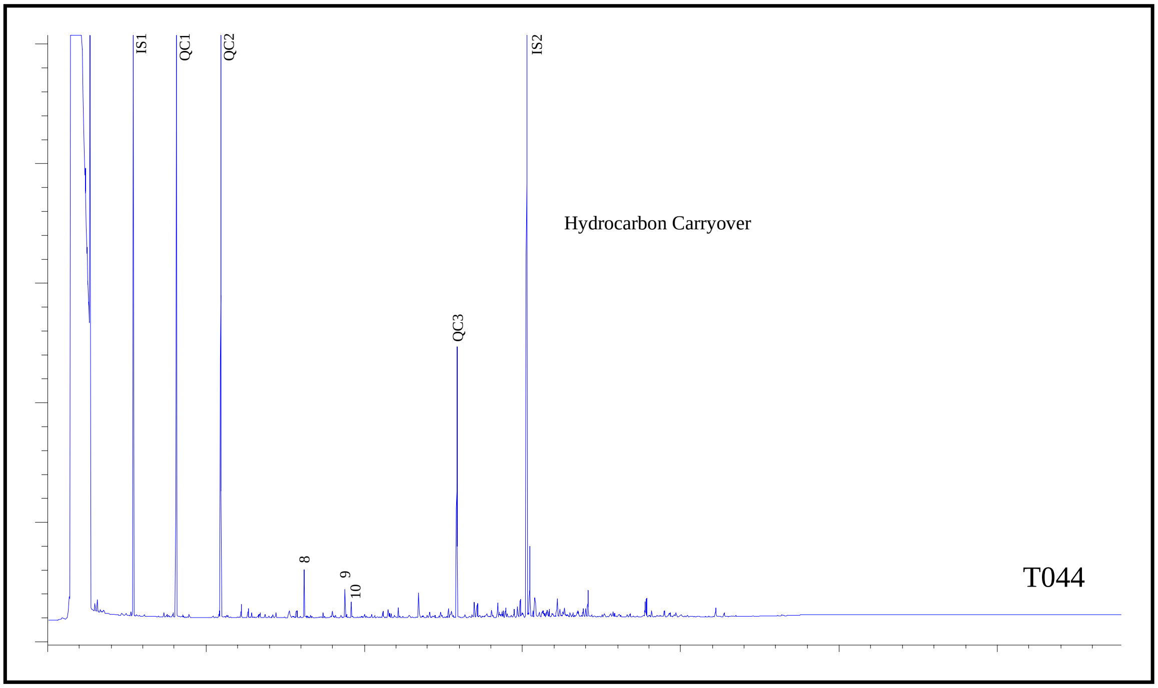

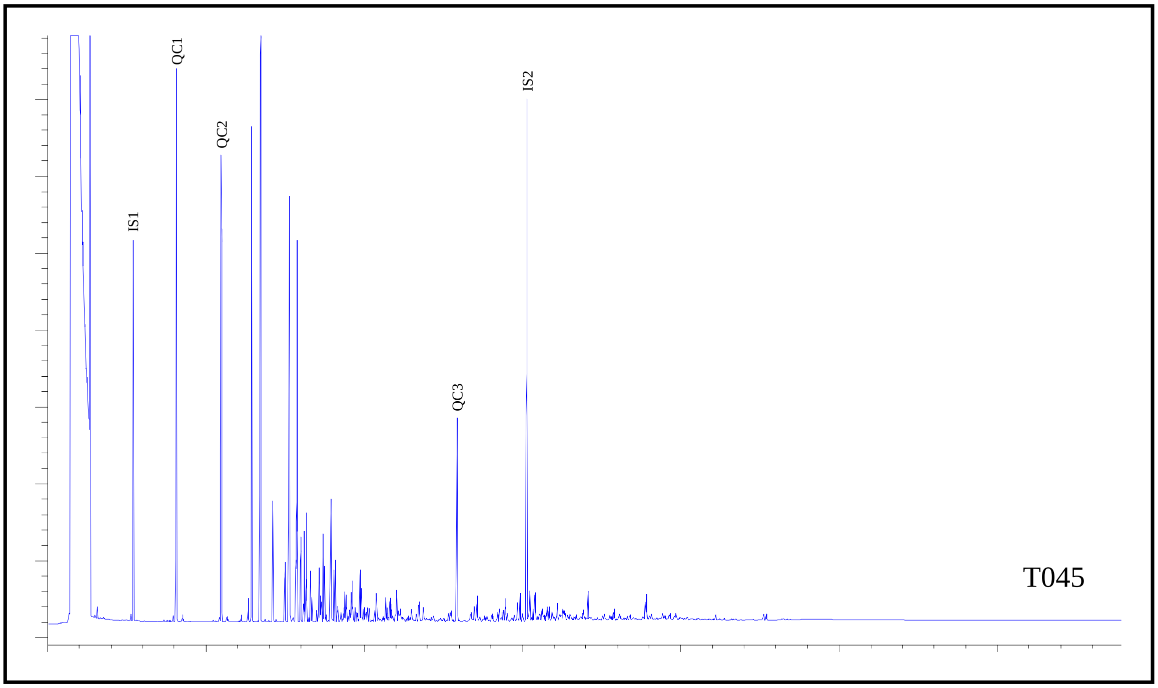

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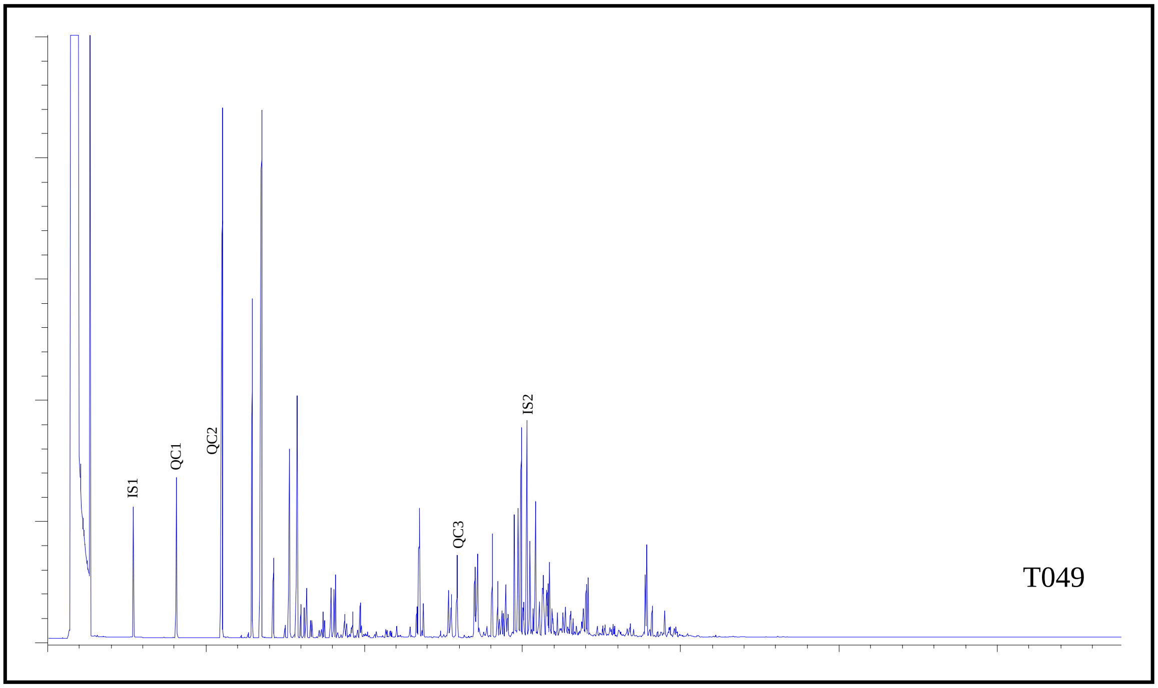

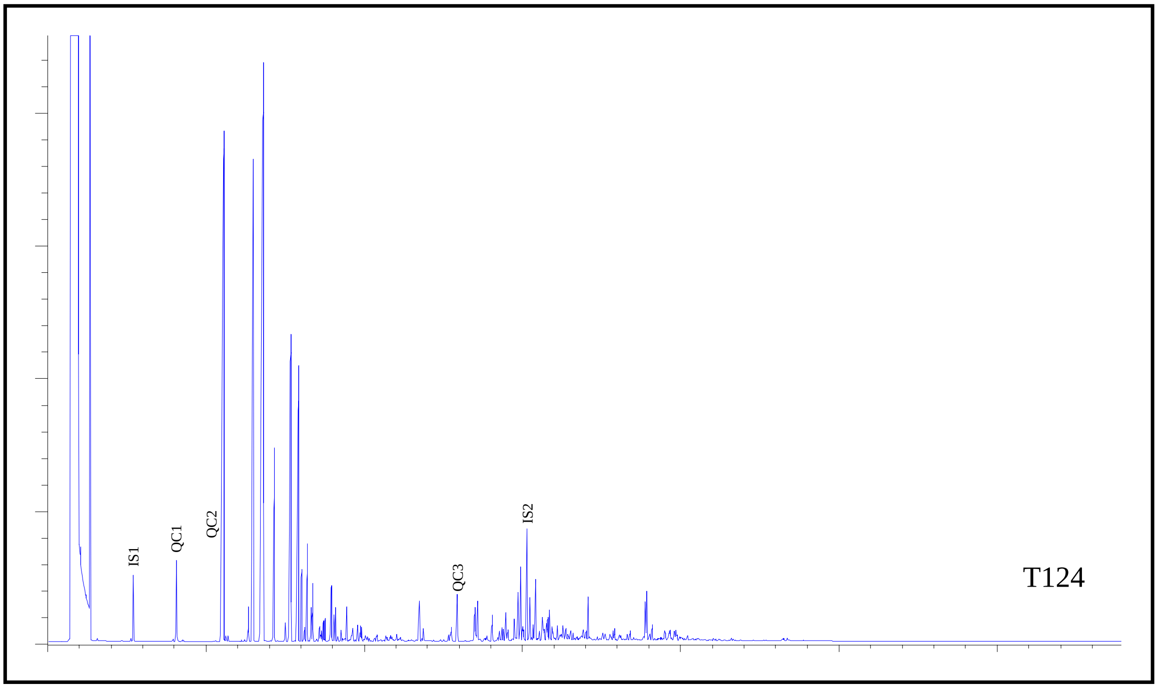

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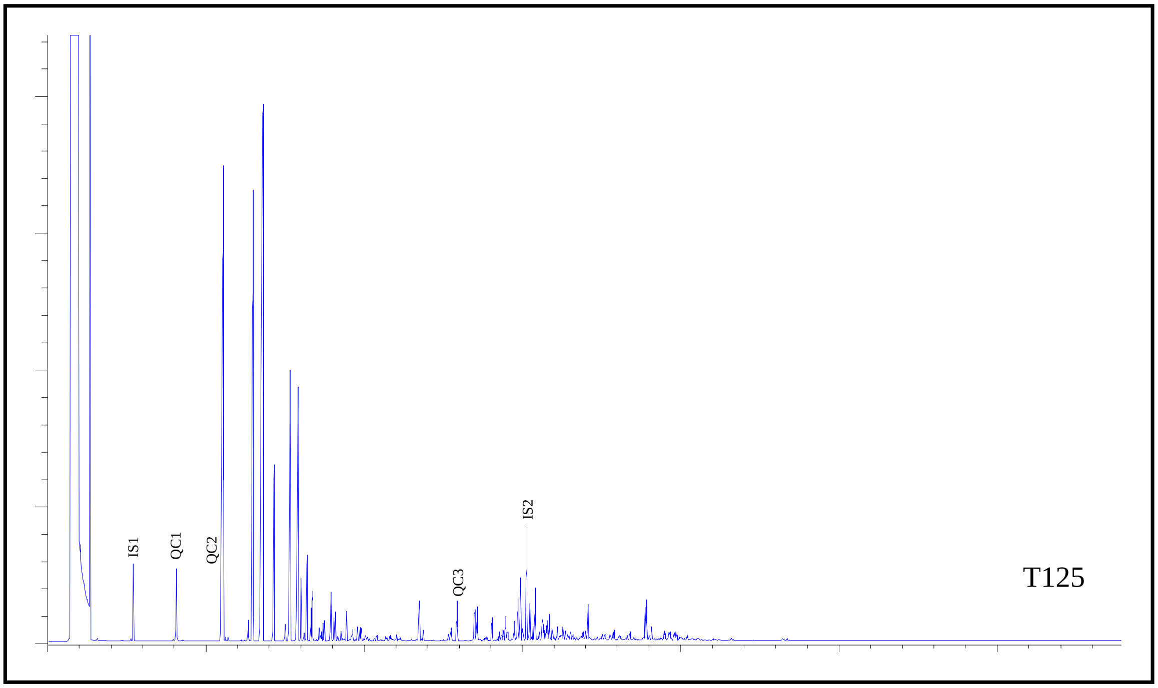

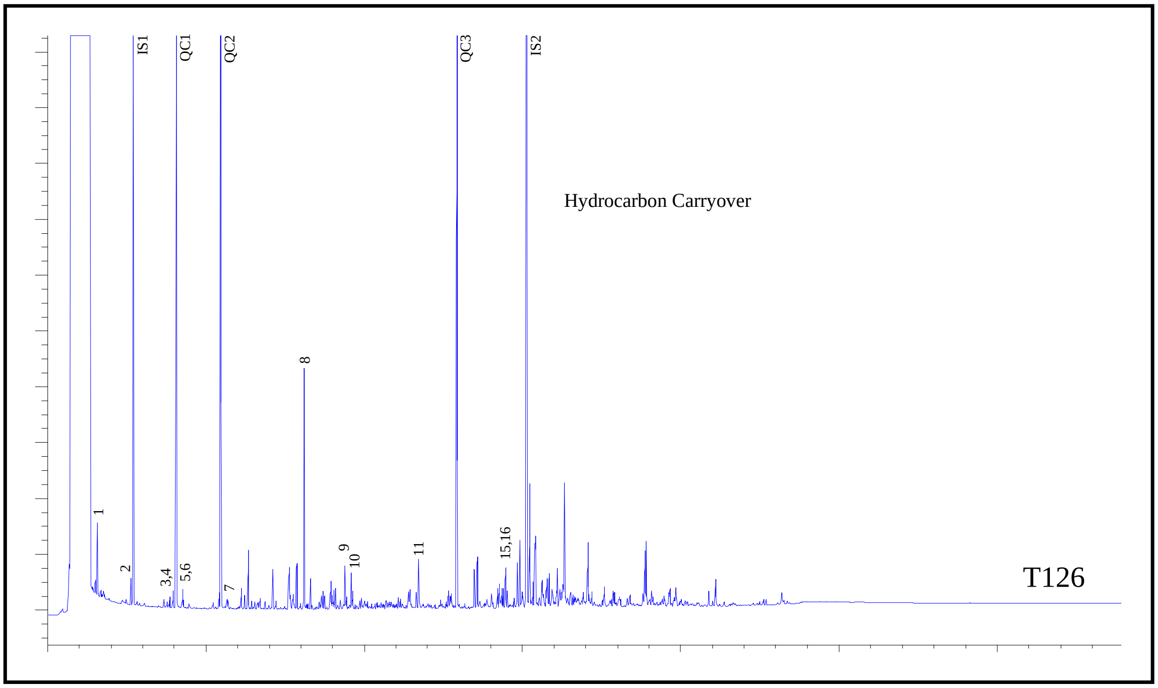

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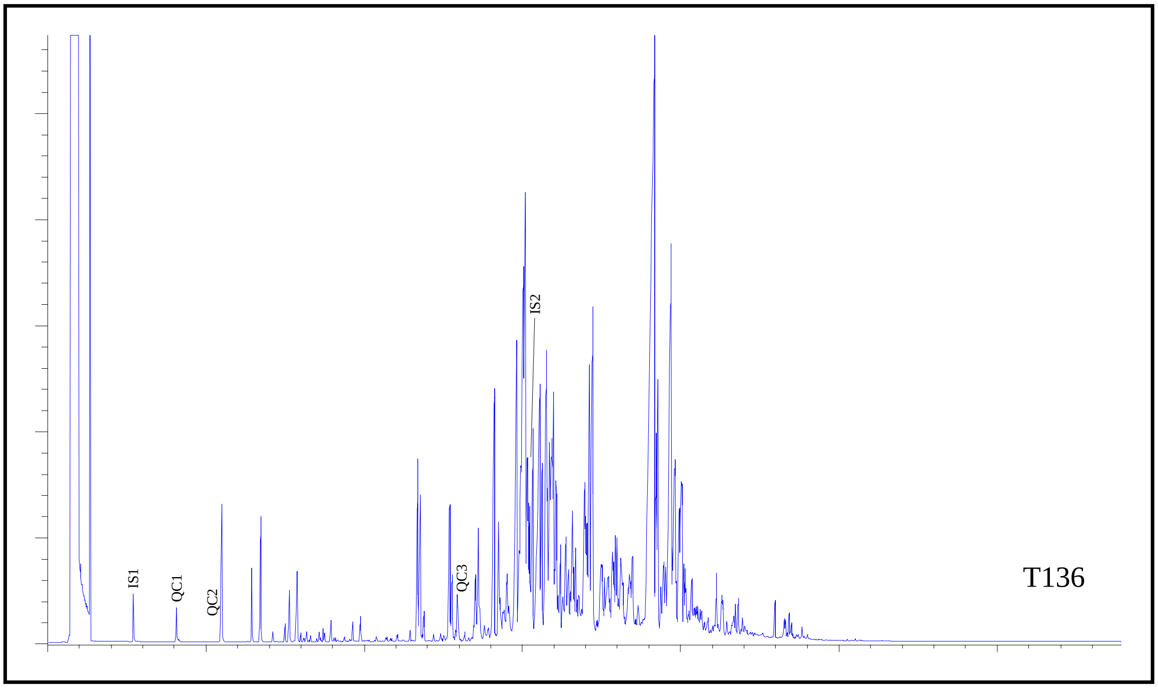

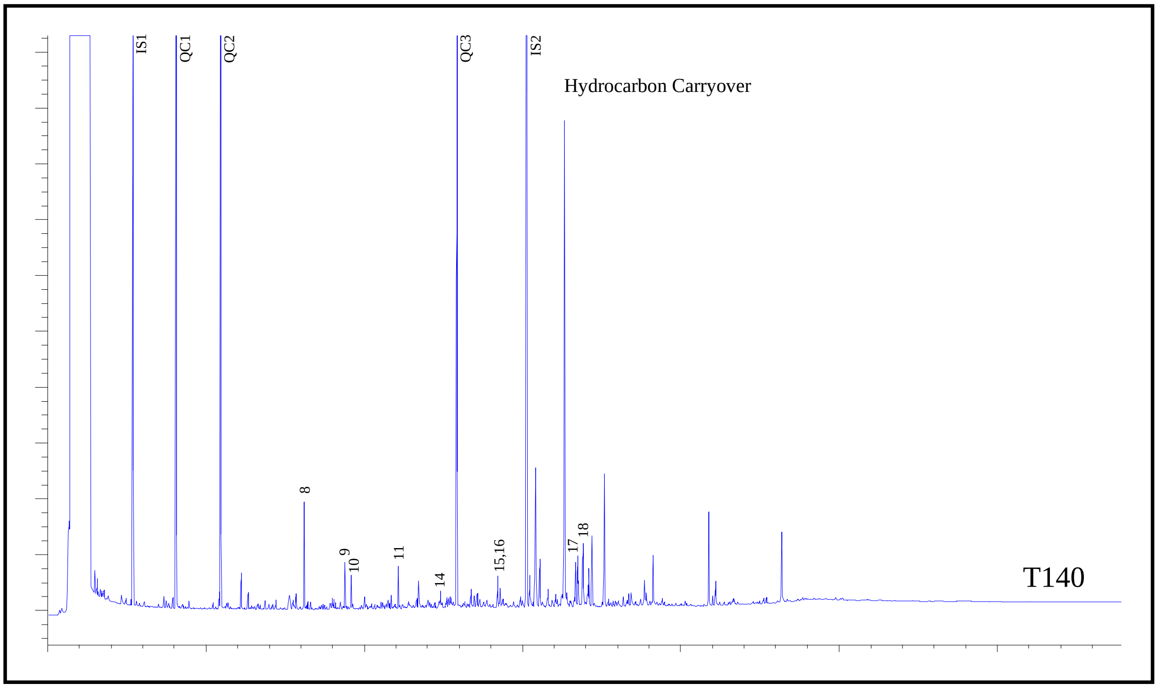

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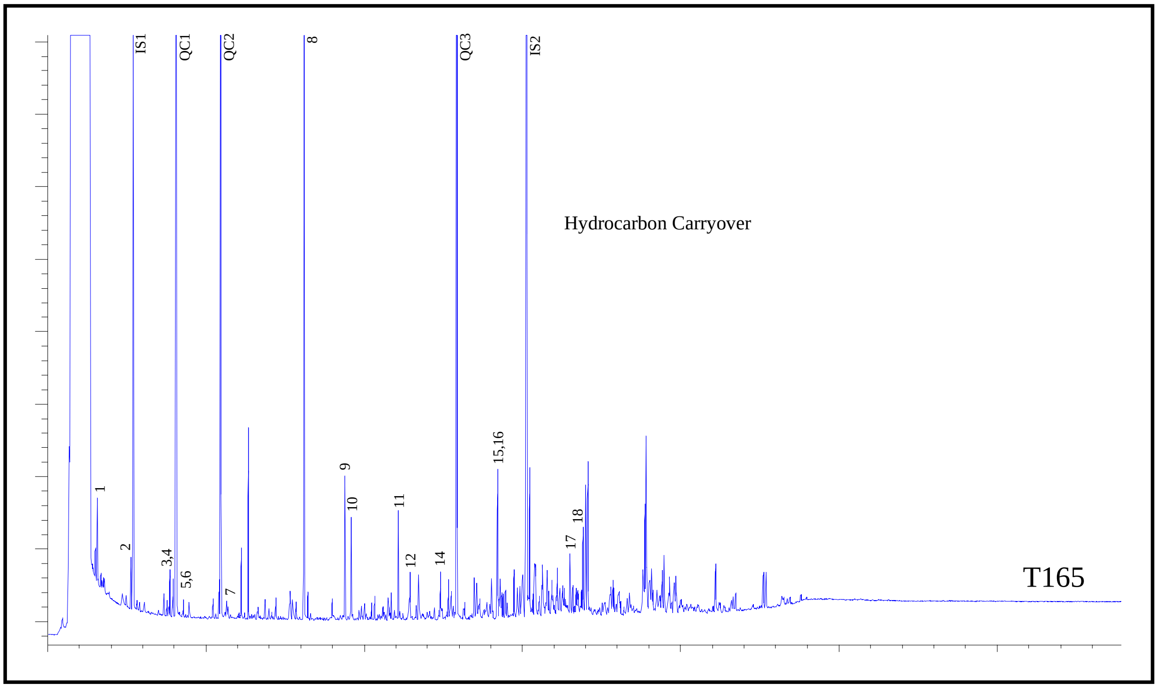

