**University Research Initiative**

# Characterization of Chronic Sources and Impacts of Tar along the Louisiana Coast

University Research Initiative

# Characterization of Chronic Sources and Impacts of Tar along the Louisiana Coast

Authors

Charles B. Henry, Jr.
Paulene O. Roberts
Edward B. Overton
Institute for Environmental Studies
Louisiana State University
Baton Rouge, Louisiana

October 1993

## DISCLAIMER

This report was prepared under contract between the Minerals Management Service (MMS) and Louisiana State University, Institute for Environmental Studies. This report has been reviewed by the MMS and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Service, nor does mention of trade names or commercial products constitute endorsement or recommendation for use. It is, however, exempt from review and compliance with MMS editorial standards.

## REPORT AVAILABILITY

Extra copies of the report may be obtained from the Public Information Unit (Mail Stop 5034) at the following address:

## CITATION

## ACKNOWLEDGMENTS

## FOREWARD

This study originated from surveys of the western Louisiana coast during the 1990 T/V *Mega Borg* oil spill which occurred off the Texas coast near Galveston. It was observed that a high density of tar balls and fresh oil patties littered the predicted landfall beaches which caused considerable confusion sorting out which oil was "background" and which was from the *Mega Borg* spill for both response and damage assessment activities. Four random samples of a "mystery" black oil at Holly Beach, Louisiana was collected and returned to Louisiana State University for source-fingerprint analysis. All four tar balls were nonmatches to the T/V *Mega Borg* and from unrelated spills. Oil sourced from the T/V *Mega Borg* was collected on Louisiana beaches, but this oil appeared as tiny reddish-brown tar balls and was difficult to spot when intermixed with the more abundant background oil. As a result of this observation, we became interested in the sources of the background tar. No studies of the abundance, distribution, and source of stranded oil along the Louisiana coast could be found, though reports for areas within the Gulf of Mexico such as Texas and the Caribbean were available. This report may well represent the first systematic study of tar ball deposition specific to Louisiana. While many comb the beaches of Louisiana collecting sea shells and curious objects that have drifted ashore, we spent much of 1992 walking beaches, collecting curious objects of tar, and applying detailed analytical chemistry to determine from where did they come.

# ABSTRACT

Along the southern coast of Louisiana, nine beach stations, covering an approximate distance of 200 miles between the farthest east and west stations, were selected for collection of deposited pelagic tar and oil during 1992. There existed an extreme difference in petroleum distribution, with 9.6 tar balls per 50 meter station in the east compared to 40 tar balls per station for the west. The samples collected from these stations were analyzed by detailed GC/MS and compared for similarities using a source-fingerprinting data synthesis process. The data indicate a wide range of petroleum sources with unweathered high paraffin and bimodal wax oils being the most abundant. These are generally associated with bunker oils and crude oil washings or sludge discharges and represent 26% of the tar balls analyzed. An assessment by detailed GC/MS characterization and source fingerprinting, utilizing selective ion monitoring (SIM) was completed for 124 of the 528 samples collected. The results indicated 18 sources with multiple occurrences and 47 unrelated sources of which 55% of the samples were sourced from the 18 multiple sources and 45% were from the unrelated sources. Ratio indexes were compiled and processed by principle component and cluster analysis algorithms to indicate or highlight the number of possible sources and the chemical characteristics of the petroleum found.

# TABLE OF CONTENTS

# LIST OF FIGURES

LIST OF FIGURES
(CONTINUED)

# LIST OF TABLES

# INTRODUCTION

*Background*

Chronic beach oiling is potentially degrading to the ecological and social economic interest of Louisiana. This preliminary study was designed to assess not only the abundance of tar balls which have been observed on Louisiana Beaches, but more specifically, their relationship to each other. Are the observed tar balls along the Louisiana coast the result of small unrelated activities? Or, are they connected? The focus of this study was the collection of preliminary data on coastal Louisiana tar ball abundance and distribution. A goal was to develop a combination of field and analytical methods for identifying chronic sources of coastal marine petroleum pollution which can aid in coastal resource management.

Why study tar balls? Their presence indicates that oil had been spilled or released during the recent past resulting in possible impacts to marine resources. It is generally accepted that oil pollution is a particular threat to immature marine animals, i.e., egg, larvae, and juvenile (RPI International, 1987). Exposure to oil pollution may have the following adverse effects: reduced growth rate, changes in normal physiology, and death. Many species of marine organism release epipelagic eggs and larvae which are at high risk to surface oil slicks. Petroleum contamination of Louisiana's coastal resources may result in additional anthropogenic stresses on already stressed commercial and sport fisheries. In addition, oil contamination on beaches detract from recreational uses such as sun bathing and surf fishing. Stranded oil and tar is a potential indicator of this unreported oil spillage.

Once oil is discharged into the marine environment it undergoes various physical and chemical interactions which include spreading, drifting, dispersion, evaporation, dissolution, emulsification, photochemical degradation, and biodegradation (Blumer et al. 1973; Butt et al. 1986; Mackay and McAuliffe, 1988.). These affects on bulk oil composition are collectively called weathering and may result in the formation of residual tar or tar balls. Factors which influence the formation of tar balls include the weather conditions, the environment, and most importantly, the type of oil. Light petroleum products and light crude oils such as many South Louisiana production oils spread rapidly and are often removed from the ocean surface by dispersion during high sea state conditions. The very heavy crude oils, refined heavy bunker oils, and other petroleum products with high pour points are slow to spread, exposing little surface area for the natural degradation processes. These heavier oils are the most persistent in the environment and often found stranded as lumps of tar. The formation of a stable water-in-oil emulsification may enhance the process of tar ball formation.