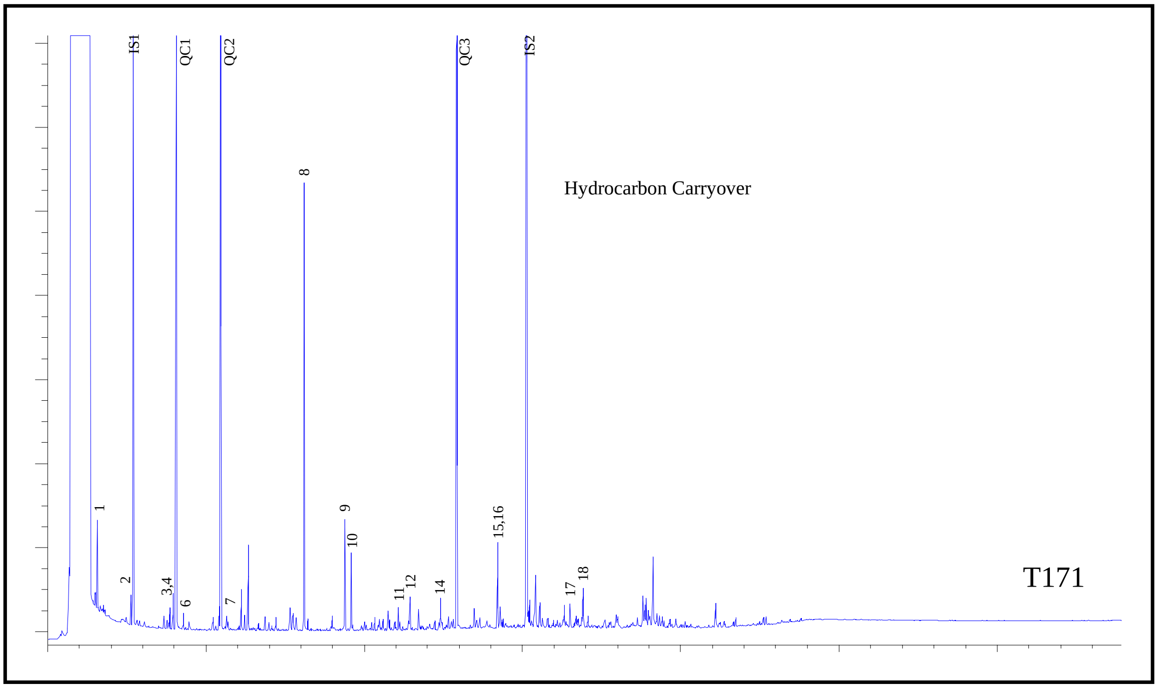

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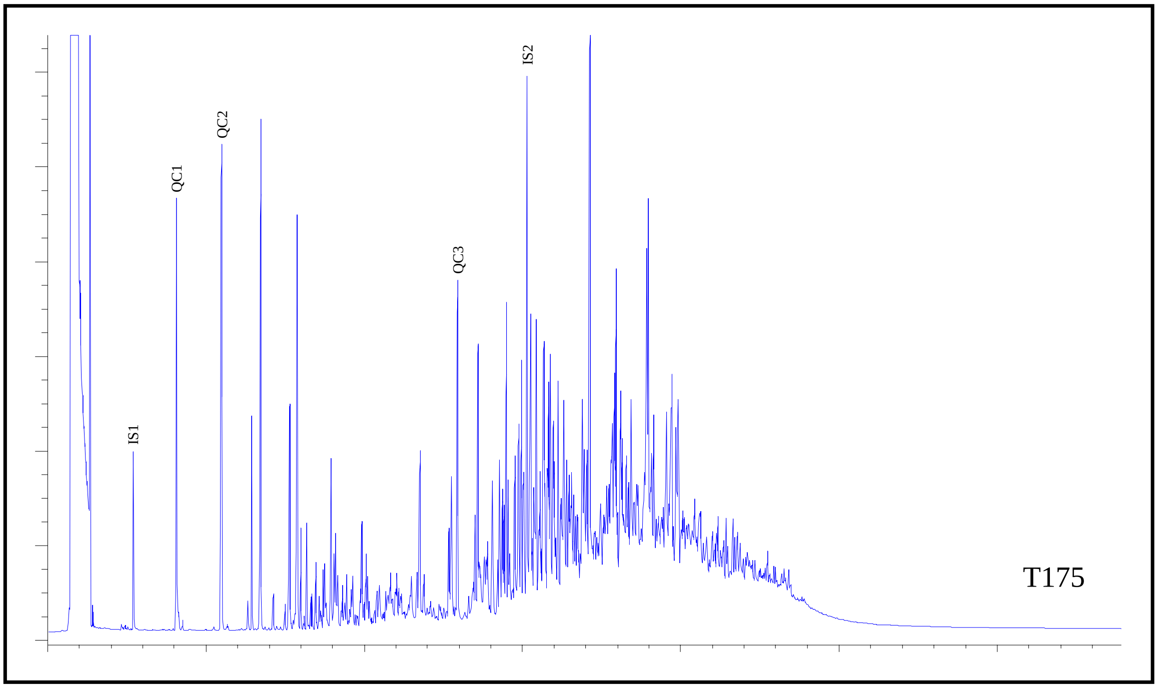

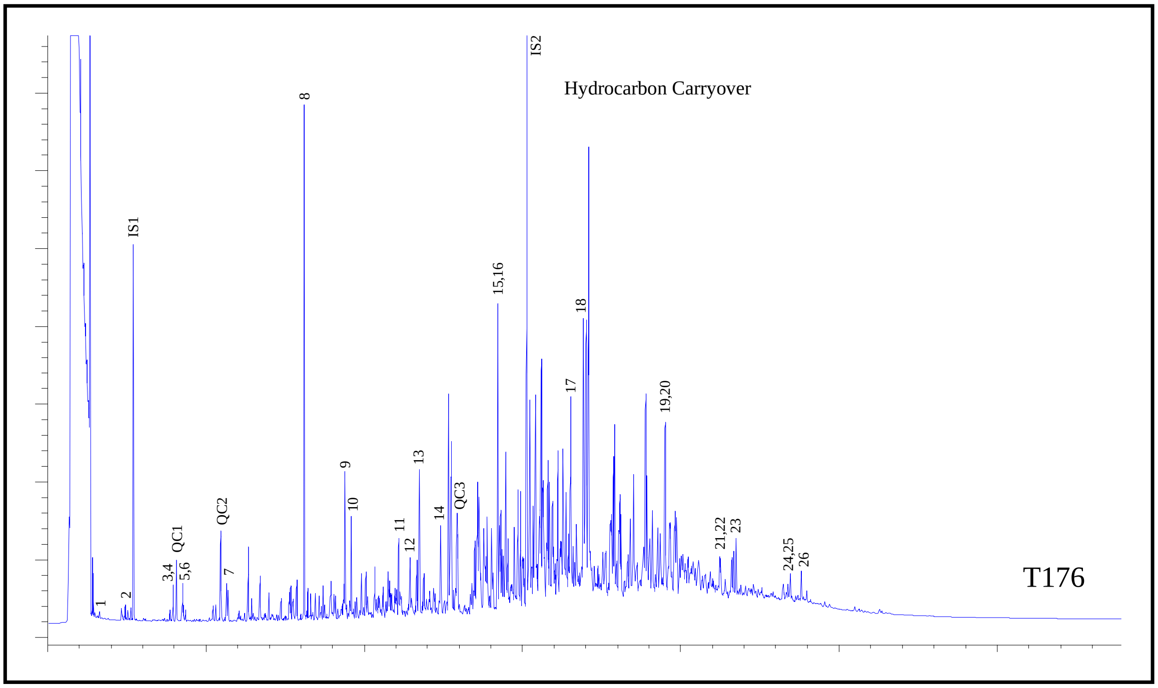

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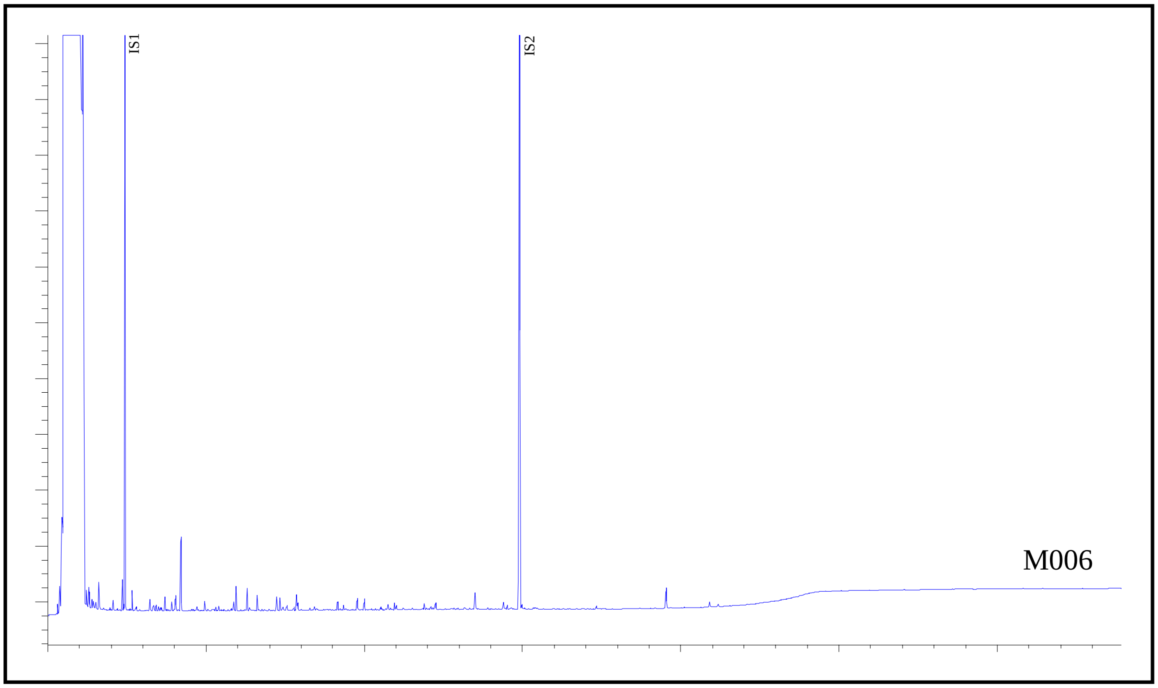

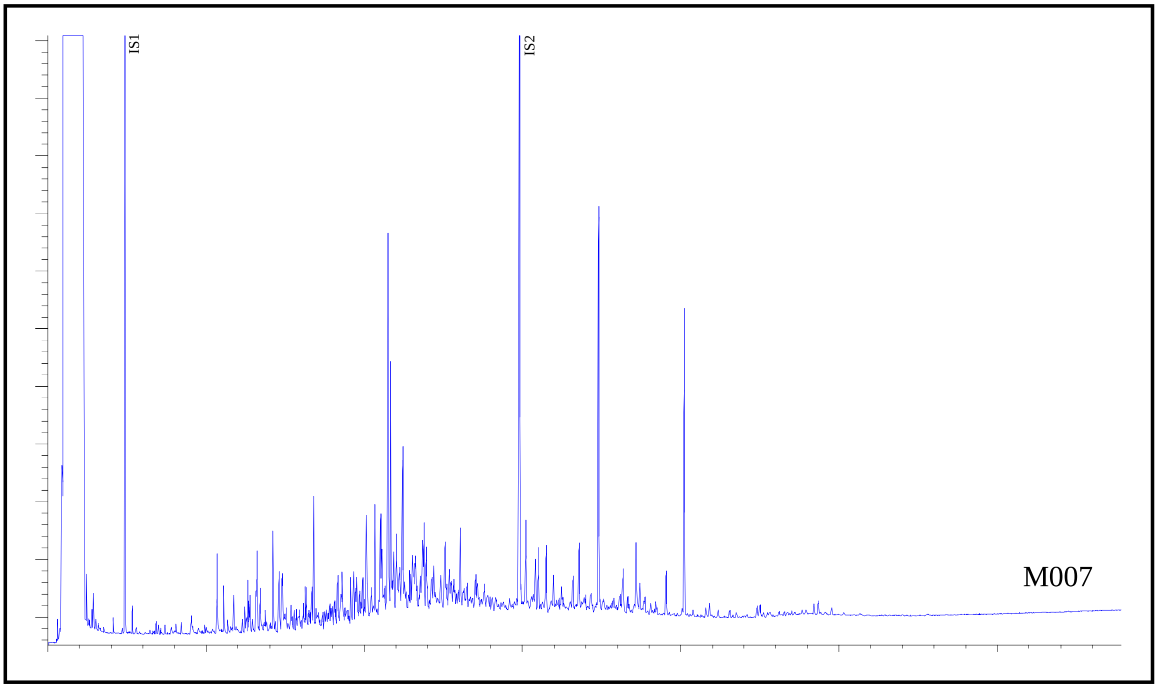

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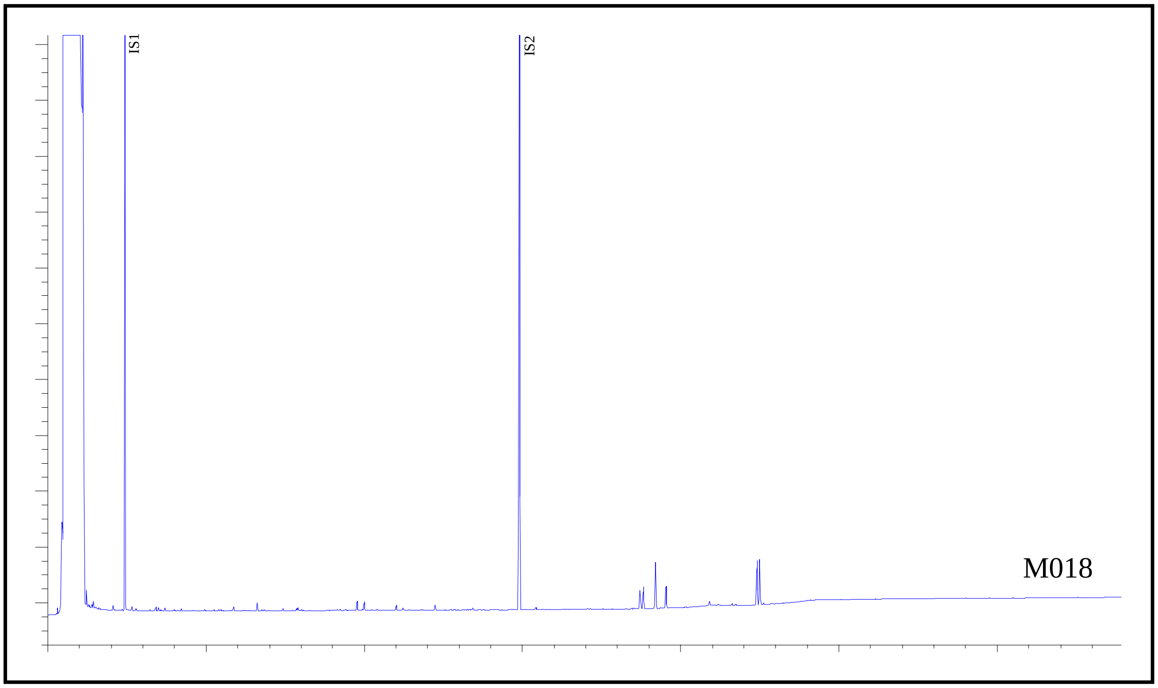

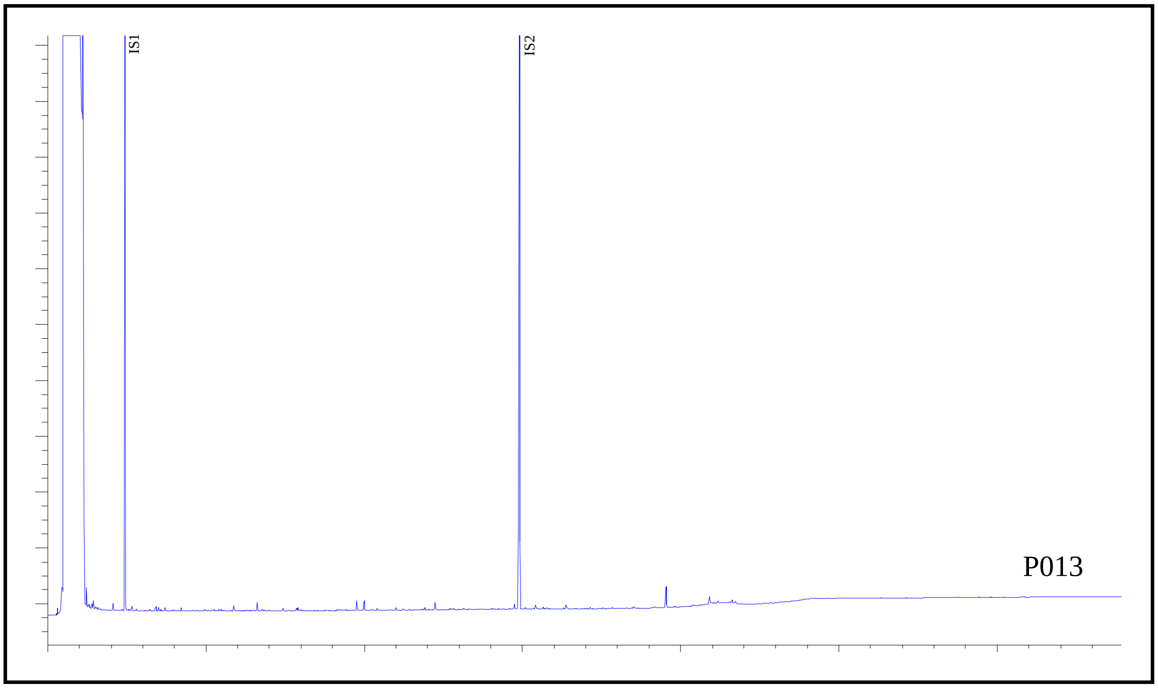

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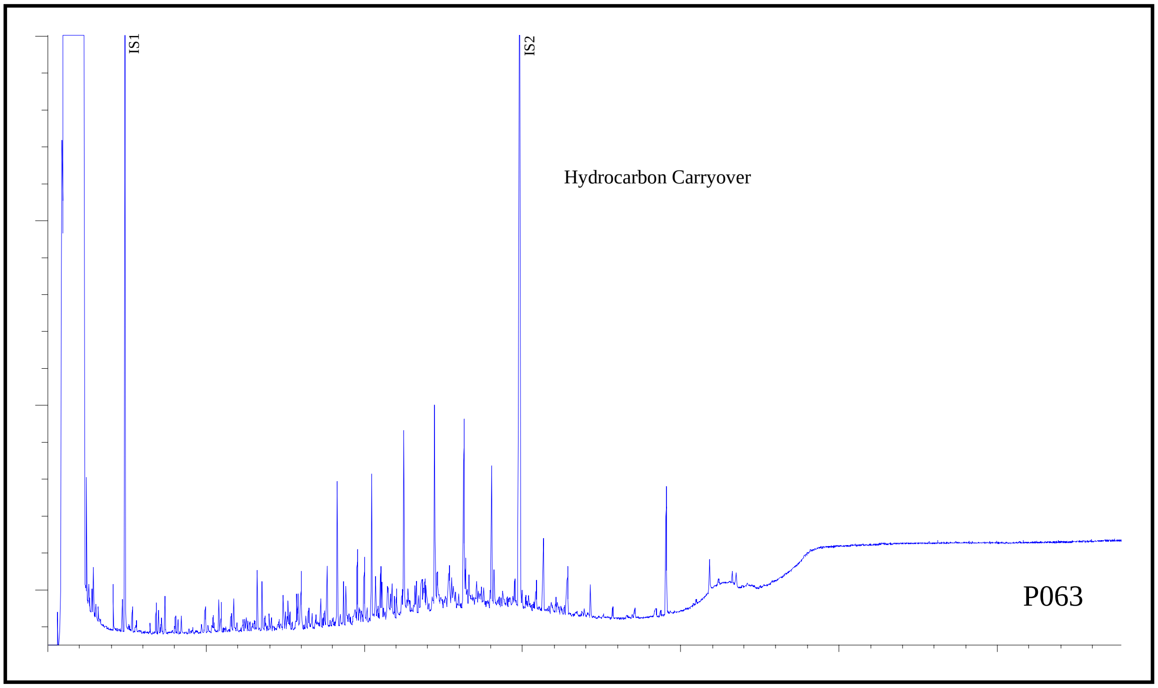

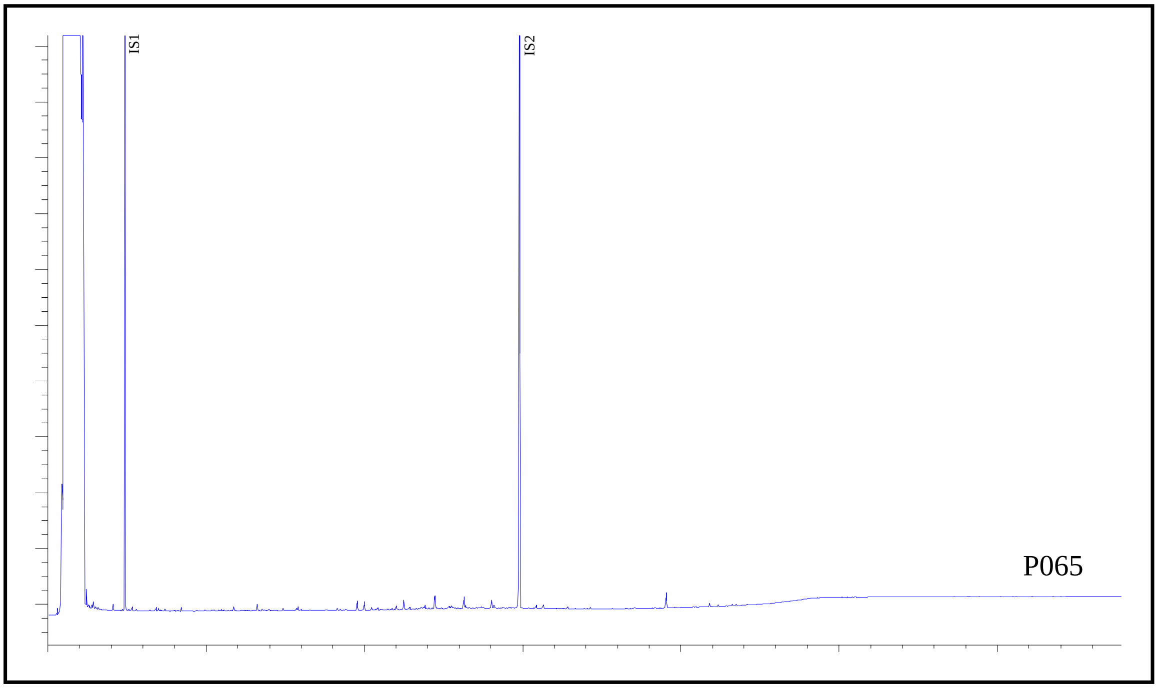

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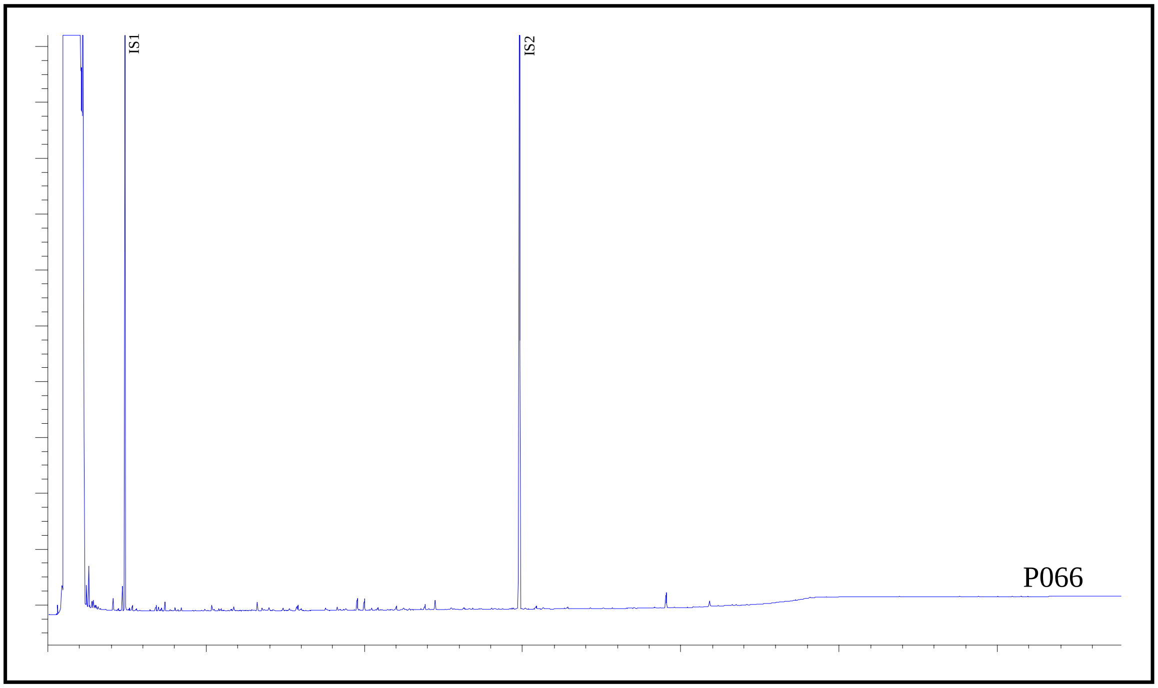

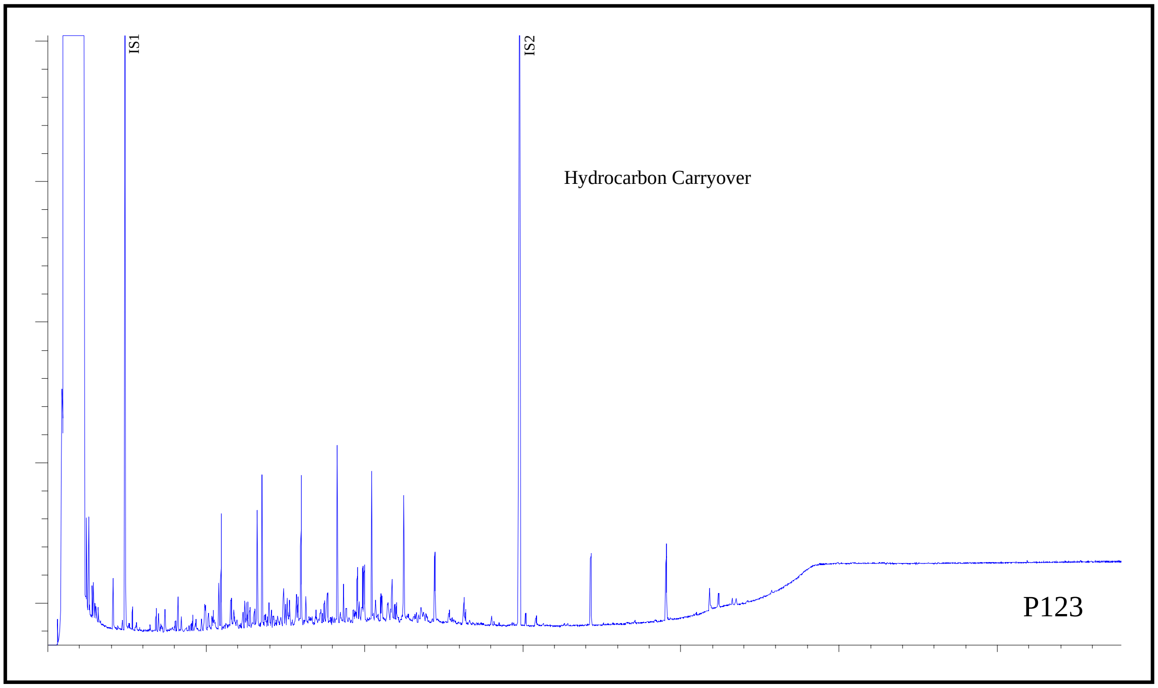

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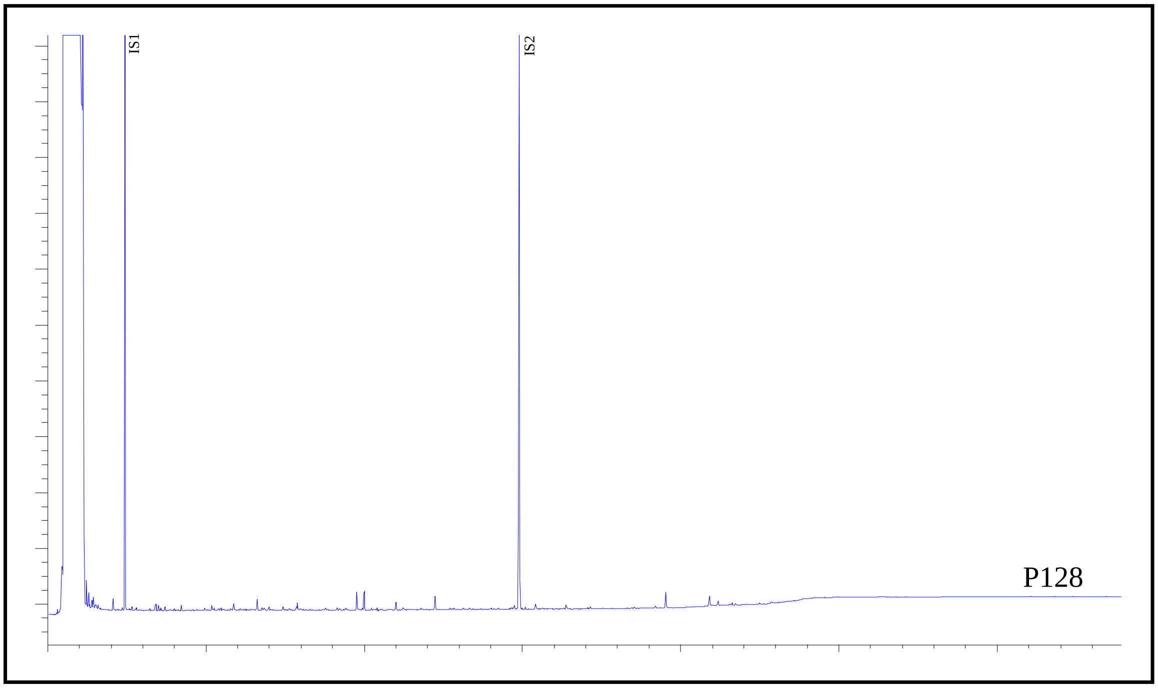

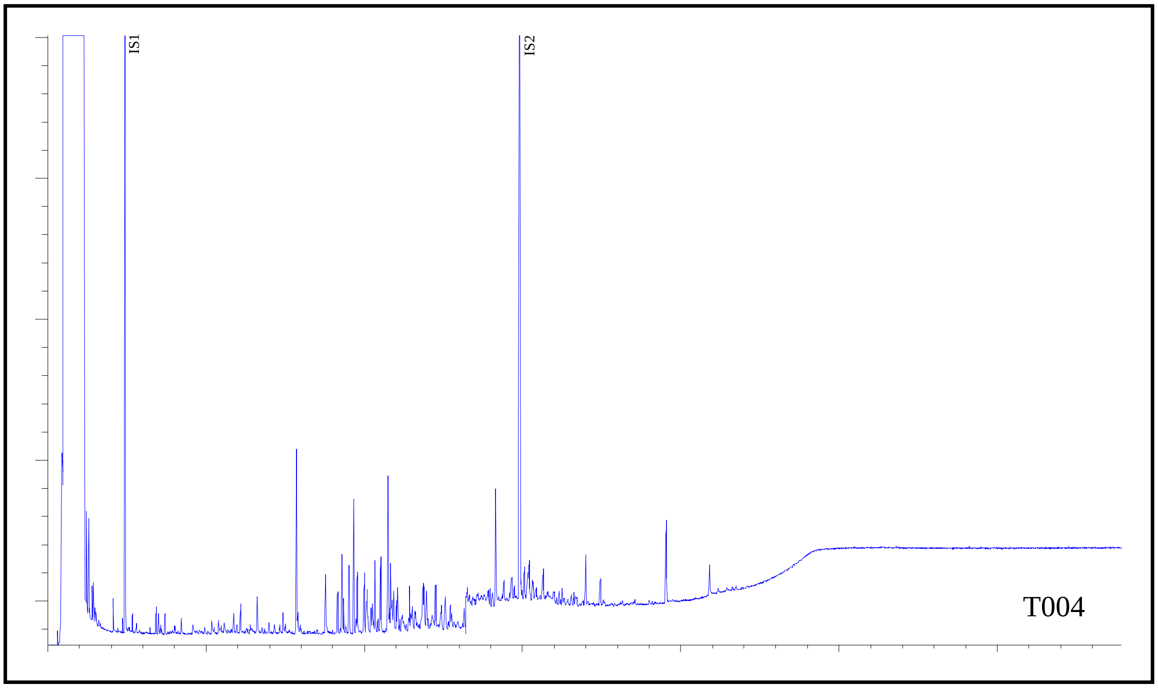

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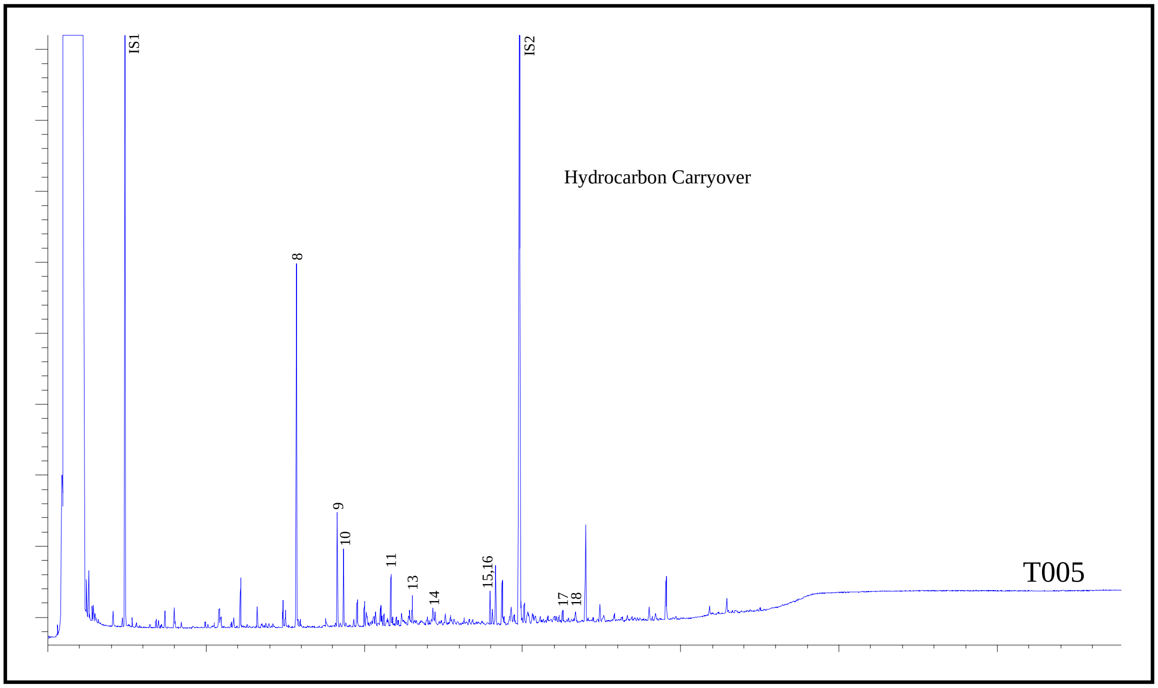

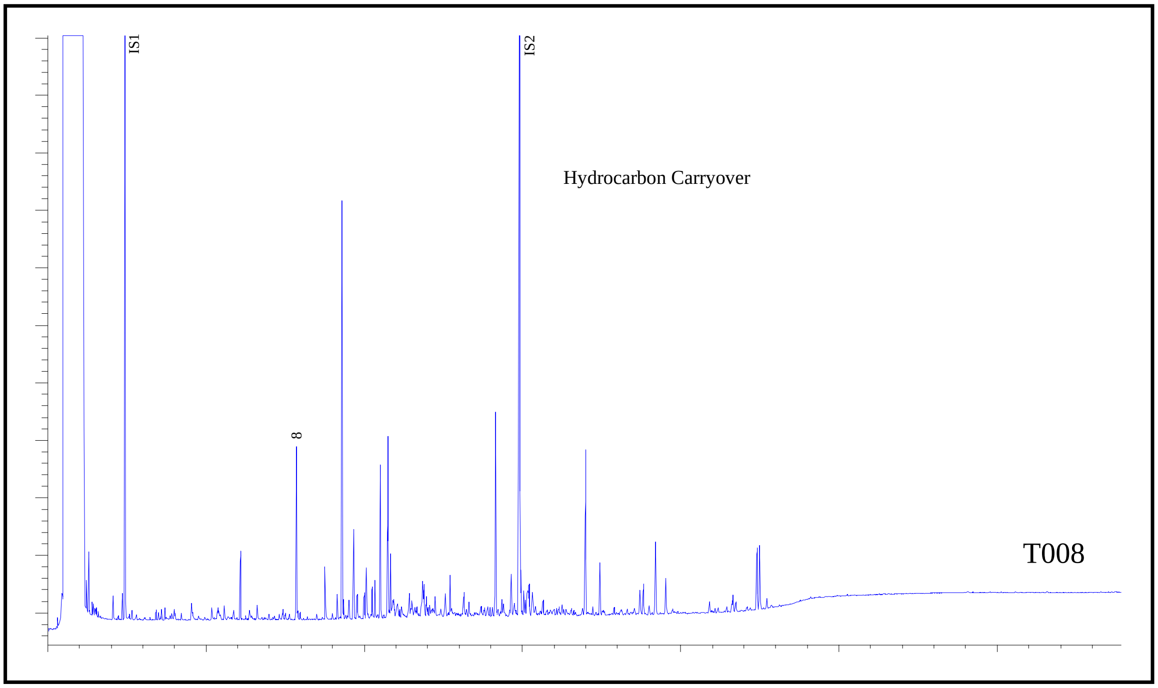

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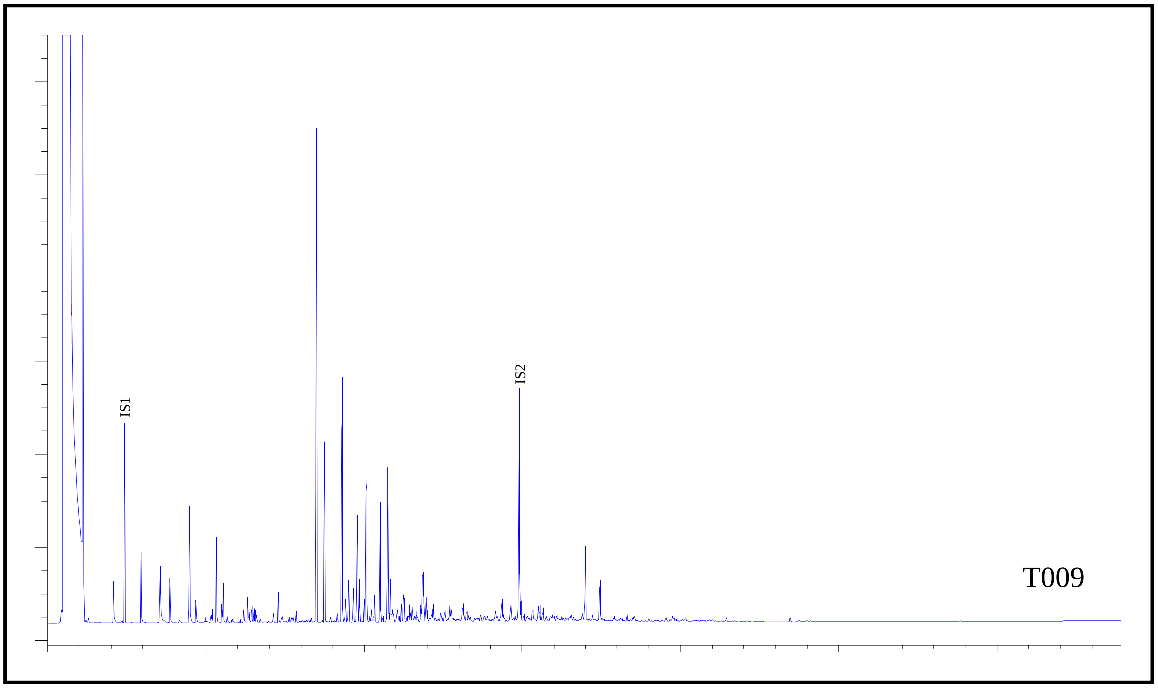