When spilled oil is weathered to the state of a tar ball, the oil is generally considered less acutely toxic than the fresh crude oil or the refined petroleum it was derived. This is due to the loss of the more water soluble mono- and di- aromatic

1

hydrocarbons (AH), such as benzenes and naphthalenes, by evaporation and dissolution processes. Yet, by the loss of these easily weathered components from the bulk oil, the remaining oil is actually enriched with the possibly carcinogenic and chronically toxic 3, 4, and 5 ring AH such as chrysene and benzo(a)pyrene. These toxic constituents of weathered tar residues are generally less available to marine animals unless ingested. Stranded oil and mousse is often washed on and off beaches by tides and storm currents. Weathered heavy oils are often "sticky-tacky" in nature and readily pick up extraneous beach material such as sand and shell fragments resulting in reduced tar ball buoyancy. When the density on the tar ball is greater than sea waters, the tar ball sinks and is transported to the benthic environment (Iliffe and Knap, 1979). Another physical process is the interactions with heavy seas and surf which tend to reduce the physical size of tar balls making them smaller, enhancing the natural rate of biodegradation but also creating sizes more easily ingested by marine species.

Studies in the gulf of Mexico have shown that endangered sea turtles have been affected (possibly killed) as a result of ingesting tar; the stomachs of dead sea turtles often contain tar balls or tar pellets (Carr, 1987). These concerns postponed the release of juvenile hawksbill sea turtles from the Nation Marine Fisheries Service facility in Galveston, Texas during the T/V *Mega Borg* oil spill due to fear that the year old turtles would feed on (ingest) the smaller tar balls resulting from the oil spill. This fear was due to the strong similarity between pellet food to the tar balls derived from the T/V *Mega Borg* spill.

The analytical methods used in this study were developed for source-fingerprinting spilled crude oil and refined petroleum products during oil spill response activities to determine if a spilled oil is compositional the same, and therefore, a positive match to a suspected or known source (e.g., a leaking tanker or pipeline). The fundamental aspects of the analytical methods used are widely accepted in the scientific literature and have been used in our laboratory for both oil spill response activities and fate and effects studies. The match-nonmatch determinations are generally derived from quantitative comparisons of the chromatographic profiles of specific AH and petroleum biomarker compounds such as the steranes and hopanes as well as indexes derived from specific compound ratios and index cluster plots. In this study, data synthesis was augmented with statistical cluster and principal component analyses in an attempt to develop statistical approaches to aid in identification of related tar balls.

*Reported Abundance, Distribution, and Sources of Tar Balls*

Scientific publications reporting the abundance and distribution of tar balls on beaches along the northern Gulf Coast appears limited. Currently, this data is the only information specific to Louisiana. Numerous studies were conducted by Texas A&M University during the 1970's, but referenced as project reports and not easily acquired. The only published data reviewed on Texas beaches reported only the characterization of sources, not abundance values. The studies in Texas suggest

2

three primary sources or types of oil found on the beaches: weathered crude oil, 55.3%; tanker sludge, 33.3%; and fuel oil residues, 7.6% (Geyer, 1980). The source information is of specific interest to this study. Current or historical abundance and distribution information for the northern Gulf of Mexico area is needed for a regional comparison to Louisiana beaches. Some evidence has been reported that suggest 10-50% of the tar observed in the eastern Gulf of Mexico waters off Florida is sourced from tar balls which have entered the northern Gulf of Mexico through the Yucatan Straits and the Gulf Loop Current (Van Vleet et al. 1984).

Scientific publications on the abundance of tar balls in the Caribbean region from the 1970's to present was readily available (Sleeter et al. 1976; Georges and Oostdam, 1983; Burton, 1987; Botello et al. 1991; Jones and Bacon, 1990; Lizarraga-Partida et al. 1990). A major study in the 'Wider Caribbean' region, which includes the Gulf of Mexico, assessed the abundance and distribution of tar balls and was supported by the Intergovernmental Oceanographic Commission's Regional Subcommission for the Caribbean and Adjacent Regions. Greater than 9000 data points between 1979 and 1987 were collected for this study in an effort to assess tar on beaches, pelagic tar, and dissolved/dispersed hydrocarbons (Atwood et al. 1987). From these surveys, beaches that contain concentrations of tar approaching 100 g/m were considered unusable for tourist purposes. A wide range of values have been reported in the Caribbean with many beaches exceeding the 100 g/m mark. It was estimated that as much as 50% of the oiling was derived from tank cleaning and ballast discharge within the region; additional inputs were suspected to be derived from outside sources transported into the region through the North Atlantic gyre system.

Outside the Gulf of Mexico, other studies within the U.S. have provided some tar ball abundance data for the Atlantic coast and California but the majority of these studies were conducted in the early 1970's. International interest in tar ball beach pollution has been continuous since 1970's, providing more recent data. Bermuda has received a great deal of study over the last 20 years (Morris, 1971; Sleeter et al. 1974; Iliffe and Knap, 1979; Knap et al. 1980; Smith and Knap, 1985) providing quantitative surveys of beach tars. One study (Knap et al. 1980) has shown a decline in the abundance of beached tar which roughly corresponds to decreases in marine discharges from improved tanker operations during this period. Quantitative tar ball studies in Oman have reported some of the highest values in the world; 'standing stocks' of tar balls were found between 5 and 2325 g/m along its coastline (Burns et al. 1982). Tar ball studies in Nigeria suggest that most of the oiling is a result of drilling operations and oil tanker terminal operations (Asuquo, 1991). Open ocean studies for pelagic tar ball distribution in the Pacific suggested that, like many beach surveys, tanker traffic and specifically tanker sludge discharges are the primary source of tar balls (Wong et al. 1976).