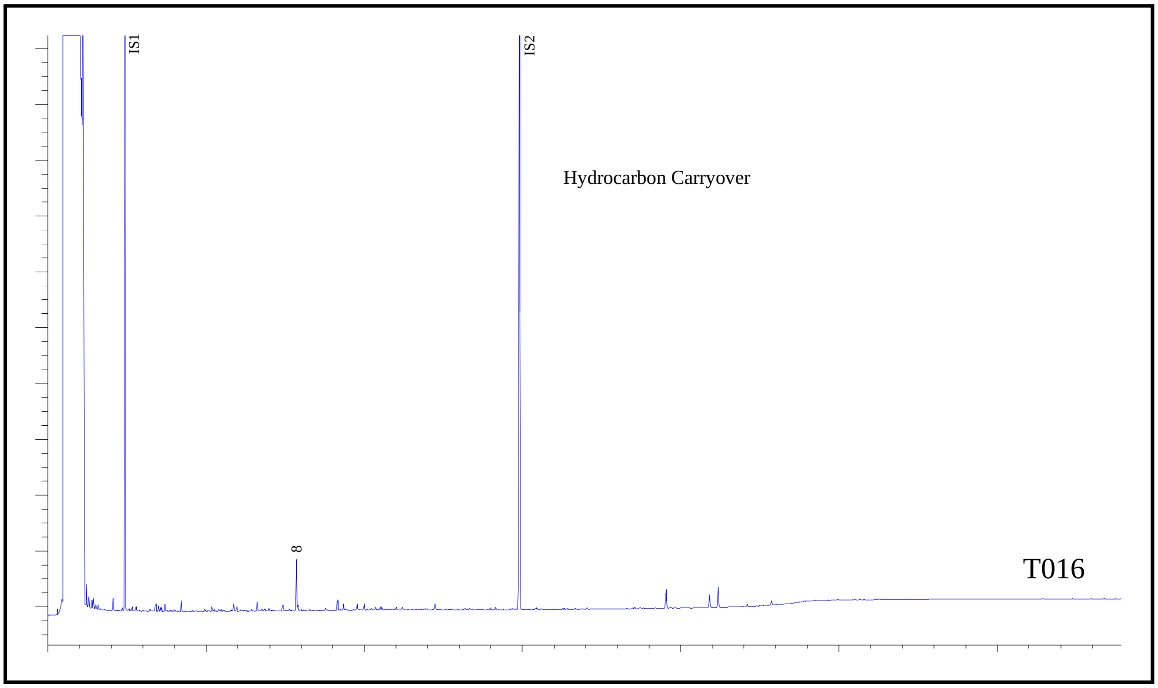

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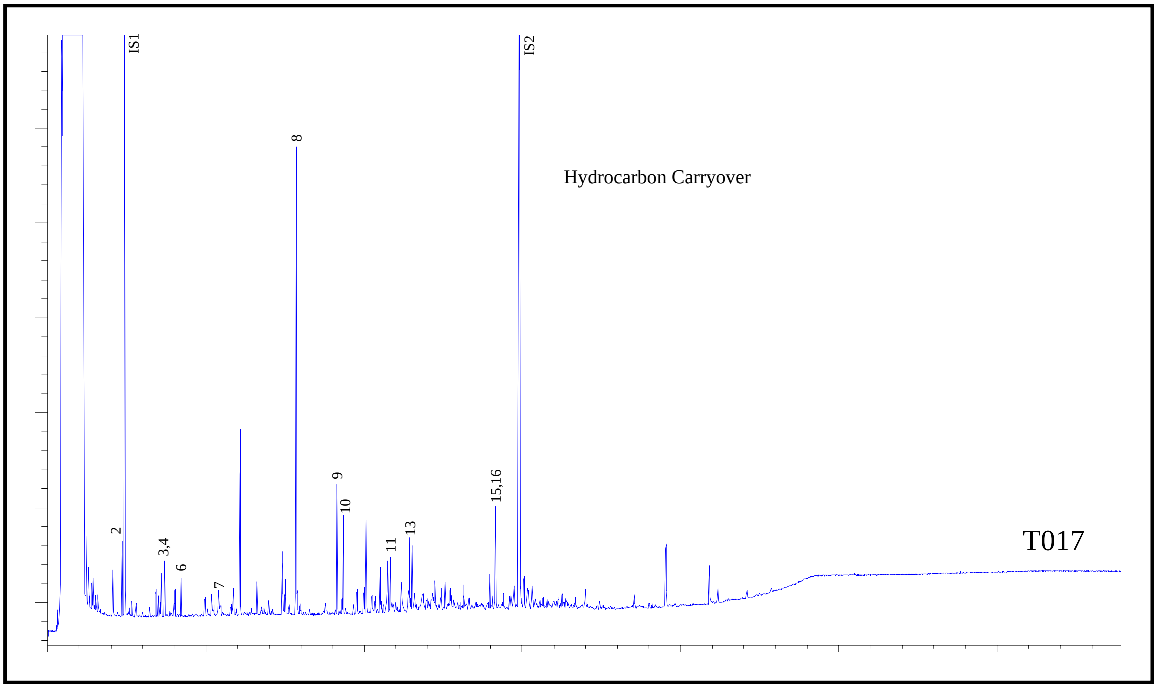

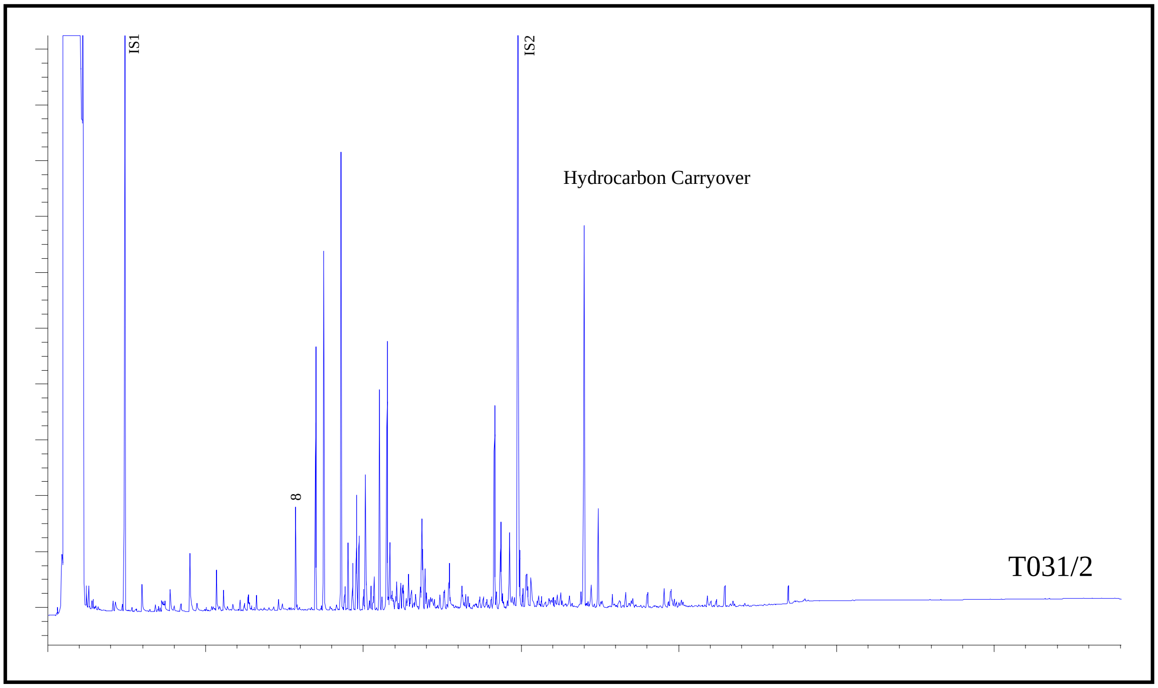

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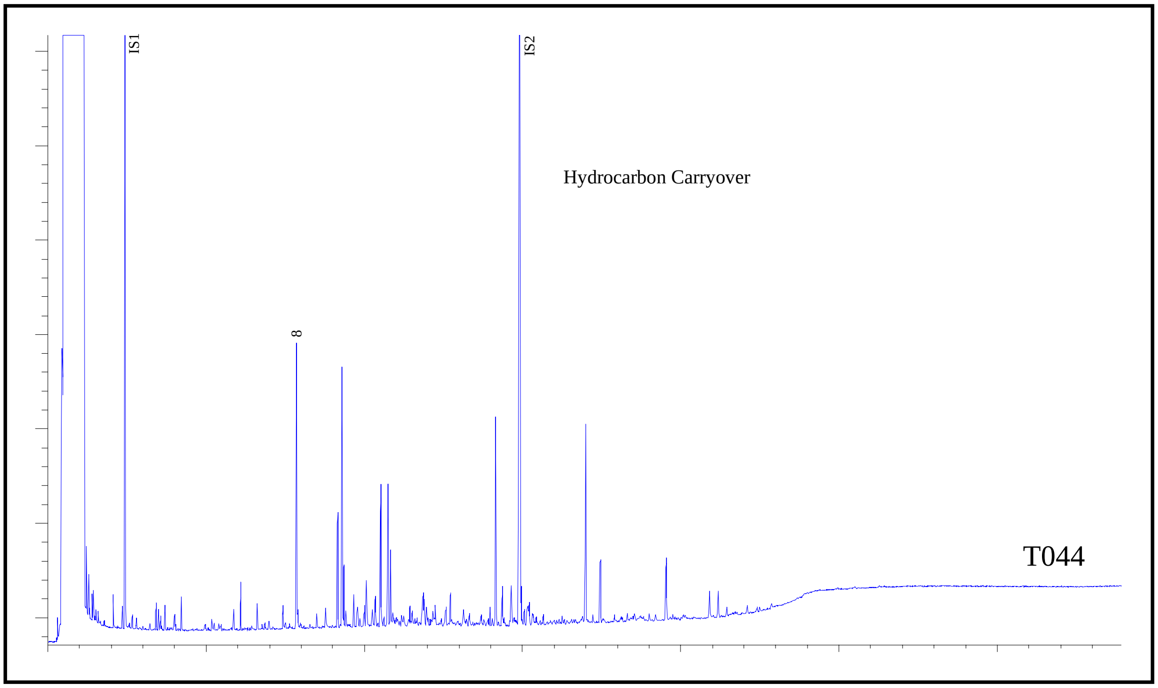

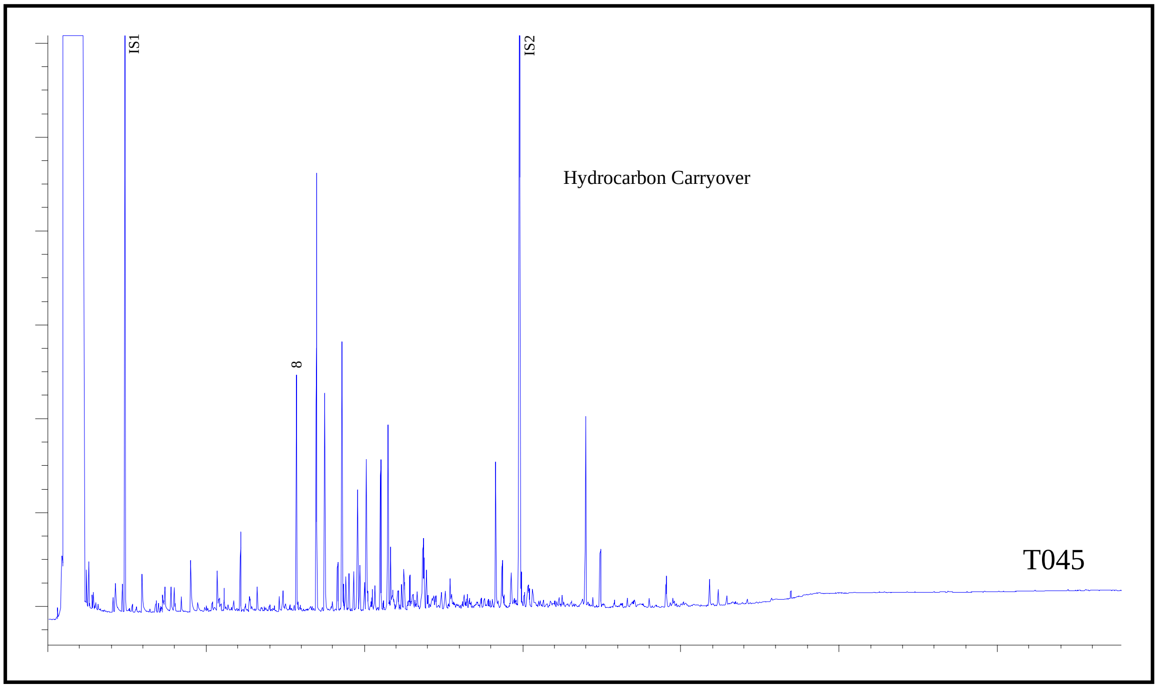

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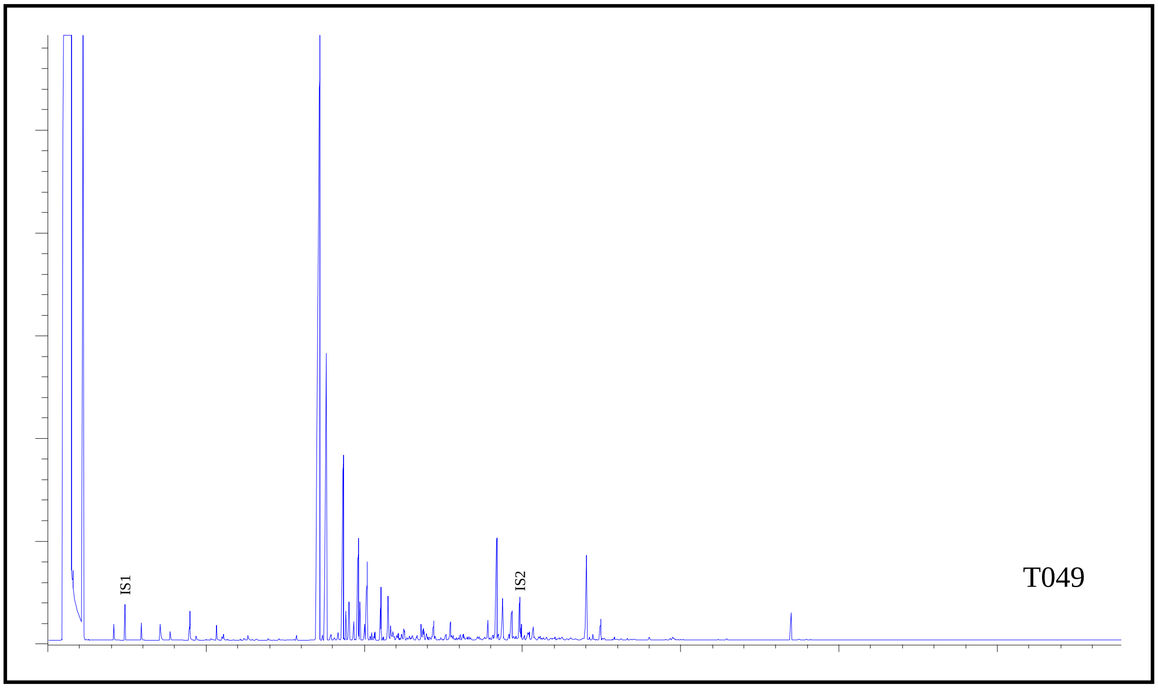

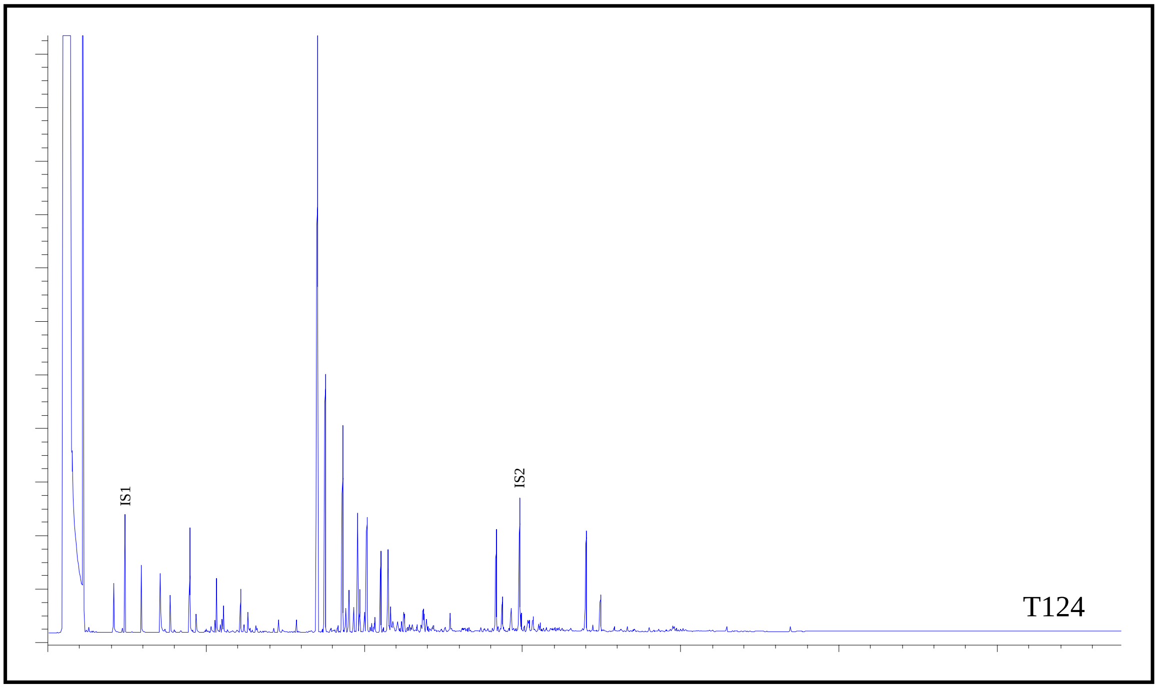

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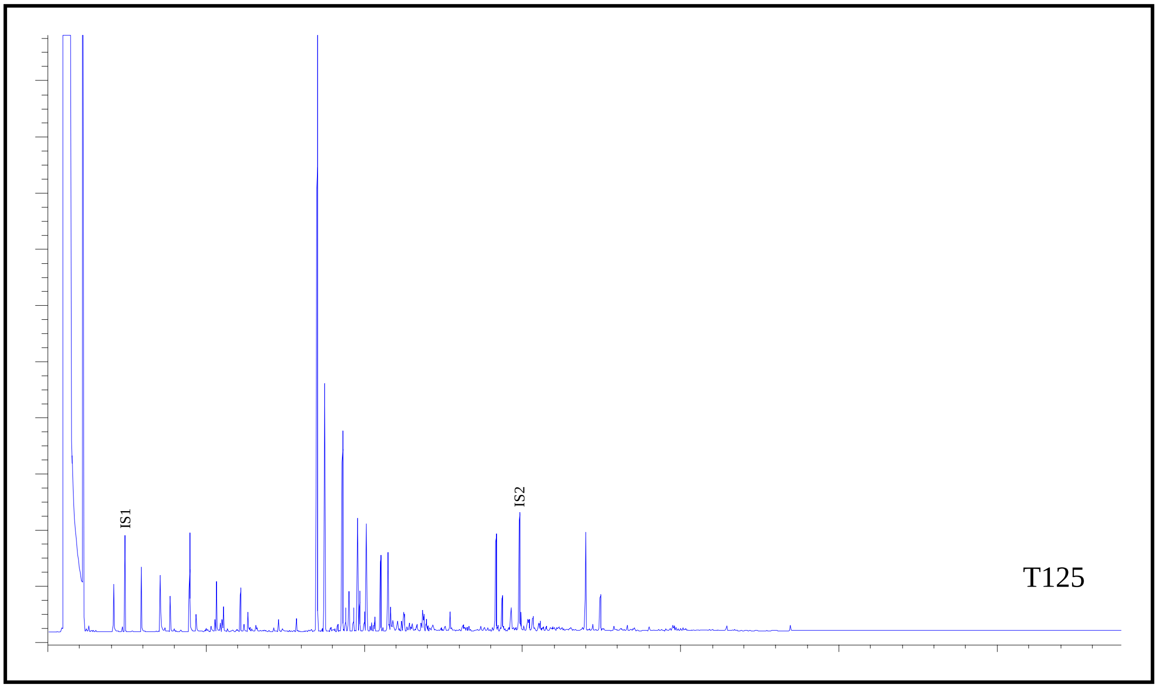

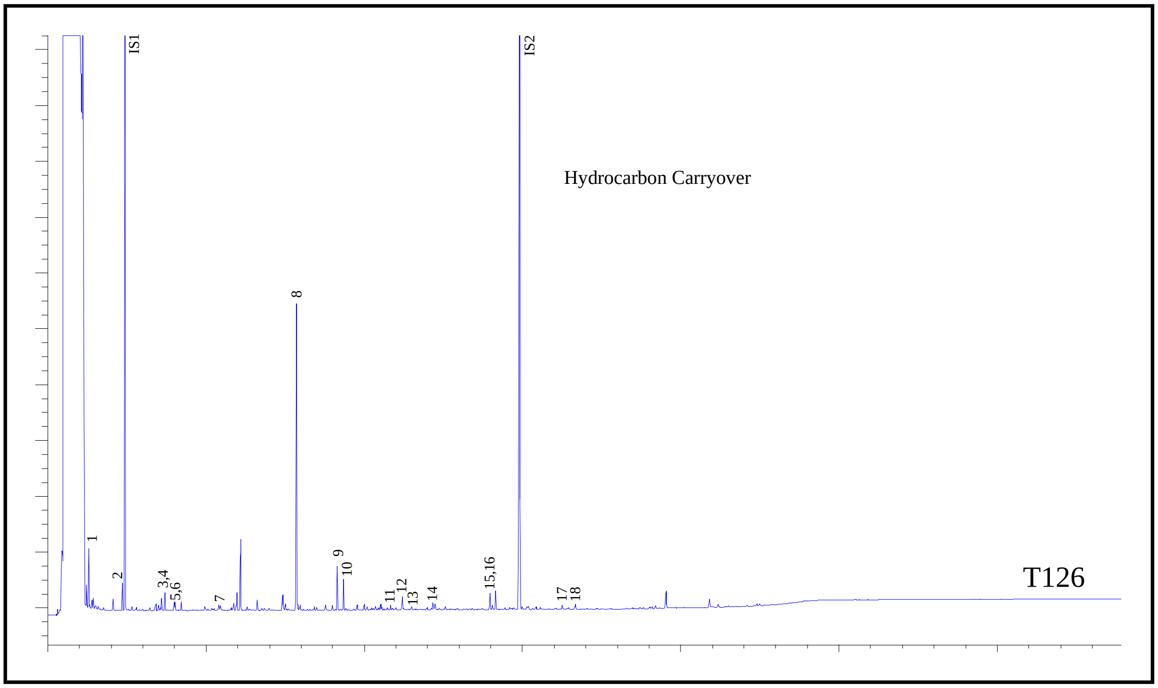

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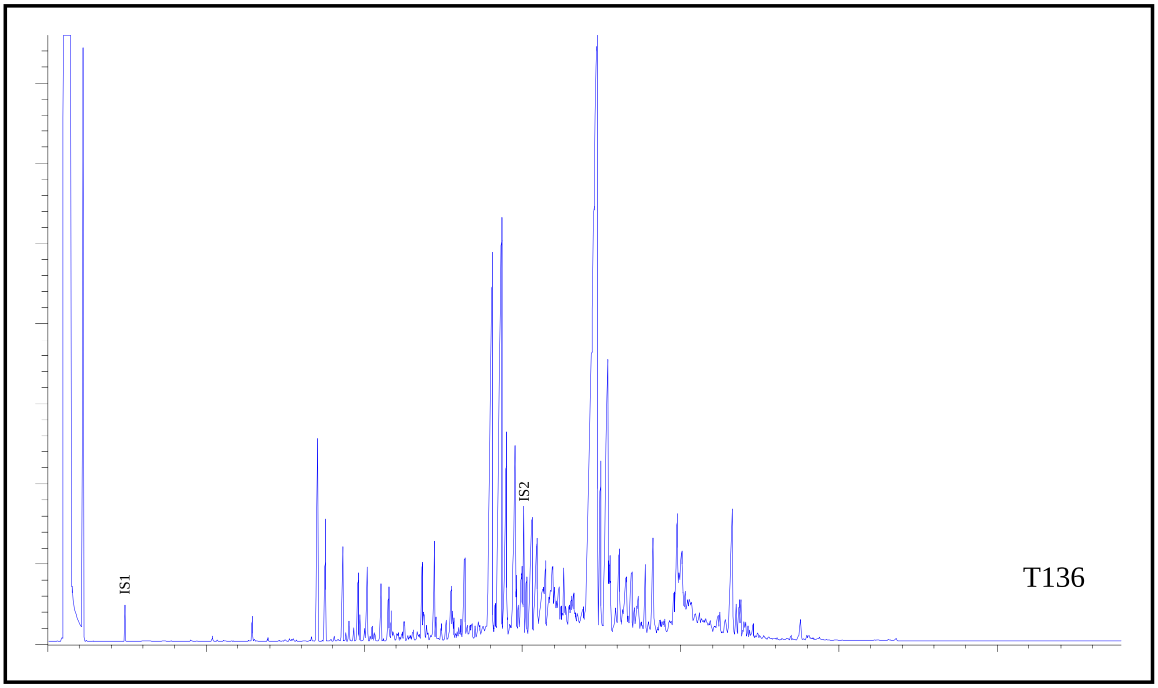

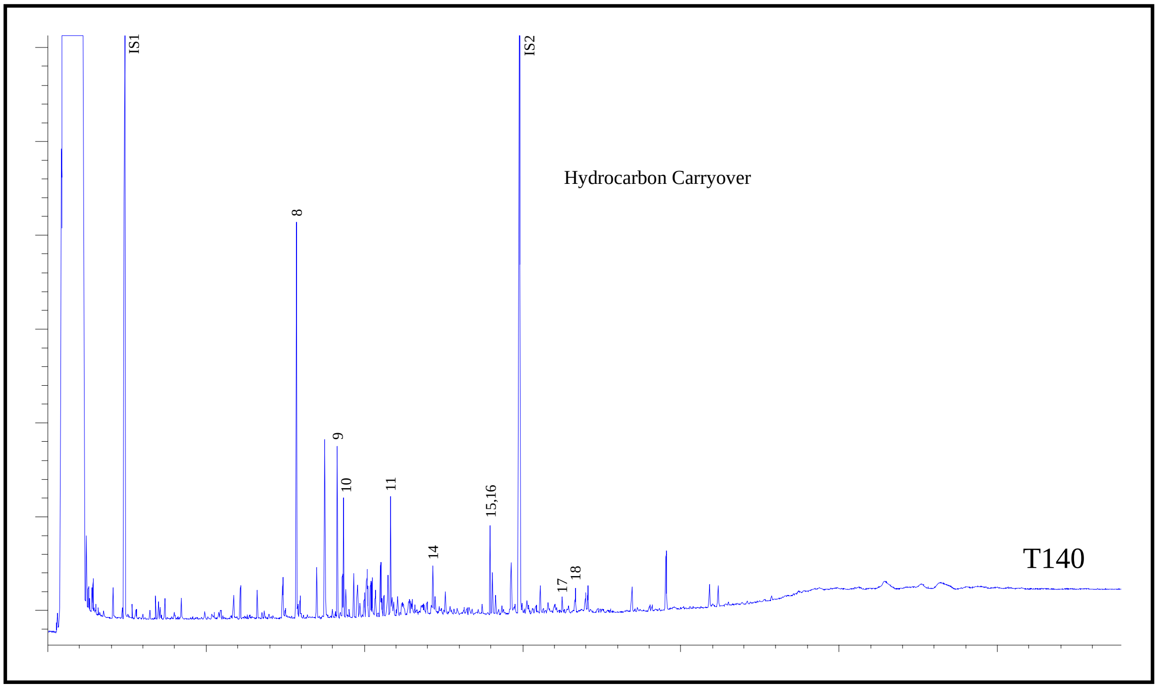

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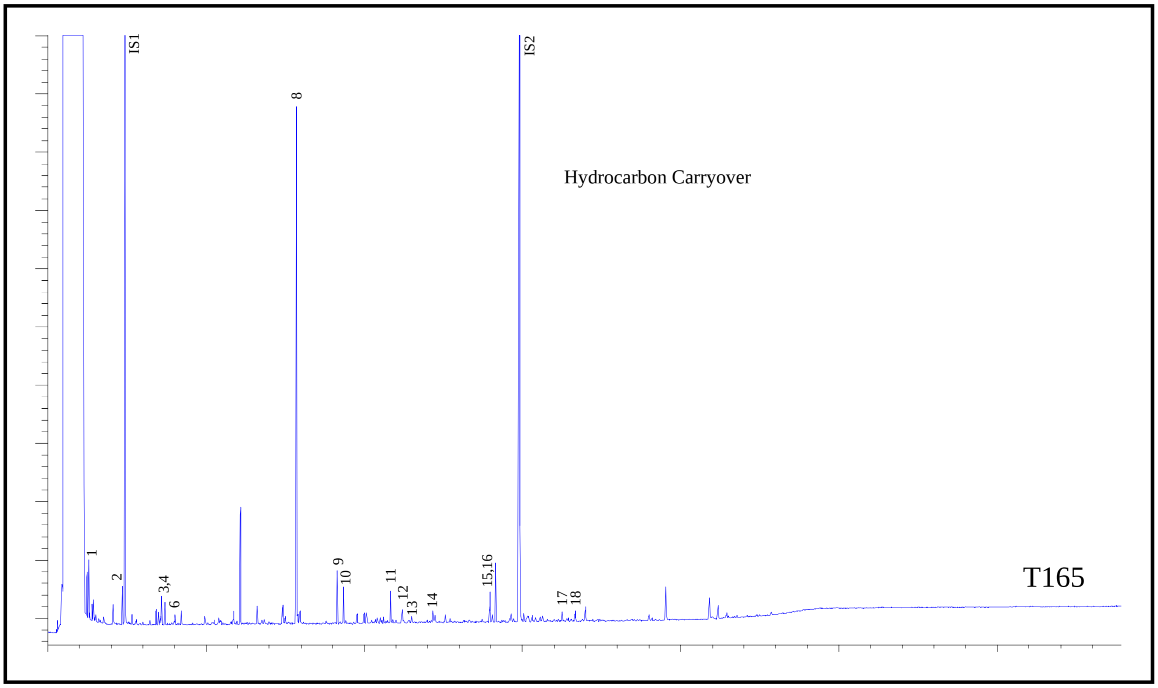

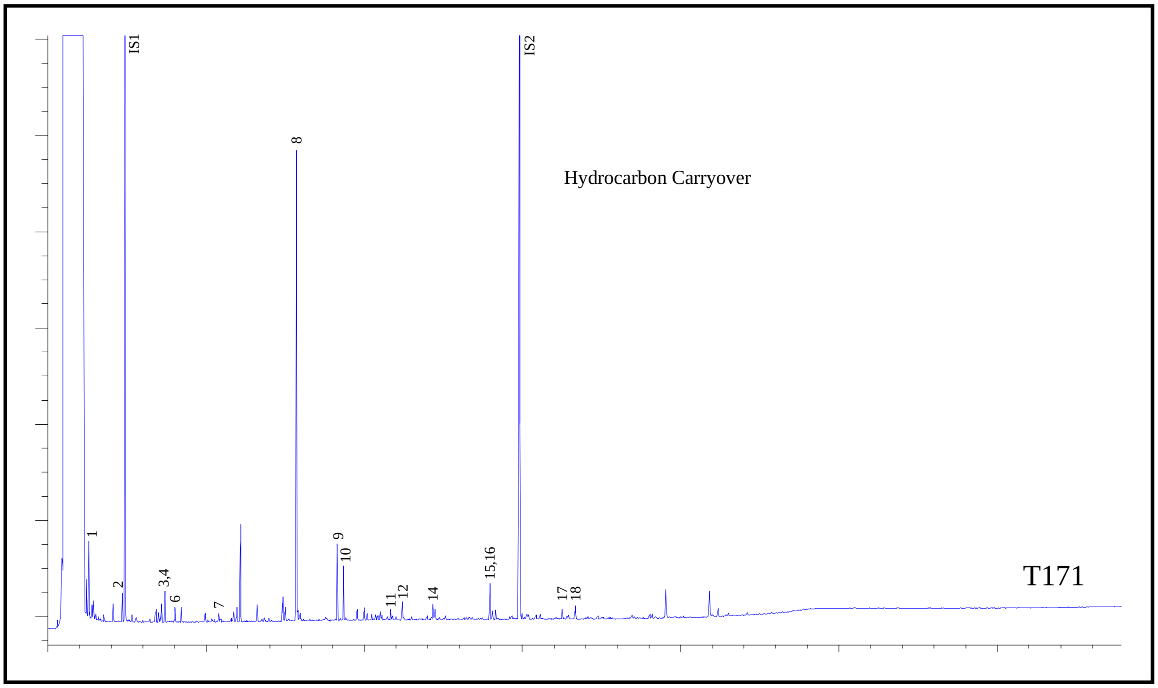

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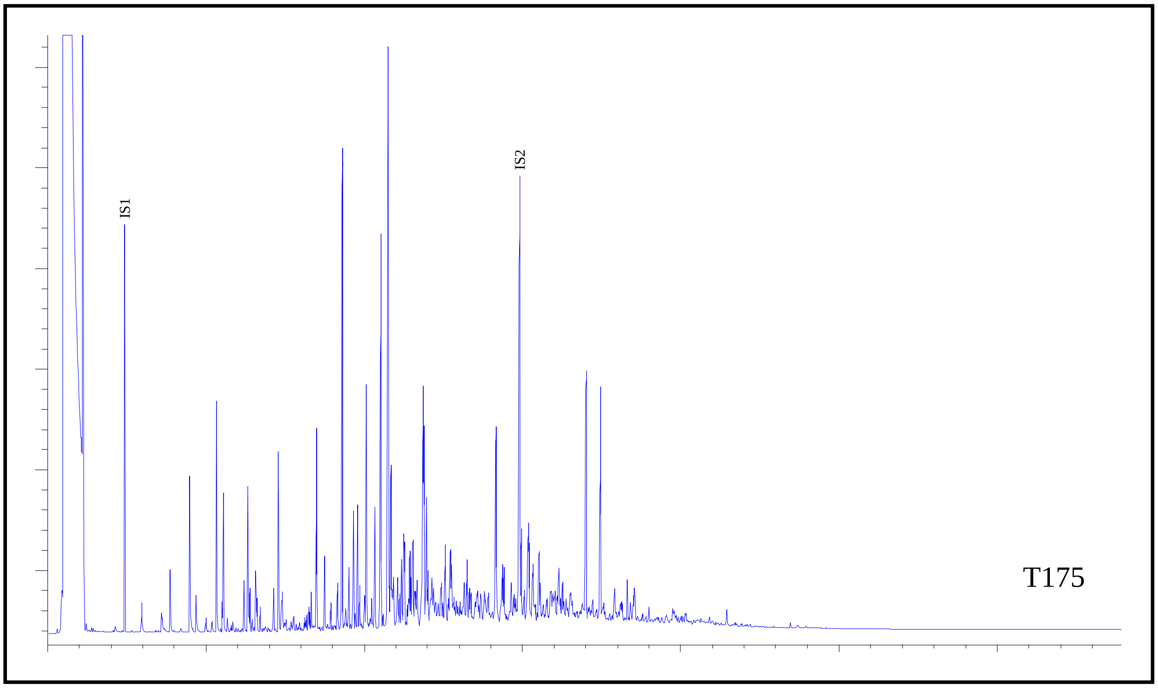

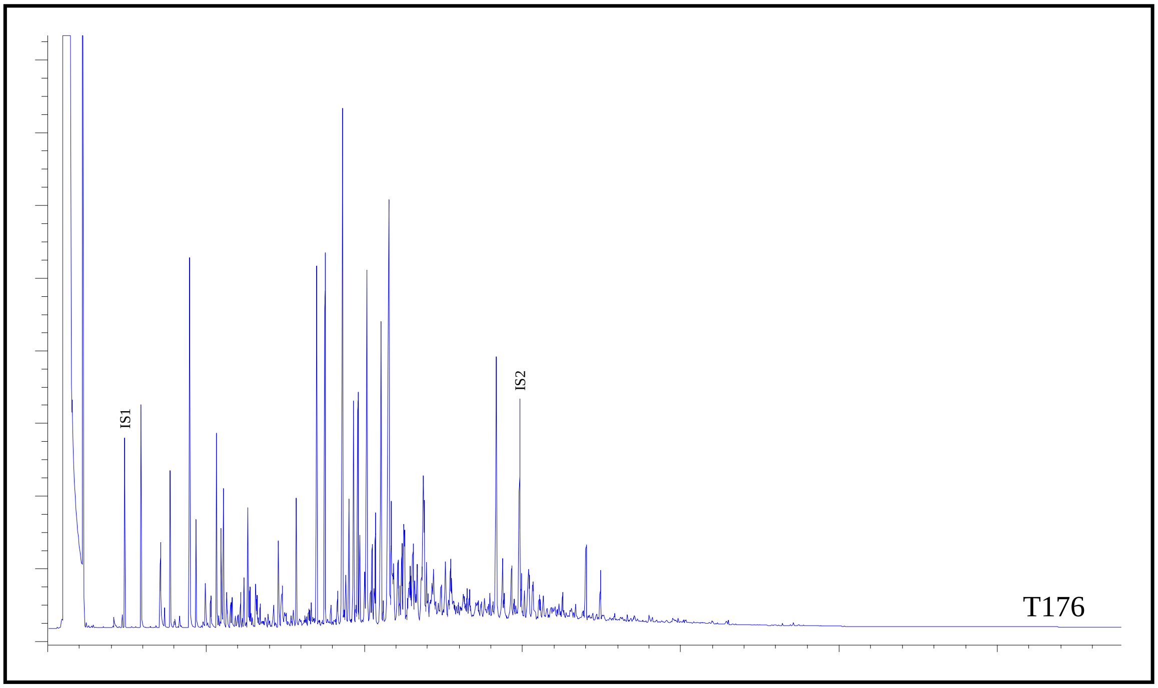

C
DATA TABLES

Table C-1
MAHs and PAHs by GC/FID (mg/kg)

Compounds	T004	T006	T009	T045	T049
benzene		1,390	1,330	1,020	294
toluene	189	2,680	4,300	2,220	911
ethylbenzene	160	4,830	888	880	402
m/p-Xylene	463	3,630	6,140	3,490	1,530
styrene	112	1,330	1,440	2,340	652
o-xylene	321	1,760	2,910	1,490	449
1,2,4-trimethylbenzene	627	4,760	4,900	5,750	1,140
naphthalene	8,100	131,000	108,000	41,900	99,900
2-methylnaphthalene	5,090	28,600	34,500	21,500	50,700
1-methylnaphthalene	3,830	16,900	19,000	10,700	19,800
acenaphthylene	1,140	16,700	6,300	4,350	3,860
acenaphthene	1,250	2,080	5,760	1,070	47,600
dibenzofuran	269	2,640	12,800	765	25,800
fluorene	1,460	10,100	15,200	2,020	27,500
phenanthrene	4,510	31,200	40,300	5,000	97,200
anthracene	1,060	9,310	9,300	1,370	6,920
fluoranthene	1,800	13,300	21,400	2,100	64,200
pyrene	2,390	17,100	21,800	2,360	44,000
benz(a)anthracene	999	7,430	12,000	1,280	12,500
chrysene	1,070	5,570	10,500	1,030	7,990
benzo(b)fluoranthene	384	2,680	5,840	429	4,130
benzo(k)fluoranthene	552	3,580	6,440	707	3,890
benzo(a)pyrene	761	6,070	10,200	935	3,800
indeno(123-cd)pyrene	372	2,380	5,270	370	985
dibenzo(ah)anthracene	91.9	564	1,430	108	206
benzo(ghi)perylene	464	2,480	5,530	334	735

Table C-1 (cont.)
MAHs and PAHs by GC/FID (mg/kg)

Compounds	T060	T095	T124	T125	T136
benzene	98.2	0.40	4,480	5,180	
toluene	121	0.75	10,400	11,300	3.08
ethylbenzene		1.97	2,560	2,690	2.57
m/p-Xylene	187	1.43	17,300	18,200	3.17
styrene	119	1.03	8,210	8,590	
o-xylene	103	0.38	6,220	6,440	2.87
1,2,4-trimethylbenzene	402	2.60	17,500	17,900	
naphthalene	34,300	26.9	68,000	66,800	283
2-methylnaphthalene	12,800	26.4	13,100	12,800	130
1-methylnaphthalene	6,890	18.8	5,670	5,540	60.2
acenaphthylene	13,700	9.26	6,800	6,650	8.18
acenaphthene	1,510	27.1	2,180	2,130	1,300
dibenzofuran	11,500	5.78	7,620	7,450	490
fluorene	14,700	22.4	10,100	9,820	914
phenanthrene	42,900	70.0	27,000	26,200	9,890
anthracene	11,100	27.5	7,290	6,810	2,150
fluoranthene	27,600	54.0	15,900	15,400	14,700
pyrene	22,000	71.4	11,200	10,900	13,800
benz(a)anthracene	13,000	35.1	7,420	7,230	6,760
chrysene	10,300	33.3	5,710	5,310	7,740
benzo(b)fluoranthene	6,350	2.49	3,560	3,430	8,540
benzo(k)fluoranthene	7,590	39.4	4,260	4,170	2,480
benzo(a)pyrene	9,350	35.6	5,310	5,140	7,040
indeno(123-cd)pyrene	3,570	11.2	2,490	2,410	3,590
dibenzo(ah)anthracene	1,190	2.97	833	801	763
benzo(ghi)perylene	2,500	16.2	2,300	2,200	2,460

Table C-1 (cont.)
MAHs and PAHs by GC/FID (mg/kg)

Compounds	T140	T165	T171	T174	T175
benzene				1,870	0.48
toluene	19.2	16.5	23.0	6,430	1.51
ethylbenzene	20.7	4,520	2,580	3,690	1.60
m/p-Xylene	171	2,050	3,690	5,790	3.67
styrene	353	98.5	71.7	1,920	2.37
o-xylene	108	1,040	1,590	2,580	1.27
1,2,4-trimethylbenzene	1,170	1,730	1,920	6,050	5.70
naphthalene	48,100	65,800	35,200	147,000	26.9
2-methylnaphthalene	39,400	19,000	17,500	58,200	19.7
1-methylnaphthalene	23,900	11,400	9,710	33,300	17.1
acenaphthylene	18,400	9,970	2,300	9,030	11.4
acenaphthene	3,370	6,390	5,090	9,560	22.2
dibenzofuran	1,820	1,370	631	7,510	14.0
fluorene	11,600	6,820	5,330	14,100	25.2
phenanthrene	23,400	18,600	11,900	34,300	87.6
anthracene	17,700	4,960	3,710	9,160	21.8
fluoranthene	4,970	6,700	3,590	13,000	61.3
pyrene	7,290	9,040	5,190	14,200	58.9
benz(a)anthracene	2,830	2,530	2,460	5,520	35.7
chrysene	2,220	2,310	1,900	4,880	27.7
benzo(b)fluoranthene	539	999	662	2,050	17.8
benzo(k)fluoranthene	1,160	1,770	1,060	2,880	24.1
benzo(a)pyrene	1,710	2,620	1,710	3,980	33.4
indeno(123-cd)pyrene	441	1,010	531	1,730	13.5
dibenzo(ah)anthracene	152	212	179	442	4.37
benzo(ghi)perylene	367	1,150	573	1,530	13.5

Table C-1 (cont.)
MAHs and PAHs by GC/FID (mg/kg)

Compounds	T176	T185	T192	T198	T199
benzene	5.29	5,060	8,650	61.9	850
toluene	61.8	3,360	4,570	25.1	2,840
ethylbenzene	49.2	83.3	226	1,710	2,390
m/p-Xylene	213	2,630	2,420	1,360	2,590
styrene	63.6	2,830	4,050		743
o-xylene	79.3	21.7	1,050	1,230	1,450
1,2,4-trimethylbenzene	200	2,070	2,840	2,720	3,740
naphthalene	1,670	98,300	85,800	41,400	31,500
2-methylnaphthalene	517	16,100	15,900	32,500	18,500
1-methylnaphthalene	287	6,350	9,070	22,300	14,000
acenaphthylene	169	23,000	11,100	1,970	6,290
acenaphthene	195	931	515	8,820	1,980
dibenzofuran	105	10,700	615	2,840	1,290
fluorene	270	16,500	3,530	6,140	5,200
phenanthrene	920	45,400	16,400	16,700	14,600
anthracene	285	14,400	3,980	4,270	3,590
fluoranthene	517	30,800	8,480	6,660	4,440
pyrene	594	22,500	10,800	7,610	6,550
benz(a)anthracene	222	15,100	3,370	3,590	3,490
chrysene	176	11,600	4,590	3,100	3,630
benzo(b)fluoranthene	105	7,780	2,210	1,400	973
benzo(k)fluoranthene	124	7,540	2,780	1,820	1,750
benzo(a)pyrene	218	10,500	4,600	2,330	2,020
indeno(123-cd)pyrene	96.5	4,900	2,640	1,080	694
dibenzo(ah)anthracene	24.6	1,400	436	327	249
benzo(ghi)perylene	113	4,320	3,200	865	702