The occurrence of tar on beaches is not new. Natural sources of oil such as riverine and ocean seeps have been releasing petroleum into the marine environment for millions of years; it would not be unreasonable to suspect that a fraction of this seep oil is being transported to and deposited on coastal shorelines. The amount of oil

released to the ocean has unquestionably increased as a result of anthropogenic activities such as petroleum transportation and on and offshore oil exploration/production. No baseline study, to our knowledge, has been completed that would aid in estimating what the concentration of tar was prior to the contribution from man's activities; therefore, any data gathered at this point in time must be considered as a contribution from both <u>natural</u> and <u>anthropogenic</u> activities. This report documents information gathered as part of a preliminary assessment of the abundance, distribution, and sources of stranded tar balls along the Louisiana coast. The initial field studies began on 21 March, 1992 and were completed on 29 September, 1992.


## METHODOLOGY

This study involved both a field and laboratory component. The study area was restricted to beaches along the Louisiana coast. All of the analytical analyses were conducted at the Institute for Environmental Studies (IES) at Louisiana State University.

*Site Selections*

Prior to site selection, Parish maps, NOAA coastal charts, USGS topographical maps, pervious research on beach trash collection and coastal residents were consulted. The following criteria was used in site selection: 1) easy access, 2) relatively unpopulated area, 3) low beach maintenance by human activities. Several beach surveys or beach walks were conducted to ground-truth sites for potential selection. In the end, 9 sites were selected: 6 along the western and 3 along the east/central Louisiana coastline. For ease of identification, the study regions are defined simply as east and west. The west sites were located from Martin's Beach to Rockerfeller Refuge. The east sites were located at Pass Fourchon to Grand Isle. The majority of the beaches were within a short walking distance from maintained roads, with the one exception being Rockerfeller Refuge (RR) which was located within the Rockerfeller Wildlife Refuge in Cameron Parish and accessible only after a 3 mile hike along the levee. The 5 remaining west sites were: Rutherford Beach (RB), Holly Beach (HB), Old Pavillion (OP) along highway 82, Constance Beach (CB), and Martin's Beach (MB). The 3 east sites are Grand Isle (GI), Elmer's Island (EI), and Pass Fourchon (PF). Figure 1 identifies the general locations of the selected sites. The distance between the west sites, from Martin's Beach to Holly Beach was 13 miles. Beginning from Martin's Beach, at mile 14 marker of highway 82, Constance beach station was approximately 6 miles distant, Old Pavilion was 11 miles, and Holly Beach was 13 miles.

The stations were semi-randomly selected within each study site. A fixed marker, either natural or manmade, was used as a site landmark. From this landmark, the station distance and direction (east or west from the landmark) was randomly selected.