Table C-1 (cont.)
MAHs and PAHs by GC/FID (mg/kg)

Compounds	**T201**	**T202**	**T203**	**T204**	**T206**
benzene	269	728	943	83.1	9,860
toluene	385	651	1,010	59.0	19,800
ethylbenzene	57.4	38.6	204	1,050	1,530
m/p-Xylene	298	647	1,160	979	11,700
styrene	392	279	108		12,300
o-xylene	140	243	513	809	4,830
1,2,4-trimethylbenzene	387	768	771	1,910	11,000
naphthalene	17,800	52,400	54,400	43,400	77,400
2-methylnaphthalene	3,820	14,000	11,400	19,800	34,500
1-methylnaphthalene	1,960	6,640	6,440	16,000	20,900
acenaphthylene	3,120	14,900	5,040	3,090	14,200
acenaphthene	440	1,140	3,960	9,330	1,140
dibenzofuran	2,280	11,500	8,690	5,990	1,880
fluorene	2,500	10,300	10,800	10,500	5,450
phenanthrene	9,610	38,700	38,600	30,300	14,600
anthracene	3,740	11,900	7,970	7,420	4,450
fluoranthene	5,530	23,400	23,900	15,900	4,640
pyrene	5,040	18,800	22,100	15,700	6,060
benz(a)anthracene	2,590	11,900	10,100	7,580	3,180
chrysene	2,180	9,630	7,690	6,620	2,170
benzo(b)fluoranthene	1,260	6,430	6,300	3,920	810
benzo(k)fluoranthene	1,570	6,050	6,150	4,310	1,260
benzo(a)pyrene	2,080	8,630	8,880	5,610	1,780
indeno(123-cd)pyrene	1,040	4,280	4,830	3,050	590
dibenzo(ah)anthracene	295	1,300	1,220	828	192
benzo(ghi)perylene	912	3,500	3,790	2,370	490

Table C-1 (cont.)
MAHs and PAHs by GC/FID (mg/kg)

Compounds	T207	T208
benzene		2,710
toluene		3,010
ethylbenzene	23.8	1,980
m/p-Xylene	385	2,700
styrene	43.9	951
o-xylene	181	1,300
1,2,4-trimethylbenzene	867	2,760
naphthalene	4,830	82,300
2-methylnaphthalene	2,370	31,700
1-methylnaphthalene	1,440	19,300
acenaphthylene	1,250	13,400
acenaphthene	250	6,720
dibenzofuran	1,010	4,090
fluorene	1,380	14,800
phenanthrene	2,910	43,900
anthracene	1,100	8,640
fluoranthene	1,660	15,800
pyrene	1,440	20,500
benz(a)anthracene	787	8,380
chrysene	651	5,800
benzo(b)fluoranthene	307	2,910
benzo(k)fluoranthene	446	3,560
benzo(a)pyrene	473	5,850
indeno(123-cd)pyrene	202	2,310
dibenzo(ah)anthracene	66.6	621
benzo(ghi)perylene	142	2,230

Table C-2
PAHs and Alkylated PAHs by GC/MS (mg/kg)

Compound	T004	T006	T009	T045	T049	T060	T095
C0B	23.2	1,170	17.7	821	142	68.9	0.02
C1B		2,540		2,710	808	154	
C2B		11,200		10,500	2,910	308	
C3B		5,930		9,720	2,280	605	
C4B		2,220		5,620	102	561	
C5B		127		1,870	2,160	86.0	
toluene	88.9	1,970	43.2	2,320	690	120	0.14
ethylbenene	948	3,710	21.7	1,040	345		0.53
m/p-xylene	1,140	2,910	126	3,910	1,200	147	0.36
styrene	2,920	1,230	96.4	2,460	551	81.0	1.04
o-xylene	788	1,470	68.0	1,660	375	69.8	0.10
1,2,4-trimethylbenzene	3,530	2,050	239	2,890	640	249	0.73
C0N	114,000	131,000	13,000	41,600	69,000	34,300	23.6
C1N	153,000	45,500	8,440	36,600	55,700	11,800	41.4
C2N	61,800	11,300	3,230	7,460	7,120	8,790	44.8
C3N	28,200	2,400	1,770	1,490	1,720	3,000	32.7
C4N	7,270	440	543	303	414	838	4.23
2-methylnaphthalene	84,800	28,600	5,180	24,200	38,500	11,700	24.9
1-methylnaphthalene	68,500	16,900	3,260	12,400	17,200	5,730	16.5
acenaphthylene	19,700	11,700	1,280	4,530	3,410	9,460	8.78
acenaphthene	17,500	1,720	771	563	38,200	1,430	26.1
dibenzofuran	3,550	2,510	2,240	808	21,100	9,940	5.73
C0F	32,900	7,400	3,130	2,390	25,100	11,600	22.8
C1F	38,600	3,560	1,730	1,700	5,160	4,690	33.3
C2F	21,600	893	1,020	426	1,020	1,300	17.4
C3F	7,340	235	646	105	705	211	12.1
phenanthrene	85,800	31,200	7,980	5,600	79,400	42,900	73.4
anthracene	21,400	9,310	1,760	1,700	5,620	11,100	29.2
C0PA	107,000	40,500	9,740	7,290	85,000	54,000	103
C1PA	67,800	10,300	4,290	3,560	13,400	10,900	143
C2PA	34,400	2,860	1,910	1,380	3,110	4,130	69.6
C3PA	13,000	708	773	350	778	1,140	30.3
C4PA	9,630	138	653	75.7	95.5	303	20.9
C0D	14,800	2,490	527	338	5,060	2,690	8.36
C1D	17,300	1,750	304	307	1,050	1,370	13.2
C2D	13,500	936	234	193	440	689	24.9
C3D	12,100	424	743	250	289	479	15.6
fluoranthene	34,300	11,100	5,790	2,580	59,100	17,200	29.2
pyrene	47,800	13,200	5,820	2,910	42,600	13,600	50.3
C0FP	82,000	25,200	11,600	5,490	102,000	31,700	79.5
C1FP	45,200	10,200	3,940	2,900	10,300	13,300	61.9
C2FP	30,400	2,120	1,680	919	2,340	3,900	33.3
C3FP	16,800	482	890	169	465	1,270	13.4
benz(a)anthracene	17,100	6,250	2,720	1,370	13,500	10,100	33.7
chrysene	20,600	5,190	2,790	1,300	7,110	6,930	34.2
C0BC	37,700	12,100	5,510	2,670	20,600	17,900	67.9
C1BC	42,100	3,460	3,610	1,120	2,020	3,900	68.9
C2BC	22,900	764	1,740	263	315	1,670	32.9
C3BC	10,100	175	798	122	157	656	12.5
C4BC	5,830	124	305	44.9	39.9	435	10.0
benzo(b)fluoranthene	7,810	3,060	1,710	673	3,210	5,780	18.7
benzo(k)fluoranthene	5,140	3,220	1,890	774	2,410	5,170	20.5
benzo(a)pyrene	15,700	6,060	2,490	1,120	2,590	7,250	30.1
indeno(1,2,3-cd)pyrene	5,320	3,280	1,340	466	700	4,150	12.8
dibenzo(a,h)anthracene	1,650	805	304	96.5	132	1,520	5.25
benzo(g,h,i)perylene	4,970	2,760	1,480	512	653	2,240	12.2

Table C-2 (cont.)
PAHs and Alkylated PAHs by GC/MS (mg/kg)

Compound	T124	T125	T136	T140	T165	T171	T174
C0B	1,900	1,770		18.0	443	1,190	1,340
C1B	7,570	6,860	330		2,890	2,990	5,310
C2B	27,600	35,400	17.2		13,000	16,500	12,500
C3B	27,700	36,200	107		9,720	15,000	11,000
C4B	215	13,200	57.8		4,130	9,480	8,000
C5B	1,820	14,400	8,230		7,790	7,030	684
toluene	6,470	5,870	287	12.0	2,470	2,550	4,130
ethylbenene	2,020	1,800			5,420	4,180	2,820
m/p-xylene	13,400	15,400		38.4	2,540	5,760	4,360
styrene	5,850	5,360		68.9	158	180	1,720
o-xylene	4,540	4,170		22.3	1,340	2,620	2,120
1,2,4-trimethylbenzene	9,660	11,300		176	1,730	3,000	3,490
C0N	51,200	51,200	233	26,100	44,000	70,100	147,000
C1N	17,100	20,000	108	42,000	25,800	67,000	91,500
C2N	3,620	3,350	82.4	14,600	11,300	20,700	28,000
C3N	982	994	35.6	4,040	3,000	5,350	8,910
C4N	246	281	22.7	686	858	1,640	2,430
2-methylnaphthalene	11,700	13,600	121	25,200	24,900	41,800	58,200
1-methylnaphthalene	5,410	6,450	64.1	16,900	16,600	25,200	33,300
acenaphthylene	5,140	4,980	20.6	13,500	14,600	5,920	6,560
acenaphthene	1,210	1,180	1,690	1,370	27.9	12,800	7,060
dibenzofuran	5,940	5,700	663	1,210	1,830	1,080	5,880
C0F	10,200	11,900	1,270	11,100	10,300	13,800	9,600
C1F	2,190	2,230	407	5,650	5,270	12,100	5,060
C2F	573	592	59.3	1,640	1,330	3,470	1,540
C3F	141	247	133	377	513	1,030	471
phenanthrene	25,900	29,400	13,100	20,300	28,300	34,900	34,300
anthracene	6,450	7,300	2,780	14,800	8,250	10,100	9,160
C0PA	32,400	36,700	15,800	35,100	36,500	45,000	43,500
C1PA	5,940	6,320	2,750	7,070	11,500	21,000	11,900
C2PA	2,050	2,270	866	1,650	3,410	7,400	4,400
C3PA	557	587	291	329	765	1,760	899
C4PA	125	107	39.1	466	143	240	365
C0D	709	634	398	2,170	1,180	966	1,990
C1D	273	277	114	1,230	740	921	1,630
C2D	138	164	40.2	434	462	609	807
C3D	243	259	1,100	725	1,040	939	520
fluoranthene	17,600	19,500	19,500	4,030	11,000	10,400	10,000
pyrene	13,100	14,700	16,100	5,800	15,100	15,100	10,100
C0FP	30,600	34,300	30,100	9,840	32,000	31,300	20,800
C1FP	7,350	10,600	7,510	4,390	9,590	14,900	7,820
C2FP	1,920	2,270	2,090	1,130	2,160	4,660	2,510
C3FP	448	467	600	320	433	1,050	569
benz(a)anthracene	5,090	5,950	10,500	1,990	5,390	6,500	4,500
chrysene	4,500	4,240	11,000	2,120	4,740	6,180	3,870
C0BC	9,610	10,200	21,600	4,110	10,200	12,700	8,890
C1BC	2,330	2,800	3,620	2,160	2,560	5,020	2,760
C2BC	579	725	935	623	684	1,270	977
C3BC	268	322	386	173	193	420	321
C4BC	79.7	113	77.8	148	50.6	97.0	157
benzo(b)fluoranthene	3,000	4,260	9,710	582	2,860	2,090	2,520
benzo(k)fluoranthene	3,050	3,310	8,570	1,010	3,230	3,080	2,000
benzo(a)pyrene	3,850	4,890	10,400	1,300	5,760	5,040	3,700
indeno(1,2,3-cd)pyrene	2,180	2,310	5,440	459	1,890	1,420	1,790
dibenzo(a,h)anthracene	321	338	752	167	251	254	653
benzo(g,h,i)perylene	2,200	2,300	6,050	373	2,490	1,810	1,310

Table C-2 (cont.)
PAHs and Alkylated PAHs by GC/MS (mg/kg)

Compound	T175	T176	T185	T192	T198	T199	T202
C0B		1.70	3,880	5,540	35.9	682	623
C1B			3,070	4,550	28.9	2,570	673
C2B			3,640	4,850	4,410	6,950	995
C3B			2,490	3,450	7,320	4,620	989
C4B			974	1,610	7,550	2,480	568
C5B			77.8	204	720	179	67.8
toluene	0.09	29.8	2,390	3,540	22.4	2,000	523
ethylbenene	0.34	29.4	71.4	242	1,270	1,880	31.0
m/p-xylene	0.61	163	2,030	2,340	1,060	2,060	490
styrene	1.28	45.9	1,510	4,220	135	682	251
o-xylene	0.31	56.0	734	1,160	879	1,150	208
1,2,4-trimethylbenzene	2.35	151	1,040	1,470	2,350	1,580	404
C0N	38.1	1,590	98,300	85,800	41,400	31,500	52,400
C1N	31.4	796	12,300	18,500	54,800	18,900	11,800
C2N	35.8	382	4,480	8,450	19,300	12,600	6,990
C3N	24.5	220	910	2,180	4,800	3,860	1,980
C4N	7.16	93.5	226	431	1,050	1,140	713
2-methylnaphthalene	21.7	492	12,700	17,700	32,500	16,700	11,800
1-methylnaphthalene	22.7	304	5,460	9,410	22,300	10,800	5,600
acenaphthylene	9.83	142	13,900	11,000	1,600	6,050	11,500
acenaphthene	22.3	161	759	627	6,680	1,860	1,060
dibenzofuran	16.0	93.7	9,470	676	1,980	825	9,760
C0F	33.5	305	12,600	4,550	4,800	4,730	7,790
C1F	22.4	212	2,710	3,410	5,150	6,860	3,440
C2F	11.2	82.5	419	954	1,730	2,720	931
C3F	10.4	51.1	131	274	372	804	445
phenanthrene	114	957	45,400	16,200	16,700	12,800	38,700
anthracene	18.5	335	11,200	5,170	3,980	3,840	11,900
C0PA	132	1,290	56,600	21,400	20,700	16,600	50,600
C1PA	122	664	7,310	8,780	9,480	13,300	8,820
C2PA	34.0	238	1,800	2,430	3,560	6,740	3,000
C3PA	16.7	102	434	782	691	1,270	1,010
C4PA	16.7	71.5	166	337	317	896	505
C0D	4.65	28.1	2,660	2,670	1,490	3,920	2,520
C1D	6.99	34.6	738	1,650	1,610	6,730	1,120
C2D	6.28	19.2	301	1,110	1,030	6,600	642
C3D	7.51	21.3	189	612	472	3,380	456
fluoranthene	78.9	521	19,200	10,600	5,520	3,950	17,200
pyrene	76.0	608	15,100	12,900	5,780	5,390	13,200
C0FP	155	1,130	35,300	24,400	11,700	9,700	31,200
C1FP	44.5	228	12,800	9,150	6,920	10,500	9,530
C2FP	35.1	117	2,670	3,050	2,730	5,230	2,870
C3FP	26.9	56.6	471	791	705	1,510	898
benz(a)anthracene	34.4	199	11,000	5,520	3,120	3,190	9,110
chrysene	30.9	169	8,600	5,720	2,490	3,160	7,210
C0BC	65.3	368	20,700	12,000	5,940	6,760	17,300
C1BC	68.0	231	4,170	4,040	2,470	4,820	3,650
C2BC	37.5	104	993	1,350	892	1,890	1,300
C3BC	21.6	52.6	356	366	264	564	532
C4BC	11.3	22.4	166	250	124	280	253
benzo(b)fluoranthene	29.1	95.1	7,790	3,880	1,430	1,080	5,760
benzo(k)fluoranthene	14.6	124	5,430	2,900	1,450	1,050	4,870
benzo(a)pyrene	29.1	181	8,260	6,210	2,270	2,000	7,050
indeno(1,2,3-cd)pyrene	14.7	81.0	6,090	4,260	1,190	770	5,350
dibenzo(a,h)anthracene	6.06	19.7	660	1,360	572	394	591
benzo(g,h,i)perylene	13.6	101	3,870	3,460	724	575	3,160

Table C-2 (cont.)
PAHs and Alkylated PAHs by GC/MS (mg/kg)

Compound	P013	P066	P120	P121	P122	P123	P125
C0B		1,260	51.2		1.52	0.54	0.81
C1B	44.8						
C2B	241						
C3B	620						
C4B	1,130						
C5B	11,800						
toluene	28.0	3,860	348	1.08	65.7	4.68	13.5
ethylbenene	22.1	1,280	114	1.02	37.3	9.69	11.3
m/p-xylene	90.6	3,960	488	13.1	201	48.4	60.0
styrene			7.82	0.54	3.80	1.32	
o-xylene	31.1	1,600	276	19.1	131	45.5	54.3
1,2,4-trimethylbenzene	128	1,690	243	172	214	217	184
C0N	127	815	22.1	54.0	29.0	80.6	75.9
C1N	632	1,730	18.0	104	54.8	187	145
C2N	1,270	1,750	10.5	89.0	28.6	213	119
C3N	1,090	1,360		9.73	4.97	104	55.7
C4N	721	595		3.39	4.09	19.6	9.55
2-methylnaphthalene	512	1,480		89.7	48.7	153	126
1-methylnaphthalene	390	1,110		65.7	30.2	122	87.6
acenaphthylene				0.53		1.52	0.88
acenaphthene	45.9					1.71	0.92
dibenzofuran	41.4	70.6		1.04	4.84	2.89	1.50
C0F	83.0	115		1.24	4.29	4.50	3.09
C1F	182	340				7.91	6.74
C2F	352	412					
C3F	245	523					
phenanthrene	309	289				0.99	0.59
anthracene	16.1	282					0.58
C0PA	321	571				0.99	1.17
C1PA	949	566					
C2PA	1,100	510					
C3PA	593	374					
C4PA	277	287					
C0D	147	235				0.66	0.61
C1D	478	389				6.17	
C2D	748	420					
C3D	646	716					
fluoranthene		2.19					
pyrene	60.0	10.9					
C0FP	110	13.1					
C1FP	160	108					
C2FP	188	140					
C3FP	183	192					
benz(a)anthracene	10.7	21.9					
chrysene	68.0	43.9					
C0BC	108	65.9					
C1BC	114	146					
C2BC	128	205					
C3BC	117	142					
C4BC	103	209					
benzo(b)fluoranthene							
benzo(k)fluoranthene							
benzo(a)pyrene		14.8					
indeno(1,2,3-cd)pyrene							
dibenzo(a,h)anthracene							
benzo(g,h,i)perylene							

Table C-2 (cont.)
PAHs and Alkylated PAHs by GC/MS (mg/kg)

Compound	P126	P127	P128
C0B	0.90	0.58	
C1B			
C2B			
C3B			
C4B			
C5B			
toluene	9.56	3.80	1.77
ethylbenene	8.12	1.55	1.01
m/p-xylene	32.1	12.9	6.94
styrene			
o-xylene	21.0	8.47	5.08
1,2,4-trimethylbenzene	64.3	35.5	23.3
C0N	55.0	41.7	20.9
C1N	182	163	86.2
C2N	254	251	153
C3N	264	245	133
C4N	70.2	74.1	40.5
2-methylnaphthalene	165	149	78.0
1-methylnaphthalene	105	93.3	50.5
acenaphthylene	2.16	2.24	1.36
acenaphthene	5.96	6.87	4.85
dibenzofuran	5.26	6.74	4.64
C0F	17.2	15.9	9.97
C1F	32.8	37.6	25.8
C2F	48.0	59.4	44.9
C3F	27.0	39.2	43.7
phenanthrene	21.1	36.4	41.7
anthracene		2.09	4.15
C0PA	21.1	38.5	45.9
C1PA	28.2	93.0	145
C2PA	17.9	103	180
C3PA	7.88	64.2	122
C4PA		35.8	67.9
C0D	6.57	11.2	20.5
C1D	36.1	36.1	65.1
C2D	3.27	48.6	99.8
C3D	2.77	72.7	152
fluoranthene	0.09	0.30	0.41
pyrene	1.02	11.5	25.3
C0FP	1.10	11.8	25.7
C1FP		34.5	69.5
C2FP		46.1	81.5
C3FP		36.7	71.0
benz(a)anthracene	0.68	3.27	7.96
chrysene	0.81	7.56	16.7
C0BC	1.49	10.8	24.6
C1BC		32.8	69.1
C2BC		34.5	79.7
C3BC		23.6	49.5
C4BC		10.5	27.5
benzo(b)fluoranthene		0.75	1.54
benzo(k)fluoranthene			0.83
benzo(a)pyrene		2.50	6.05
indeno(1,2,3-cd)pyrene			
dibenzo(a,h)anthracene			0.98
benzo(g,h,i)perylene		1.26	2.56

Table C-3
Biomarker Compounds in Selected Samples (mg/kg)