4

# Louisiana Coastline Stations
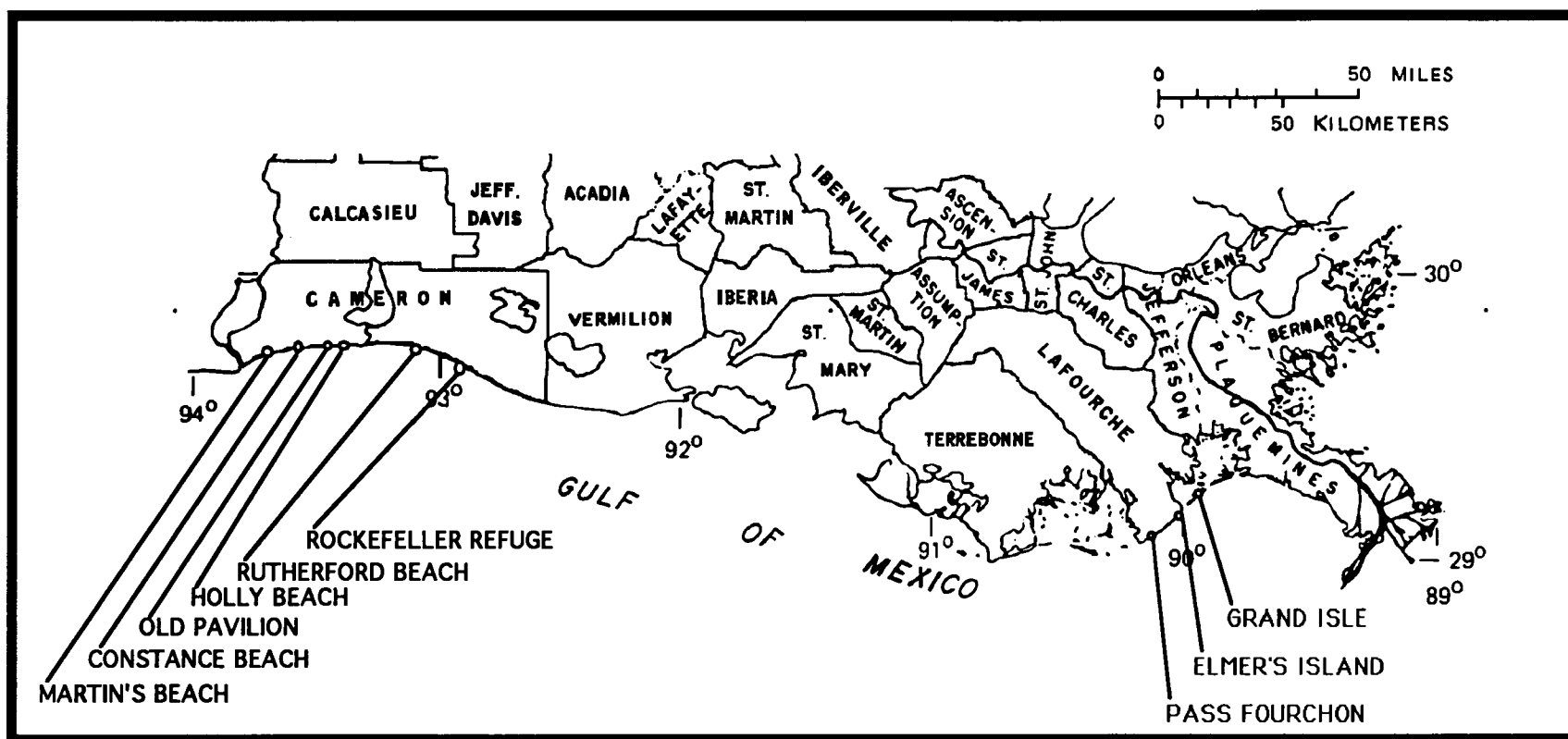


Figure 1. Station locations for stranded oil and tar survey, 1992

Once selected, the station was marked in the northeast and northwest corners by flagged stakes and the distance from the landmark was recorded. All stations were a 50 meter-wide swath perpendicular to the shoreline which extended to the upper beach storm berm or beach stabilizing material, such as rip-rap and sand bags. The station widths ranged from 10 to 75 meters. Each station was further subdivided during sampling into backshore and foreshore regions; the backshore region is defined as the area behind any recent tidal debris lines including the storm berm area, while the foreshore area included the high tide debris line down to the waters edge. Photographs were taken of each site and of any interesting findings, and are archived at IES.

*Field Surveys and Sample Collection*

Tar ball collection was performed by systematically walking each station, collecting all tar balls which were greater than a few millimeters in size, and wrapping each individually in aluminum foil. Sampling was performed only during low tide or falling tidal conditions. Pits were dug between the high and low tide lines to document and collect any subsurface oiling found. All samples were stored in coolers while in the field. Upon return to IES, each sample was logged into the laboratory and given a unique identification number followed by refrigeration storage until morphological descriptions and GC/MS analyses were completed. The sampling was conducted during two seasonal periods. The two sampling periods were at the beginning of Spring and the end of Summer. The Spring sampling began on 21 March, 1992 and was completed on 1 May, 1992. The end of Summer sampling began on 24 August, 1992 and was completed on 29 September, 1992.

*Morphological Characterization*

Visual descriptions and physical characterization were made for each sample collected. Morphological characterizations included: color, extraneous material, texture, pliability, core hardness, diameter, and individual tar ball weight measurements. The color categories determined were black, brown, dark gray, dark green, amber, and dark red. Extraneous materials were classified as a percentage of organic, sand, and shell by visual appearance only. Occasionally, other materials such as plastics, feathers, and hypodermic needles were found incorporated in the tar balls and noted. The pliability classification was judged and ranked from 0 to 5 by the extent the tar ball would bend when manual pressure was applied. A value of 0 represents tar ball that was solid and without any pliability, while 5 indicated that no force beyond gravity was required for the material to bend or flow at ambient laboratory temperature. This pliability characteristic can be related to some degree to the residual oil's pour-point and provide insight to the extent of weathering. Each tar ball was cut in half to determine core hardness. The classifications were soft (beads of fresh oil), medium (past-like), and hard. All these descriptions were used to develop a general classification of the oil and to determine the gross amount of oil found at each station.

*Gas Chromatography/Mass Spectrometry Analyses*

The GC/MS analysis provides highly selective source-fingerprinting information as well as compound specific quantitative results for specific aromatic hydrocarbons that are potential sources of stress to shoreline communities. Fingerprinting is a term used to describe the analytical process of characterizing a petroleum sample and comparing the results to a known crude oil or petroleum product to determine if the sample is characteristically the same and, therefore, possibly from the same source. These target compounds utilized are also useful for monitoring oil weathering and biodegradation. Petrogenic (oil or petroleum derived) and pyrogenic (combustion derived) AH are monitored as well as alkanes, sulfur heterocycles, sterane, triterpanes, and hopanes. Table 1 identifies the 43 components (either individual compounds or isomer groups) and the primary ion monitored for each.

Mass spectrometry has long been used by many researchers to detect the presence of oil and to study oil weathering processes, such as evaporative loss, photolytic and biological degradation, and fate of oil spilled into the environment (Overton et al. 1980; Kennicutt, 1988; Michel et al. 1991; Henry and Overton, 1993b; and many others). Information derived from published papers, in addition to years of actual experience analyzing and interpreting oil contaminated samples in support of oil spill response activities with NOAA, supports GC/MS as currently the most powerful tool for detailed chemical analysis of crude oil and refined products. Crude oil is a very complex mixture of compounds that cannot be completely resolved by gas chromatography, but by using a highly selective detector such as a mass spectrometer in conjunction with a high resolution chemical separation system (the GC), we are able to discriminate specific target compounds from the bulk oil. Typically for crude oils, the target AH represent less than 2% of the bulk oil composition by weight, and many of the target analytes are present at the low ppm level in whole oil. Detailed chemical analyses of oil and proper interpretation of the derived data is not a trivial task. The method was designed to accomplish the following tasks, detect the presence of oil, compositional analysis, compound specific quantification, and source-fingerprinting.

The interpretation of the data produced requires a high degree of knowledge in practical GC/MS, petroleum chemistry, and environmental chemistry. Many of the compounds of interest have no standards commercially available and identification is often based on extensive qualitative MS analyses that occurred during the method development process. These selected compounds were determined to provide the most useful information and could not be replaced by other compounds with standards. The majority of these target constituents exist as complex mixtures of isomers such as the C-3 alkylated phenanthrenes which are quantified as a single component by this approach.

Table 1.  Target compounds for qualitative and semi-quantitative assessment of tar ball samples by GC/MS.

| compound | quant.. ion |
|---|---|
| alkanes (nC-10 thru nC-31) | 85 |
| decalin* | 138 |
| A- decalin | 152 |
| B- decalin | 166 |
| C- decalin | 180 |
| naphthalene | 128 |
| D- naphthalenes | 142 |
| E- naphthalenes | 156 |
| F- naphthalenes | 170 |
| G- naphthalenes | 184 |
| fluorene | 166 |
| H- fluorenes | 180 |
| I- fluorenes | 194 |
| J- fluorenes | 208 |
| dibenzothiophene | 184 |
| K- dibenzothiophenes | 198 |
| L- dibenzothiophenes | 212 |
| M- dibenzothiophenes | 226 |
| phenanthrene | 178 |
| N- phenanthrenes | 192 |
| O- phenanthrenes | 206 |
| P- phenanthrenes | 220 |
| naphthobenzothiophene | 234 |
| Q- naphthobenzothiophenes | 248 |
| R- naphthobenzothiophenes | 262 |
| S- naphthobenzothiophenes | 276 |
| fluoranthrene/pyrene | 202 |
| T- pyrenes | 216 |
| U- pyrenes | 230 |
| chrysene | 228 |
| V- chrysenes | 242 |
| W- chrysenes | 256 |
| hopanes (191 family)* | 191 |
| sterenes (217 family)* | 217 |
| benzo(b)fluoranthene | 252 |
| benzo(k)fluoranthene | 252 |
| benzo(e)pyrene | 252 |
| benzo(a)pyrene | 252 |
| perylene | 252 |
| indeno(g,h,i)pyrene | 276 |
| dibenzo(a,h)anthracene | 278 |
| benzo(1,2,3-cd)perylene | 276 |

* Used primarily for source-fingerprinting and generally not quantified.
All of the above chromatographic profiles are used for source-fingerprinting in addition to indexes derived from the quantitative data.

8

In preparation for analysis, tar ball samples were split open to expose the fresher oil beneath the exterior, and 0.2 to 0.5 g of this less weathered oil was taken for extraction. One to two grams of sodium sulfate was added, followed by 8 mL of hexane. The vial was then sealed and sonnicated for ten minutes and stored for 8 to 24 hours to allow the asphaltenes/residuum to fall from suspension. Prior to analysis, the prepared tar ball extracts were spiked with internal standards and injected by a Hewlett-Packard 7673A auto-sampler into a Hewlett Packard 5890 GC. This instrument was configured with a DB-5 high resolution capillary column directly interfaced to a Hewlett Packard 5971 MS. The GC flow rates, etc. were optimized to provide the required degree of separation (i.e., phytane and n-C18 should be baseline resolved and pristane and n-C17 should be near baseline resolved). The GC was operated in the temperature program mode with an initial column temperature of 55° C for 3 min. then increased to 290° C at a rate of 5° C/min. and held at the upper temperature for 15 min. The injection temperature was set to 250° C and only high-temp, low thermal bleed septa were used. The interface to the MS was maintained at 290° C. All gasses used were of the highest purity available.

The MS was operated in the Multiple Ion Detection mode (MID) to maximize the detection of several trace constituents in crude oil. The instrument was operated such that the selected ions for each acquisition window are scanned at a rate greater than 1.5 scans/sec. At the start of an analysis period, the MS was tuned to PFTBA. A daily quantification standard and a reference oil (North Slope Crude Oil from the T/V *Exxon Valdez*) was analyzed prior to analysis of the extracted tar balls. An internal standard mix composed of naphthalene-d8, anthracene-d10, chrysene-d12, and perylene-d12 was coinjected with each analysis to monitor the instruments performance during each run.

The data was processed and interpreted at several levels. First, a comparison of the extracted ion chromatographic profiles determines if any of the samples containing oil appear to be related. This process compares the relative composition and extent of weathering for each sample analyzed, providing a detailed interpretation of the alkylated PNAs series, sterane, and triterpane distribution patterns. In this study all tar ball samples analyzed by GC/MS were initially compared within their sampling period; the Spring samples compared to the Spring population analyzed and the Summer samples compared the Summer population. After completion of source-fingerprinting by sampling period, all analyzed samples were compared as a total population for a total number of sources. The second level of interpretation was a comparison of source-fingerprint indexes, or ratios to determine possible source correlation.