Compounds	T004	T005	T008	T009	T016
Normal Alkanes					
decane	2.86	435	15.8	71.2	36.5
heptadecane	84.3	823	34.4	163	
octadecane	63.2	523	24.6	159	14.2
eicosane	121	275	27.4	168	16.3
triacontane	3,180	16.3	4.11	14.2	7.44
Isoprenoids					
2,4,10-trimethyldodecane (farnesane)	10.9	286	5.30	22.0	221
2,4,10-trimethyltridecane	7.29	333	10.6	39.0	375
2,6,10-trimethylpentadecane (norpristane)	12.7	310	25.1	48.2	339
2,6,10,14-tetramethylpentadecane (pristane)	9.51	306	43.7	111	448
2,6,10,14-tetramethylhexadecane (phytane)	15.1	233	35.6	68.6	197
Tricyclic terpanes					
C19 tricyclic terpane					3.52
C20 tricyclic terpane	33.0				5.56
C21 tricyclic terpane	11.6				3.80
C22 tricyclic terpane	14.6				3.03
C23 tricyclic terpane	28.9	1.73			8.16
C24 tricyclic terpane	14.6				3.69
C25 tricyclic terpane	10.2		1.59	1.67	3.26
C26 tricyclic terpane	4.64				5.08
Tetracyclic terpanes					
C27 tetracyclic terpane	2.24				1.52
C27 tetracyclic terpane	2.75	1.05			2.18
C28 tetracyclic terpane	8.99				1.60
C28 tetracyclic terpane	4.66				2.29
Pentacyclic terpanes					
18a(H),21b(H)-22,29,30-trisnorhopane (Ts)	20.4				17.9
17a(H),18a(H),21a(H)-25,28,30-trisnorhopane	1.68				
17a(H),21b(H)-22,29,30-trisnorhopane (Tm)	15.3	1.39	0.60	2.28	15.5
17a(H),18a(H),21b(H)-28,30-bisnorhopane	11.2			0.51	1.40
17b(H),21a(H)-30-norhopane	42.3	2.15	1.19	3.47	54.7
18a(H),21b(H)-30-norneohopane	6.78		0.66		17.7
17a(H),21b(H)-30-norhopane (normoretane)	8.47			1.47	11.0
17a(H),21b(H)-hopane	49.7	3.67	1.59	4.32	98.3
17b(H),21a(H)-hopane (moretane)	9.02			0.94	14.0

Table C-3 (cont.)
Biomarker Compounds in Selected Samples (mg/kg)

Compounds	T004	T005	T008	T009	T016
22S-17a(H),21b(H)-30-homohopane	9.81	1.02		1.33	19.8
22R-17a(H),21b(H)-30-homohopane	7.06			0.71	14.5
17b(H),21b(H)-hopane (hopane)			0.78	0.58	3.02
22S-17a(H),21b(H)-30,31-bishomohopane	4.95			1.35	12.1
22R-17a(H),21b(H)-30,31-bishomohopane	4.70		0.75	0.64	9.33
22S-17a(H),21b(H)-30,31,32-rishomohopane	3.05		0.52		6.72
22R-17a(H),21b(H)-30,31,32-trishomohopane	2.49				3.70
22S-17a(H),21b(H)-30,31,32,33-tetrakishomohopane					2.63
22R-17a(H),21b(H)-30,31,32,33-tetrakishomohopane					1.54
22S-17a(H),21b(H)-30,31,32,33,34-pentakishomohopane	5.44				
22R-17a(H),21b(H)-30,31,32,33,34-pentakishomohopane	8.12	1.01			
Steranes					
C20 5a(H),14a(H),17a(H)-sterane	10.3				
C21 5a(H),14b(H),17b(H)-sterane	14.9				2.22
C22 5a(H),14b(H),17b(H)-sterane	2.17				
C27 20S-13b(H),17a(H)-diasterane	1.49				
C27 20R-13b(H),17a(H)-diasterane	6.98				
C27 20S-13a(H),17b(H)-diasterane	1.90				
C27 20R-13a(H),17b(H)-diasterane	6.46	2.25			1.17
C28 20S-13b(H),17a(H)-diasterane	1.62				
C27 20S-5a(H),14a(H),17a(H)-cholestane	11.0				
C27 20R-5a(H),14b(H),17b(H)-cholestane					
C27 20S-5a(H),14b(H),17b(H)-cholestane	54.4				1.03
C29 20S-13b(H),17a(H)-diasterane	1.51				
C28 20S-5a(H),14a(H),17a(H)-ergostane	66.6				
C28 20R-5a(H),14b(H),17b(H)-ergostane	3.76				
C28 20S-5a(H),14b(H),17b(H)-ergostane	3.16				
C29 20R-13a(H),17b(H)-diasterane	8.21				
C28 20R-5a(H),14a(H),17a(H)-ergostane	23.2	18.2			4.64
C29 20S-5a(H),14a(H),17a(H)-stigmastane	14.3	2.20			
C29 20R-5a(H),14b(H),17b(H)-stigmastane	15.3				1.24
C29 20S-5a(H),14b(H),17b(H)-stigmastane	15.3				
C29 20R-5a(H),14a(H),17a(H)-stigmastane	11.0				1.99

Table C-3 (cont.)
Biomarker Compounds in Selected Samples (mg/kg)

Compounds	T017	T031/T032	T044	T045	T049
Normal Alkanes					
decane	96.1	0.51	30.3	37.4	
heptadecane	630	11.9	416	92.3	181
octadecane	464	8.86	249	61.7	118
eicosane	281	5.20	199	34.5	67.7
triacontane	21.6	0.53	386	11.2	7.73
Isoprenoids					
2,4,10-trimethyldodecane (farnesane)	176	2.20	110	48.8	5.92
2,4,10-trimethyltridecane	241	4.68	198	57.7	52.1
2,6,10-trimethylpentadecane (norpristane)	300	4.54	97.9	25.9	79.7
2,6,10,14-tetramethylpentadecane (pristane)	242	5.18	84.6	30.6	64.6
2,6,10,14-tetramethylhexadecane (phytane)	200	2.83	42.3	12.9	79.0
Tricyclic terpanes					
C19 tricyclic terpane					1.05
C20 tricyclic terpane			37.1	29.7	
C21 tricyclic terpane	2.77		13.5		
C22 tricyclic terpane	1.19		6.85		
C23 tricyclic terpane	1.30		13.4		1.37
C24 tricyclic terpane			6.40		
C25 tricyclic terpane	4.52	0.24	4.40		3.75
C26 tricyclic terpane			3.17		
Tetracyclic terpanes					
C27 tetracyclic terpane			1.21		
C27 tetracyclic terpane			1.10		
C28 tetracyclic terpane			2.37		
C28 tetracyclic terpane			1.18		
Pentacyclic terpanes					
18a(H),21b(H)-22,29,30-trisnorhopane (Ts)	1.22		6.96		
17a(H),18a(H),21a(H)-25,28,30-trisnorhopane			1.51	1.02	
17a(H),21b(H)-22,29,30-trisnorhopane (Tm)	1.03	0.12	6.74	1.20	
17a(H),18a(H),21b(H)-28,30-bisnorhopane	1.18		1.60		
17b(H),21a(H)-30-norhopane	3.23	0.15	17.7	2.19	
18a(H),21b(H)-30-norneohopane	1.05		5.05		
17a(H),21b(H)-30-norhopane (Normoretane)	1.75		3.39	1.35	
17a(H),21b(H)-hopane	2.35	0.19	26.3	1.60	
17b(H),21a(H)-hopane (moretane)			4.45		

Table C-3 (cont.)
Biomarker Compounds in Selected Samples (mg/kg)

Compounds	**T017**	**T031/T032**	**T044**	**T045**	**T049**
22S-17a(H),21b(H)-30-homohopane	1.40		5.42		
22R-17a(H),21b(H)-30-homohopane			4.08		
17b(H),21b(H)-hopane (hopane)					
22S-17a(H),21b(H)-30,31-bishomohopane			3.02		
22R-17a(H),21b(H)-30,31-bishomohopane			2.79		
22S-17a(H),21b(H)-30,31,32-rishomohopane			1.32		
22R-17a(H),21b(H)-30,31,32-trishomohopane			1.08		
22S-17a(H),21b(H)-30,31,32,33-tetrakishomohopane			1.18		
22R-17a(H),21b(H)-30,31,32,33-tetrakishomohopane					
22S-17a(H),21b(H)-30,31,32,33,34-pentakishomohopane					
22R-17a(H),21b(H)-30,31,32,33,34-pentakishomohopane					
Steranes					
C20 5a(H),14a(H),17a(H)-sterane					
C21 5a(H),14b(H),17b(H)-sterane	1.94		8.75		
C22 5a(H),14b(H),17b(H)-sterane			1.19		
C27 20S-13b(H),17a(H)-diasterane			1.60		
C27 20R-13b(H),17a(H)-diasterane			1.58		
C27 20S-13a(H),17b(H)-diasterane				2.54	
C27 20R-13a(H),17b(H)-diasterane	3.14		4.54	3.13	2.45
C28 20S-13b(H),17a(H)-diasterane					
C27 20S-5a(H),14a(H),17a(H)-cholestane			1.80		
C27 20R-5a(H),14b(H),17b(H)-cholestane			1.32		
C27 20S-5a(H),14b(H),17b(H)-cholestane			8.60		
C29 20S-13b(H),17a(H)-diasterane					
C28 20S-5a(H),14a(H),17a(H)-ergostane			9.85		
C28 20R-5a(H),14b(H),17b(H)-ergostane			1.04		
C28 20S-5a(H),14b(H),17b(H)-ergostane			1.71		
C29 20R-13a(H),17b(H)-diasterane			1.40		
C28 20R-5a(H),14a(H),17a(H)-ergostane	24.7		21.4	27.8	20.5
C29 20S-5a(H),14a(H),17a(H)-stigmastane	3.23		1.76	2.66	2.17
C29 20R-5a(H),14b(H),17b(H)-stigmastane			2.59		
C29 20S-5a(H),14b(H),17b(H)-stigmastane			1.64		
C29 20R-5a(H),14a(H),17a(H)-stigmastane			5.68		

Table C-3 (cont.)
Biomarker Compounds in Selected Samples (mg/kg)

Compounds	**T095**	**T124**	**T125**	**T126**	**T136**
Normal Alkanes					
decane	0.18	123	85.6	741	
heptadecane		16.9	145	1,200	2.69
octadecane		13.5	117	925	1.67
eicosane	1.69	10.5	104	756	
triacontane	0.59	5.16	38.2	507	6.59
Isoprenoids					
2,4,10-trimethyldodecane (farnesane)	3.39	8.19	49.3	290	
2,4,10-trimethyltridecane	5.18	13.0	90.5	387	
2,6,10-trimethylpentadecane (norpristane)	6.63	5.94	48.7	614	
2,6,10,14-tetramethylpentadecane (pristane)	11.6	6.58	63.9	470	
2,6,10,14-tetramethylhexadecane (phytane)	10.6	2.97	30.6	391	
Tricyclic terpanes					
C19 tricyclic terpane			1.55	1.17	
C20 tricyclic terpane					
C21 tricyclic terpane	0.08			7.02	
C22 tricyclic terpane	0.08			8.94	
C23 tricyclic terpane	0.15			19.0	
C24 tricyclic terpane	0.09			9.46	
C25 tricyclic terpane	0.08	3.93	10.8	6.18	2.89
C26 tricyclic terpane	0.11			3.70	
Tetracyclic terpanes					
C27 tetracyclic terpane	0.04			1.56	
C27 tetracyclic terpane	0.06			1.54	
C28 tetracyclic terpane	0.04			2.68	
C28 tetracyclic terpane	0.06			1.78	
Pentacyclic terpanes					
18a(H),21b(H)-22,29,30-trisnorhopane (Ts)	0.18			7.07	
17a(H),18a(H),21a(H)-25,28,30-trisnorhopane	0.02			1.71	
17a(H),21b(H)-22,29,30-trisnorhopane ™	0.23		1.31	6.82	
17a(H),18a(H),21b(H)-28,30-bisnorhopane	0.02		2.85	1.64	
17b(H),21a(H)-30-norhopane	0.66		2.59	17.8	
18a(H),21b(H)-30-norneohopane	0.12			5.52	
17a(H),21b(H)-30-norhopane (normoretane)	0.13			3.33	
17a(H),21b(H)-hopane	0.92		2.85	27.2	
17b(H),21a(H)-hopane (moretane)	0.15		1.10	4.35	

Table C-3 (cont.)
Biomarker Compounds in Selected Samples (mg/kg)

Compounds	T095	T124	T125	T126	T136
22S-17a(H),21b(H)-30-homohopane	0.22		1.13	5.56	
22R-17a(H),21b(H)-30-homohopane	0.16			3.61	
17b(H),21b(H)-hopane (hopane)	0.04				
22S-17a(H),21b(H)-30,31-bishomohopane	0.23			2.70	
22R-17a(H),21b(H)-30,31-bishomohopane	0.11		1.27	2.32	
22S-17a(H),21b(H)-30,31,32-rishomohopane	0.09			2.60	
22R-17a(H),21b(H)-30,31,32-trishomohopane	0.07				
22S-17a(H),21b(H)-30,31,32,33-tetrakishomohopane	0.04				
22R-17a(H),21b(H)-30,31,32,33-tetrakishomohopane	0.03				
22S-17a(H),21b(H)-30,31,32,33,34-pentakishomohopane	0.04				
22R-17a(H),21b(H)-30,31,32,33,34-pentakishomohopane	0.01				
Steranes					
C20 5a(H),14a(H),17a(H)-sterane	0.03			1.08	
C21 5a(H),14b(H),17b(H)-sterane	0.09			7.14	
C22 5a(H),14b(H),17b(H)-sterane	0.03			1.96	
C27 20S-13b(H),17a(H)-diasterane	0.08			1.48	
C27 20R-13b(H),17a(H)-diasterane	0.04			1.70	
C27 20S-13a(H),17b(H)-diasterane	0.03				
C27 20R-13a(H),17b(H)-diasterane	0.06	1.81	13.5	3.52	2.94
C28 20S-13b(H),17a(H)-diasterane	0.03				
C27 20S-5a(H),14a(H),17a(H)-cholestane	0.10			1.51	
C27 20R-5a(H),14b(H),17b(H)-cholestane	0.07			1.02	
C27 20S-5a(H),14b(H),17b(H)-cholestane	0.04			9.31	
C29 20S-13b(H),17a(H)-diasterane	0.02				
C28 20S-5a(H),14a(H),17a(H)-ergostane	0.03				
C28 20R-5a(H),14b(H),17b(H)-ergostane	0.03				
C28 20S-5a(H),14b(H),17b(H)-ergostane	0.02			1.01	
C29 20R-13a(H),17b(H)-diasterane	0.03			1.10	
C28 20R-5a(H),14a(H),17a(H)-ergostane	0.05	16.6	110	24.3	29.3
C29 20S-5a(H),14a(H),17a(H)-stigmastane	0.03	1.55	11.8	2.04	3.60
C29 20R-5a(H),14b(H),17b(H)-stigmastane	0.06			3.23	
C29 20S-5a(H),14b(H),17b(H)-stigmastane	0.02			1.20	
C29 20R-5a(H),14a(H),17a(H)-stigmastane	0.06		1.83	5.97	

Table C-3 (cont.)
Biomarker Compounds in Selected Samples (mg/kg)

Compounds	T140	T165	T171	T174	T175
Normal Alkanes					
decane	5.45	125	1,030	606	0.53
heptadecane	281	744	964	726	1.78
octadecane	148	499	731	633	1.58
eicosane	57.1	319	479	417	1.71
triacontane	11.2	9.49	10.4		0.48
Isoprenoids					
2,4,10-trimethyldodecane (farnesane)	118	235	88.1	685	0.68
2,4,10-trimethyltridecane	152	312	153	794	1.26
2,6,10-trimethylpentadecane (norpristane)	68.4	338	221	510	1.35
2,6,10,14-tetramethylpentadecane (pristane)	99.3	265	42.5	889	1.42
2,6,10,14-tetramethylhexadecane (phytane)	80.5	228	59.5	380	0.67
Tricyclic terpanes					
C19 tricyclic terpane				3.21	0.04
C20 tricyclic terpane				6.25	0.13
C21 tricyclic terpane	27.1		1.32	6.14	0.03
C22 tricyclic terpane					0.03
C23 tricyclic terpane				9.02	0.04
C24 tricyclic terpane				6.06	0.02
C25 tricyclic terpane				6.46	0.04
C26 tricyclic terpane				3.04	0.05
Tetracyclic terpanes					
C27 tetracyclic terpane				5.85	0.02
C27 tetracyclic terpane				6.14	0.02
C28 tetracyclic terpane				5.02	0.02
C28 tetracyclic terpane				5.28	
Pentacyclic terpanes					
18a(H),21b(H)-22,29,30-trisnorhopane (Ts)				3.78	0.06
17a(H),18a(H),21a(H)-25,28,30-trisnorhopane				4.12	
17a(H),21b(H)-22,29,30-trisnorhopane (Tm)			1.19	11.7	0.33
17a(H),18a(H),21b(H)-28,30-bisnorhopane	1.16			1.98	0.04
17b(H),21a(H)-30-norhopane	1.49		2.09	22.0	0.58
18a(H),21b(H)-30-norneohopane				3.67	0.12
17a(H),21b(H)-30-norhopane (normoretane)				7.16	0.15
17a(H),21b(H)-hopane	1.35		2.44	40.3	0.87
17b(H),21a(H)-hopane (moretane)				8.45	0.30

Table C-3 (cont.)
Biomarker Compounds in Selected Samples (mg/kg)

Compounds	**T140**	**T165**	**T171**	**T174**	**T175**
22S-17a(H),21b(H)-30-homohopane				9.44	0.18
22R-17a(H),21b(H)-30-homohopane				8.99	0.13
17b(H),21b(H)-hopane (hopane)					0.05
22S-17a(H),21b(H)-30,31-bishomohopane				5.22	0.13
22R-17a(H),21b(H)-30,31-bishomohopane				5.64	0.09
22S-17a(H),21b(H)-30,31,32-rishomohopane				4.33	0.08
22R-17a(H),21b(H)-30,31,32-trishomohopane					0.05
22S-17a(H),21b(H)-30,31,32,33-tetrakishomohopane					0.04
22R-17a(H),21b(H)-30,31,32,33-tetrakishomohopane				3.25	0.03
22S-17a(H),21b(H)-30,31,32,33,34-pentakishomohopane					0.03
22R-17a(H),21b(H)-30,31,32,33,34-pentakishomohopane					0.02
Steranes					
C20 5a(H),14a(H),17a(H)-sterane				3.38	
C21 5a(H),14b(H),17b(H)-sterane				6.63	0.02
C22 5a(H),14b(H),17b(H)-sterane				2.81	
C27 20S-13b(H),17a(H)-diasterane				4.05	
C27 20R-13b(H),17a(H)-diasterane				2.34	
C27 20S-13a(H),17b(H)-diasterane				2.26	
C27 20R-13a(H),17b(H)-diasterane	3.27	1.93	1.49	5.43	0.02
C28 20S-13b(H),17a(H)-diasterane				2.11	
C27 20S-5a(H),14a(H),17a(H)-cholestane				9.92	
C27 20R-5a(H),14b(H),17b(H)-cholestane				2.11	
C27 20S-5a(H),14b(H),17b(H)-cholestane				3.95	
C29 20S-13b(H),17a(H)-diasterane					
C28 20S-5a(H),14a(H),17a(H)-ergostane				5.93	0.03
C28 20R-5a(H),14b(H),17b(H)-ergostane				6.50	
C28 20S-5a(H),14b(H),17b(H)-ergostane				4.54	0.02
C29 20R-13a(H),17b(H)-diasterane				3.00	
C28 20R-5a(H),14a(H),17a(H)-ergostane	24.4	15.6	11.9	11.0	0.20
C29 20S-5a(H),14a(H),17a(H)-stigmastane		1.82	1.38	4.27	0.03
C29 20R-5a(H),14b(H),17b(H)-stigmastane				5.28	0.03
C29 20S-5a(H),14b(H),17b(H)-stigmastane				5.28	0.03
C29 20R-5a(H),14a(H),17a(H)-stigmastane				8.89	0.10

Table C-3 (cont.)
Biomarker Compounds in Selected Samples (mg/kg)

Compounds	T176	T192	P013	P063	P065
Normal Alkanes					
decane	55.3	10.5	272	5,600	344
heptadecane	26.7	24.3	7,730	12,800	5,270
octadecane	20.9	24.7	6,770	9,070	3,770
eicosane	15.8	14.6	9,920	5,860	2,190
triacontane	4.95	2.02	7,530	4,720	581
Isoprenoids					
2,4,10-trimethyldodecane (farnesane)	7.88	26.4	828	1,420	316
2,4,10-trimethyltridecane	15.3	21.4	1,620	3,730	871
2,6,10-trimethylpentadecane (norpristane)	14.7	15.4	2,610	4,750	2,130
2,6,10,14-tetramethylpentadecane (pristane)	10.5	17.5	2,410	1,950	1,240
2,6,10,14-tetramethylhexadecane (phytane)	6.33	4.46	3,950	2,710	1,560
Tricyclic terpanes					
C19 tricyclic terpane			25.0	12.2	1.07
C20 tricyclic terpane			4.44		
C21 tricyclic terpane	0.04		54.0	18.9	7.78
C22 tricyclic terpane	0.02		79.1	3.95	0.84
C23 tricyclic terpane			186	63.4	23.7
C24 tricyclic terpane			118	28.5	10.6
C25 tricyclic terpane			100	17.6	11.9
C26 tricyclic terpane	0.07		51.6	14.1	5.68
Tetracyclic terpanes					
C27 tetracyclic terpane			40.4	4.87	1.77
C27 tetracyclic terpane			39.7	3.91	1.81
C28 tetracyclic terpane			42.2	16.7	4.53
C28 tetracyclic terpane			44.9	5.93	13.4
Pentacyclic terpanes					
18a(H),21b(H)-22,29,30-trisnorhopane (Ts)	0.04		74.5	36.6	11.7
17a(H),18a(H),21a(H)-25,28,30-trisnorhopane	0.04		35.7	3.51	2.01
17a(H),21b(H)-22,29,30-trisnorhopane (Tm)	0.51		102	31.1	10.7
17a(H),18a(H),21b(H)-28,30-bisnorhopane	0.08		8.16	14.9	2.79
17b(H),21a(H)-30-norhopane	0.82		205	71.7	35.7
18a(H),21b(H)-30-norneohopane	0.82		44.4	17.6	8.05
17a(H),21b(H)-30-norhopane (normoretane)	0.24		24.8	15.2	5.91
17a(H),21b(H)-hopane	0.77		311	86.3	48.9
17b(H),21a(H)-hopane (moretane)	0.30		60.4	15.8	6.26