# RESULTS AND DISCUSSION

As expected, we did find tar balls along the Louisiana coast. A total of 528 samples of stranded oil and tar was collected within the two sampling periods for the nine study stations (considerably more than expected). This section has been subdivided into field observations and laboratory results. The field observations describe when the field activities occurred, the abundance and distribution of tar balls observed, their morphological appearance, and any interesting observations made during the beach surveys. The laboratory information presents the source classification of the tar balls collected, source-correlations, synthesized GC/MS results, index cluster plots, and statistical analysis.

*Field Results*

The initial beach surveys were intended to identify study stations and were completed by 2 April, 1992. The first round of sampling was completed by 1 May, 1992; these samples are identified as the Spring samples. Station RR was sampled twice on 22 March and 1 May, 1992; 6 tar ball samples were collected in March compared to 14 in May, yet only May data was included in the abundance and distribution comparisons. The RR station was the first created and therefore the learning station to calibrate the sampler's eyes for spotting partially buried tar balls. The end of Summer sampling period was complicated by the occurrence of Hurricane Andrew on 24 August, 1992. Andrew struck the Louisiana coast near the Atchafalaya Delta, destroying many natural and manmade landmarks. The western stations MB, CB, OP, HB were sampled before the hurricane on 23 and 24 August; the remaining western stations RB and RR were sampled three weeks after the storm along with the eastern stations EI and GI. The PF station was inaccessible after the hurricane due to bridge and road damage. No Summer samples were collected at PF. A second Summer sample was collected approximately one month after hurricane Andrew at station MB on 29 September, as a qualitative observation to determine if the tar ball deposition rates were similar to prestorm values; 58 tar balls were collected in August and 30 were collected in September. The September samples were included in this study for general information only and were not used in the abundance and distribution calculations. All sampling was completed by 29 September, 1992.

Tar Ball Numbers and Distribution. The sampling results suggest no significant difference between the Spring and Summer sampling periods. A total of 275 samples were collected during the Spring sampling and 253 were collected for the Summer. The abundance of tar balls collected between the east and west stations was significant. A total of 480 samples were collected in the west compared to 48 in the east. This can be expressed as 40 tar balls/station in the west compared to 9.6 tar balls/station in the east for the total number of 528 samples collected in 1992. Table 2 provides a summary of the number of tar samples collected by station, collection period, and beach zone. Between the backshore and foreshore beach zones, there

10

were more tar balls collected in the upper beach region than the lower with 18.8 backshore tar balls/station compared to 12.2 foreshore tar balls/station. This can be attributed to tar balls stranded in the supra-tidal zone during storm events and extreme high tides and storm events and becoming stranded in the supra-tidal zone. The lower volume of foreshore tar balls is due in part to their being frequently removed by normal tidal activity.

The total number of tar balls found at each station indicates a distinct trend of deposition along the Louisiana shoreline. The number of samples collected between the Spring and Fall sampling periods indicates a shift in the stations with the most abundant tar balls, but since the number of samplings was only two, these differences are not considered statistical. From the Spring sampling data, it appears that the distribution of stranded tar balls was more abundant towards the western most stations. The Summer sampling data were also biased toward the west stations, but distribution was apparently more random.

Table 2.    Total tar ball accumulation comparison per beach station and region.

|  | Spring Sampling | | Summer Sampling | |
|  | Backshore | Foreshore | Backshore | Foreshore |
|---|---|---|---|---|
| West Stations | | | | |
| MB | 57 | 39 | 45 | 13 |
| CB | 41 | 11 | 16 | 4 |
| OP | 13 | 39 | 50 | 29 |
| HB | 15 | 10 | 14 | 15 |
| RB | 3 | 6 | 4 | 4 |
| RR | 10 | 4 | 25 | 13 |
| Totals | 139 | 109 | 154 | 78 |
| | | | | |
| East Stations | | | | |
| PF | 14 | 4 | Not Sampled | Not Sampled |
| EI | 2 | 3 | 0 | 3 |
| GI | 3 | 1 | 8 | 10 |
| Totals | 19 | 8 | 8 | 13 |
| | | | | |
| Sampling Total | 158 | 117 | 162 | 91 |

Morphological Appearance. The tar balls collected ranged in size from one mm in diameter to 300 mm. A wide gradation of colors were observed and each tar ball was classified as black, brown, dark grey, dark green, amber (yellow to yellow/brown), and dark red. Greater than 80% of the tar balls collected were black in appearance as shown by the histogram plot in Figure 2. Brown was the next significant color and represented approximately 10% of the samples. The remaining colors were less than

5% of the total. Color often suggests an oil type. Many of the dark green and amber tar balls appeared to be old globs of a heavy grease or lube oil. The pitch black lumps of oil appear to be sourced either from high pour-point bunker oils or other refined products derived from heavy petroleum residuum. Brown tar balls often suggest oil which has been oxidized and moussed during the weathering process; often these represent spilled crude oils.

Many of the samples collected contained extraneous matter including organic debris (plant stems, seeds, seaweed, etc.), sand, and shell fragments. These observations are not unusual. Sticky-tacky oil floating on the water's surface and repeated strandings often result in the accumulation of organic debris and beach substrate. The potential for extraneous material to become incorporated in the tar ball is a function of physical weathering processes as well as the physical/chemical composition of the spilled oil. Very high pour-point oils do not easily spread and are limited to surface encrustations only. Figures 3, 4, and 5 present the relative contribution of organic matter, sand and shell fragments to the entire tar ball population studied. Organic debris is a very ubiquitous feature in the marine environment, as both pelagic material and through beach erosion, but not frequently found within the samples. Sand was the most predominant extraneous material encountered and was found in greater than 80% of the tar balls collected. These percentage values represent qualitative assessments only. Shell was not as frequently found as sand which is consistent with the distribution of beach substrates; sandy beaches are more numerous than shell beaches along the northern Gulf of Mexico. Of our selected study stations, only RR had a high percentage of shell fragments associated with the beach substrate.
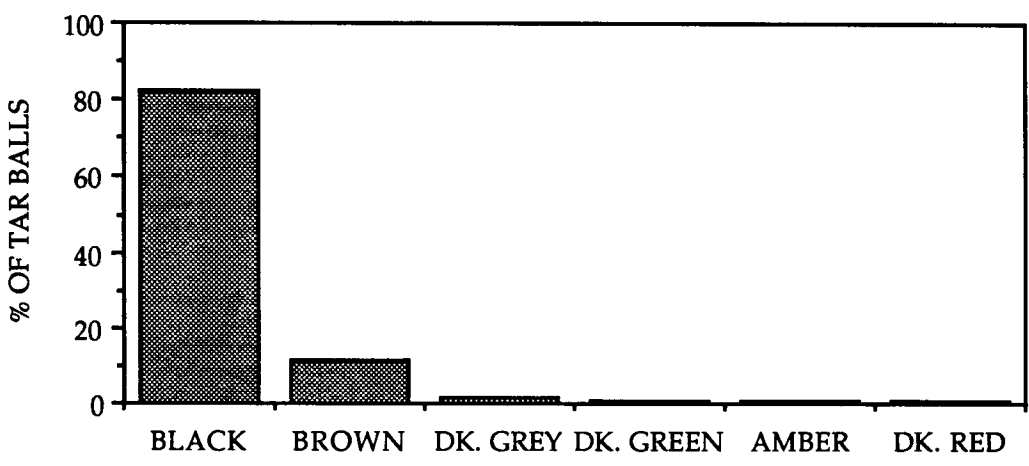


Figure 2.    Histogram plot showing the distribution of tar balls as classified by color.

Each tar ball was also characterized for its pliability. Pliability is generally associated with the physical/chemical composition of the spilled oil and the extent of

weathering which has occurred. Highly weathered tar balls tend to become nonpliable, often brittle or very difficult to break. These pliability characterizations were qualitative only. Each sample collected was rated from 0 to 5; a rating score of 0 is nonplaible and nonbreakable using normal hand pressure while a score of 5 represents stranded tar that was almost fluid. A majority of the tar balls sampled were ranked as 3, representative of tar pieces that can bend without breaking. Less than 10% of the samples collected were either nonpliable or very fluid.
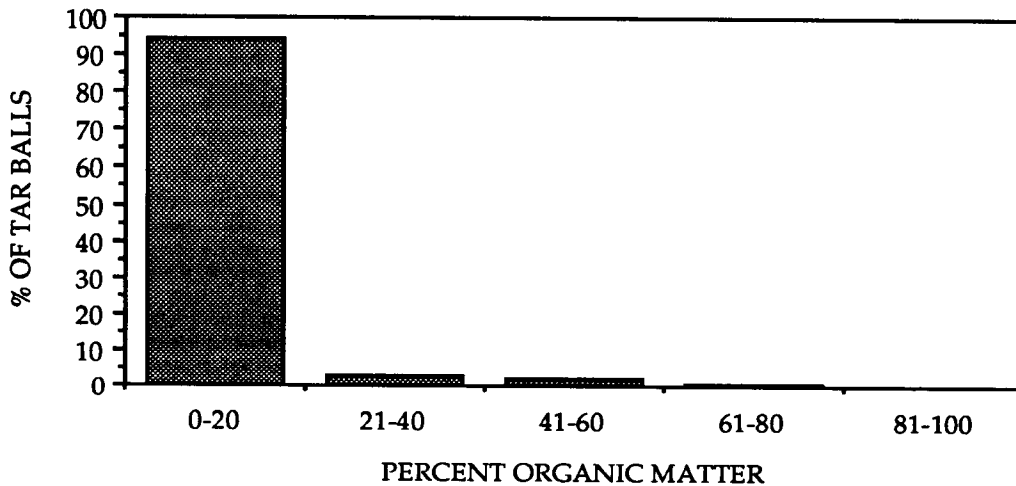
Figure 3.    Histogram presentation of the contribution of organic matter to the tar balls sampled.
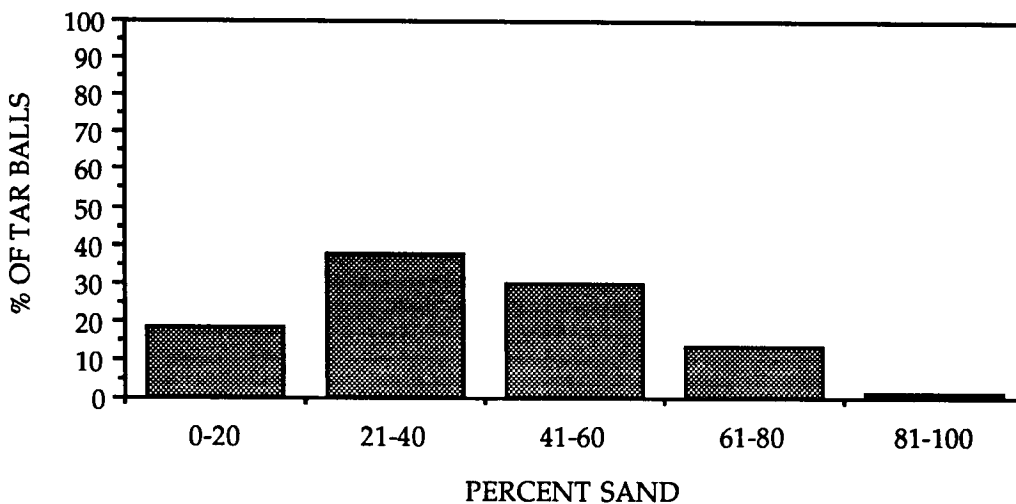
Figure 4.    Histogram presentation of the contribution of sand to the tar balls sampled.