Table C-3 (cont.)
Biomarker Compounds in Selected Samples (mg/kg)

Compounds	**T176**	**T192**	**P013**	**P063**	**P065**
22S-17a(H),21b(H)-30-homohopane	0.22		127	18.0	16.2
22R-17a(H),21b(H)-30-homohopane	0.17		77.3	12.9	11.7
17b(H),21b(H)-hopane (hopane)	0.09		10.2	3.70	2.54
22S-17a(H),21b(H)-30,31-bishomohopane	0.15		70.3	8.73	10.2
22R-17a(H),21b(H)-30,31-bishomohopane	0.11		55.4	7.91	8.05
22S-17a(H),21b(H)-30,31,32-rishomohopane	0.05		56.1	8.08	7.51
22R-17a(H),21b(H)-30,31,32-trishomohopane	0.04		44.5	4.79	6.58
22S-17a(H),21b(H)-30,31,32,33-tetrakishomohopane	0.03		30.1	0.91	3.96
22R-17a(H),21b(H)-30,31,32,33-tetrakishomohopane	0.02		17.0	0.42	2.49
22S-17a(H),21b(H)-30,31,32,33,34-pentakishomohopane			36.4	12.1	8.29
22R-17a(H),21b(H)-30,31,32,33,34-pentakishomohopane			20.2	17.7	2.72
Steranes					
C20 5a(H),14a(H),17a(H)-sterane			15.4	20.3	4.45
C21 5a(H),14b(H),17b(H)-sterane	0.02		80.3	22.3	7.34
C22 5a(H),14b(H),17b(H)-sterane			23.1	4.88	2.08
C27 20S-13b(H),17a(H)-diasterane			57.1	3.36	1.61
C27 20R-13b(H),17a(H)-diasterane			39.3	13.9	2.70
C27 20S-13a(H),17b(H)-diasterane			20.0	3.83	1.25
C27 20R-13a(H),17b(H)-diasterane	0.02		33.5	13.0	6.19
C28 20S-13b(H),17a(H)-diasterane			28.1	3.01	1.25
C27 20S-5a(H),14a(H),17a(H)-cholestane			24.6	19.4	2.75
C27 20R-5a(H),14b(H),17b(H)-cholestane			70.1	1.59	1.79
C27 20S-5a(H),14b(H),17b(H)-cholestane			82.0	111	16.4
C29 20S-13b(H),17a(H)-diasterane			8.97	3.89	17.2
C28 20S-5a(H),14a(H),17a(H)-ergostane			17.5	127	0.39
C28 20R-5a(H),14b(H),17b(H)-ergostane			18.6	9.78	2.00
C28 20S-5a(H),14b(H),17b(H)-ergostane			27.0	11.0	2.61
C29 20R-13a(H),17b(H)-diasterane			17.8	16.7	2.54
C28 20R-5a(H),14a(H),17a(H)-ergostane	0.13		63.6	47.9	29.0
C29 20S-5a(H),14a(H),17a(H)-stigmastane			35.0	5.63	3.37
C29 20R-5a(H),14b(H),17b(H)-stigmastane	0.02		53.6	13.0	4.30
C29 20S-5a(H),14b(H),17b(H)-stigmastane	0.02		34.9	14.4	3.00
C29 20R-5a(H),14a(H),17a(H)-stigmastane	0.03		59.6	211	7.42

Table C-3 (cont.)
Biomarker Compounds in Selected Samples (mg/kg)

Compounds	P066	P123	P126	P127	P128
Normal Alkanes					
decane	2,920		233	80.6	67.9
heptadecane	2,340	64.6	404	310	94.7
octadecane	1,990	19.7	283	217	77.0
eicosane	1,960	2.64	149	128	55.3
triacontane	728	0.20	0.41	1.15	2.39
Isoprenoids					
2,4,10-trimethyldodecane (farnesane)	569	139	148	78.9	30.6
2,4,10-trimethyltridecane	1,020	189	298	160	38.5
2,6,10-trimethylpentadecane (norpristane)	905	43.3	213	136	41.5
2,6,10,14-tetramethylpentadecane (pristane)	993	23.9	248	213	36.9
2,6,10,14-tetramethylhexadecane (phytane)	992	7.22	151	116	37.1
Tricyclic terpanes					
C19 tricyclic terpane	0.27		0.07	0.01	0.01
C20 tricyclic terpane	29.3				
C21 tricyclic terpane	10.9		0.31	0.21	0.14
C22 tricyclic terpane	17.7		0.36	0.24	0.24
C23 tricyclic terpane	41.2		0.23	0.53	0.92
C24 tricyclic terpane	29.5		0.12	0.11	0.13
C25 tricyclic terpane	27.8				0.26
C26 tricyclic terpane	16.5		0.04	0.05	0.09
Tetracyclic terpanes					
C27 tetracyclic terpane	10.9			0.02	0.03
C27 tetracyclic terpane	12.9			0.02	0.05
C28 tetracyclic terpane	12.7			0.03	0.03
C28 tetracyclic terpane	9.78			0.05	0.03
Pentacyclic terpanes					
18a(H),21b(H)-22,29,30-trisnorhopane (Ts)	19.9			0.19	0.16
17a(H),18a(H),21a(H)-25,28,30-trisnorhopane	11.4			0.05	0.07
17a(H),21b(H)-22,29,30-trisnorhopane (Tm)	27.4			0.13	0.20
17a(H),18a(H),21b(H)-28,30-bisnorhopane	1.74			0.02	0.01
17b(H),21a(H)-30-norhopane	52.0			0.34	0.55
18a(H),21b(H)-30-norneohopane	14.5			0.07	0.10
17a(H),21b(H)-30-norhopane (normoretane)	6.09			0.03	0.05
17a(H),21b(H)-hopane	107			0.48	0.89
17b(H),21a(H)-hopane (moretane)	7.48			0.07	0.06

Table C-3 (cont.)
Biomarker Compounds in Selected Samples (mg/kg)

Compounds	P066	P123	P126	P127	P128
22S-17a(H),21b(H)-30-homohopane	49.4			0.22	0.36
22R-17a(H),21b(H)-30-homohopane	28.0			0.12	0.22
17b(H),21b(H)-hopane (hopane)	4.24			0.03	0.04
22S-17a(H),21b(H)-30,31-bishomohopane	30.0			0.21	0.34
22R-17a(H),21b(H)-30,31-bishomohopane	22.3			0.13	0.28
22S-17a(H),21b(H)-30,31,32-rishomohopane	22.4			0.15	0.30
22R-17a(H),21b(H)-30,31,32-trishomohopane	14.6			0.09	0.27
22S-17a(H),21b(H)-30,31,32,33-tetrakishomohopane	17.0			0.20	0.31
22R-17a(H),21b(H)-30,31,32,33-tetrakishomohopane	9.72			0.12	0.15
22S-17a(H),21b(H)-30,31,32,33,34-pentakishomohopane	19.2			0.07	0.34
22R-17a(H),21b(H)-30,31,32,33,34-pentakishomohopane	12.4			0.09	0.21
Steranes					
C20 5a(H),14a(H),17a(H)-sterane	6.77		0.04	0.06	0.05
C21 5a(H),14b(H),17b(H)-sterane	18.3		0.06	0.07	0.09
C22 5a(H),14b(H),17b(H)-sterane	7.57		0.01	0.02	0.02
C27 20S-13b(H),17a(H)-diasterane	18.1			0.02	0.02
C27 20R-13b(H),17a(H)-diasterane	8.55			0.01	0.01
C27 20S-13a(H),17b(H)-diasterane	6.20			0.01	
C27 20R-13a(H),17b(H)-diasterane	19.2			0.17	
C28 20S-13b(H),17a(H)-diasterane	9.33			0.01	0.01
C27 20S-5a(H),14a(H),17a(H)-cholestane	7.88			0.01	0.01
C27 20R-5a(H),14b(H),17b(H)-cholestane	16.9			0.03	0.04
C27 20S-5a(H),14b(H),17b(H)-cholestane	8.78			0.01	0.02
C29 20S-13b(H),17a(H)-diasterane	5.92			0.01	
C28 20S-5a(H),14a(H),17a(H)-ergostane	9.54				0.02
C28 20R-5a(H),14b(H),17b(H)-ergostane	10.2				0.02
C28 20S-5a(H),14b(H),17b(H)-ergostane	7.72			0.02	0.02
C29 20R-13a(H),17b(H)-diasterane	5.61			0.01	0.01
C28 20R-5a(H),14a(H),17a(H)-ergostane	43.1				1.35
C29 20S-5a(H),14a(H),17a(H)-stigmastane	7.17				0.16
C29 20R-5a(H),14b(H),17b(H)-stigmastane	16.7			0.02	0.04
C29 20S-5a(H),14b(H),17b(H)-stigmastane	5.59			0.02	0.02
C29 20R-5a(H),14a(H),17a(H)-stigmastane	17.2			0.05	0.08

Table C-3 (cont.)
Biomarker Compounds in Selected Samples (mg/kg)

Compounds	**M006**	**M007**	**M018**
Normal Alkanes			
decane	0.01	0.01	0.55
heptadecane	5.19	0.48	50.2
octadecane	4.27	0.41	39.9
eicosane	4.22	0.69	30.7
triacontane	1.91	2.08	11.3
Isoprenoids			
2,4,10-trimethyldodecane (farnesane)	1.44	0.33	8.89
2,4,10-trimethyltridecane	4.22	1.29	20.8
2,6,10-trimethylpentadecane (norpristane)	2.45	0.41	20.7
2,6,10,14-tetramethylpentadecane (pristane)	8.52	2.73	19.7
2,6,10,14-tetramethylhexadecane (phytane)	1.93	0.42	17.2
Tricyclic terpanes			
C19 tricyclic terpane	0.03	3.17	0.08
C20 tricyclic terpane		8.07	0.15
C21 tricyclic terpane	0.02	3.60	0.09
C22 tricyclic terpane	0.01		0.11
C23 tricyclic terpane	0.01		0.33
C24 tricyclic terpane			0.14
C25 tricyclic terpane	0.01	0.02	1.02
C26 tricyclic terpane	0.04	0.01	0.35
Tetracyclic terpanes			
C27 tetracyclic terpane	0.01	0.01	0.16
C27 tetracyclic terpane	0.01	0.03	0.14
C28 tetracyclic terpane	0.01	0.03	0.15
C28 tetracyclic terpane	0.01	0.04	0.18
Pentacyclic terpanes			
18a(H),21b(H)-22,29,30-trisnorhopane (Ts)	0.01	0.03	0.73
17a(H),18a(H),21a(H)-25,28,30-trisnorhopane	0.03		0.97
17a(H),21b(H)-22,29,30-trisnorhopane (Tm)	0.48	0.13	1.35
17a(H),18a(H),21b(H)-28,30-bisnorhopane	0.03	0.53	0.48
17b(H),21a(H)-30-norhopane	0.69	1.20	7.02
18a(H),21b(H)-30-norneohopane	0.11	0.16	0.61
17a(H),21b(H)-30-norhopane (normoretane)	0.08	0.18	0.55
17a(H),21b(H)-hopane	1.39	0.34	7.59
17b(H),21a(H)-hopane (moretane)	0.23	0.54	0.49

Table C-3 (cont.)
Biomarker Compounds in Selected Samples (mg/kg)

Compounds	**M006**	**M007**	**M018**
22S-17a(H),21b(H)-30-homohopane	0.44	0.25	4.38
22R-17a(H),21b(H)-30-homohopane	0.29	1.58	3.03
17b(H),21b(H)-hopane (hopane)	0.10	0.91	0.44
22S-17a(H),21b(H)-30,31-bishomohopane	0.28	0.02	3.09
22R-17a(H),21b(H)-30,31-bishomohopane	0.20	0.11	2.15
22S-17a(H),21b(H)-30,31,32-rishomohopane	0.12	0.59	2.47
22R-17a(H),21b(H)-30,31,32-trishomohopane	0.08	0.03	1.66
22S-17a(H),21b(H)-30,31,32,33-tetrakishomohopane	0.06	0.10	2.18
22R-17a(H),21b(H)-30,31,32,33-tetrakishomohopane	0.04	0.01	1.34
22S-17a(H),21b(H)-30,31,32,33,34-pentakishomohopane	0.02	0.02	2.93
22R-17a(H),21b(H)-30,31,32,33,34-pentakishomohopane	0.02		2.15
Steranes			
C20 5a(H),14a(H),17a(H)-sterane			0.03
C21 5a(H),14b(H),17b(H)-sterane	0.01		0.10
C22 5a(H),14b(H),17b(H)-sterane		0.03	0.05
C27 20S-13b(H),17a(H)-diasterane		0.01	0.08
C27 20R-13b(H),17a(H)-diasterane			0.03
C27 20S-13a(H),17b(H)-diasterane			0.01
C27 20R-13a(H),17b(H)-diasterane	0.01		0.06
C28 20S-13b(H),17a(H)-diasterane		0.01	0.11
C27 20S-5a(H),14a(H),17a(H)-cholestane		0.02	0.14
C27 20R-5a(H),14b(H),17b(H)-cholestane	0.02	0.02	0.20
C27 20S-5a(H),14b(H),17b(H)-cholestane	0.01	0.02	0.12
C29 20S-13b(H),17a(H)-diasterane	0.01	0.01	0.02
C28 20S-5a(H),14a(H),17a(H)-ergostane	0.01	0.02	0.15
C28 20R-5a(H),14b(H),17b(H)-ergostane	0.01	0.01	0.15
C28 20S-5a(H),14b(H),17b(H)-ergostane	0.02	0.02	0.17
C29 20R-13a(H),17b(H)-diasterane			0.13
C28 20R-5a(H),14a(H),17a(H)-ergostane	0.01	0.04	0.14
C29 20S-5a(H),14a(H),17a(H)-stigmastane	0.03	0.01	0.22
C29 20R-5a(H),14b(H),17b(H)-stigmastane	0.01	0.03	0.30
C29 20S-5a(H),14b(H),17b(H)-stigmastane	0.01	0.03	0.22
C29 20R-5a(H),14a(H),17a(H)-stigmastane	0.02	0.08	0.28

Table C-4
Stable Carbon Isotope Ratios ($\delta^{13}C$, ‰)

Compounds	Code	T006	T044	T045	T060	T124	T136
naphthalene	*NAP*		-26.24	-24.92	-23.745		
2-methylnaphthalene	*2MN*	-28.29	-24.93	-24.465	-23.895	-23.1	
1-methylnaphthalene	*1MN*	-27.76	-25.23	-23.54	-22.375	-24.93	
acenaphthylene	*ACY*	-27.62	-24.45	-24.645	-21.13	-22.7	
fluorene	*FLU*	-28.21	-25.38	-25.03	-23.625	-24.79	
phenanthrene	*PHE*	-29.11	-26.14	-25.795	-23.83	-23.78	-23.52
anthracene	*ANT*	-28.76	-26.20	-25.595	-23.64	-23.89	-23.25
fluoranthene	*FLR*	-29.3	-26.25	-25.72	-23.835	-24.04	-23.73
pyrene	*PYR*	-29.57	-26.42	-26.06	-23.695	-24.01	-23.37
benzofluoranthenes	*BBK*	-29.22	-27.64	-26.2	-20.98	-24.665	-21.3
benz(a)anthracene	*BAA*	-28.3	-24.99	-25.4	-22.7	-23.82	-23.175
chrysene	*CHR*	-29.16	-28.07	-26.41	-25.905	-25.135	-24.74
benzo(a)pyrene	*BAP*	-29.84	-27.92	-26.275	-23.5	-25.24	-23.3
internal standard	*9D*	-30.06	-30.42	-28.115	-30.54	-30.365	-30.72
internal standard	*10D*	-30.84	-30.70	-32.09		-27.88	
internal standard	*16D*	-29.69	-25.87	-28.945	-29.775	-28.875	-29.915
internal standard	*19D*	-27.69	-27.54	-27.66	-27.44	-28.845	-26.82
internal standard	*24D*	-26.12	-26.19	-25.995	-25.5	-28.675	-25.595
internal standard	*32D*	-29.56	-29.31	-29.25	-29.45	-29.005	-28.685
Batch		oct99	oct99	oct99	feb99	oct99	feb99

Table C-4 (cont.)
Stable Carbon Isotope Ratios (δ^{13}C, ‰)

Compounds	**Code**	**T140**	**T165**	**T171**	**T174**	**T174**	**T185**
naphthalene	*NAP*		-29.31	-29.31		-24.19	
2-methylnaphthalene	*2MN*	-26.71	-26.83	-26.77		-23.12	-22.15
1-methylnaphthalene	*1MN*	-26.68	-28.86	-27.77		-27.61	-21.87
acenaphthylene	*ACY*	-26.67	-26.69	-26.68	-19.49	-21.53	-22.51
fluorene	*FLU*	-26.18	-28.42	-27.30	-23.67	-23.81	-23.65
phenanthrene	*PHE*	-27.79	-28.56	-26.62	-23.99	-24.16	-23.57
anthracene	*ANT*	-27.28	-28.75	-26.43	-23.56	-23.83	-23.81
fluoranthene	*FLR*	-27.67	-29.01	-26.80	-24.69	-24.91	-23.77
pyrene	*PYR*	-28.26	-28.66	-26.76	-23.5	-24.55	-23.52
benzofluoranthenes	*BBK*	-26.67		-23.99	-25.71	-22.79	-23.77
benz(a)anthracene	*BAA*	-26.91	-26.90	-25.66	-23.66	-23.27	-22.65
chrysene	*CHR*	-26.85	-30.19	-27.26	-24.27	-25.59	-26.45
benzo(a)pyrene	*BAP*	-27.12		-25.21		-23.24	-23.62
internal standard	*9D*	-30.60	-32.52	-31.28	-30.69	-31.01	-29.49
internal standard	*10D*	-31.97			-31.29		-31.77
internal standard	*16D*	-26.63	-29.60	-28.71	-27.86	-29.58	-29.26
internal standard	*19D*	-27.04	-26.58	-26.81	-26.75	-27.06	-27.22
internal standard	*24D*	-26.00	-23.52	-25.04	-26.03	-25.63	-27.26
internal standard	*32D*	-29.35	-21.74	-26.59	-29.47	-30.78	-28.85
Batch		aug00	feb99	feb99	feb00	feb99	oct99

Table C-4 (cont.)
Stable Carbon Isotope Ratios ($\delta^{13}C$, ‰)

Compounds	**Code**	**T185**	**T192**	**T198**	**T199**	**T201**	**T202**
naphthalene	*NAP*		-21.1		-25.61		
2-methylnaphthalene	*2MN*	-22.74		-22.45	-25.60	-22.45	-22.97
1-methylnaphthalene	*1MN*	-22.42		-22.15	-24.81	-22.15	-22.33
acenaphthylene	*ACY*	-21.98	-21	-22.25	-24.99	-21.62	-21.97
fluorene	*FLU*	-22.59	-22.2	-23.12	-24.98	-22.66	-22.97
phenanthrene	*PHE*	-21.23	-22.3	-22.40	-25.19	-22.35	-21.48
anthracene	*ANT*	-21.22	-22.8	-22.52	-25.86	-22.66	-22.26
fluoranthene	*FLR*	-22.26	-23.8	-23.01	-24.66	-23.41	-22.82
pyrene	*PYR*	-22.44	-22.1	-22.98	-26.42	-22.54	-22.72
benzofluoranthenes	*BBK*	-22.51	-25			-25.00	-22.40
benz(a)anthracene	*BAA*	-21.30	-22.5	-21.97	-25.40	-22.24	-21.67
chrysene	*CHR*	-22.74	-24.7	-24.60	-27.62	-24.65	-23.32
benzo(a)pyrene	*BAP*	-23.74	-23.2	-23.68	-26.65	-23.44	-23.09
internal standard	*9D*	-30.27	-31.5	-29.88	-30.65	-30.69	-30.15
internal standard	*10D*	-31.93	-32	-31.85	-31.44	-31.92	-32.00
internal standard	*16D*	-28.27	-28.5	-28.76	-28.53	-28.63	-27.36
internal standard	*19D*	-26.32	-26.6	-26.77	-27.04	-26.68	-26.25
internal standard	*24D*	-24.43	-26.4	-25.84	-26.06	-26.12	-25.49
internal standard	*32D*	-28.65	-29.2	-28.75	-29.64	-28.98	-29.51
Batch		aug00	feb00	aug00	aug00	aug00	aug00

Table C-4 (cont.)
Stable Carbon Isotope Ratios ($\delta^{13}C$, ‰)

Compounds	**Code**	**T203**	**T204**	**T206**
naphthalene	*NAP*		-24.76	
2-methylnaphthalene	*2MN*	-23.4	-25.885	-24.42
1-methylnaphthalene	*1MN*	-22.65	-24.62	-24.73
acenaphthylene	*ACY*	-22.175	-24.305	-25.605
fluorene	*FLU*	-23.44	-23.71	-25.42
phenanthrene	*PHE*	-22.36	-23.28	-26.17
anthracene	*ANT*	-22.395	-23.205	-26.045
fluoranthene	*FLR*	-22.93	-23.475	-27.1
pyrene	*PYR*	-22.61	-23.445	-27.33
benzofluoranthenes	*BBK*	-23.43	-23.38	
benz(a)anthracene	*BAA*	-22.14	-22.415	-25.785
chrysene	*CHR*	-23.8	-23.83	-27.71
benzo(a)pyrene	*BAP*	-22.815	-23.79	
internal standard	*9D*	-30.46	-30.21	-30.355
internal standard	*10D*	-31.59	-31.44	-30.57
internal standard	*16D*	-28.095	-27.86	-27.265
internal standard	*19D*	-25.98	-25.95	-26.47
internal standard	*24D*	-25.19	-25.31	-25.73
internal standard	*32D*	-29.23	-29.23	-29.68
Batch		aug00	aug00	aug00

Targets:

MGP Site Management

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