13
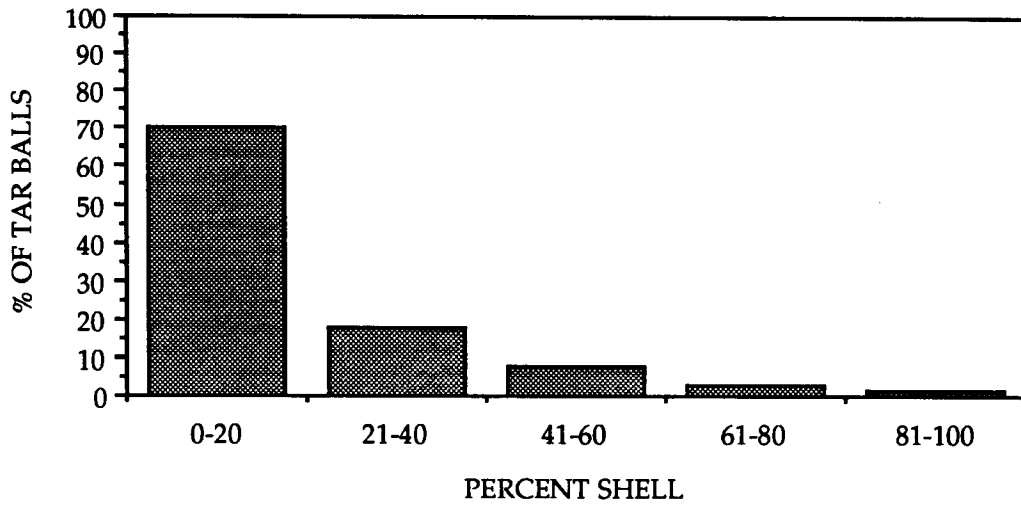
Figure 5.     Histogram presentation of the contribution of shell fragments to the tar
              ball sampled.
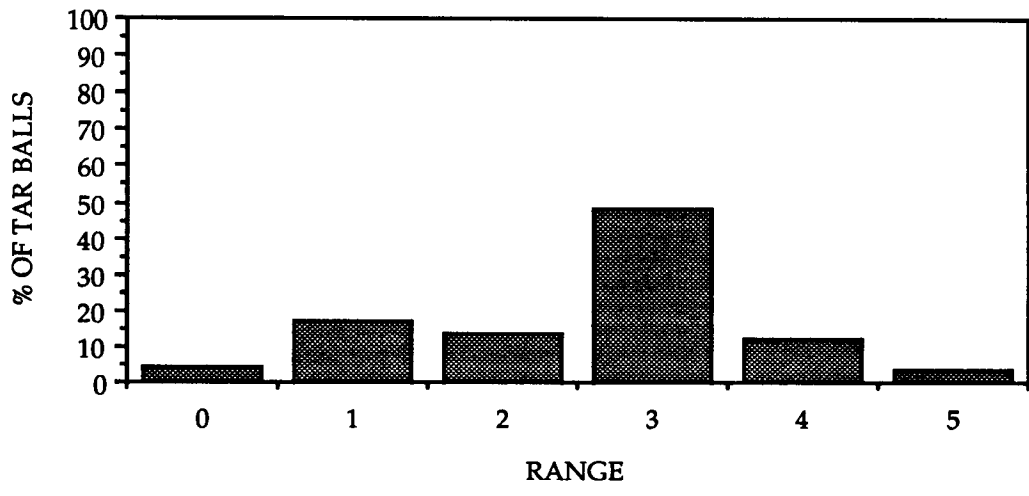


Figure 6.     Histogram presentation of tar ball pliability. Pliability was rated from 0
              to 5; 0 is a hard, nonpliable piece of tar and a score of 5 is stranded tar
              that is almost fluid oil. Most of the tar balls were classified as 3, or
              easily bent under slight hand pressure.

14

Abundance and Distribution. The weight distribution is a function of the amount of oil and the amount of adsorbed material. As indicated by the morphological characterizations, numerous samples contained sand and other extraneous debris. The percentage of weight contributed from debris (not oil) could possibly account for 50% of the weight of some samples. It is practically impossible to remove these included materials; therefore, the weight values presented are over estimations of the true values.

A similar trend was observed in the total tar ball weight collected between the west and east stations that was noted for total number of tar balls. A total of 4416.42 g were collected in west compared to 627.65 g in the east during the Spring, 1992 sampling period, or 736.07 g/station in the west compared to 209.22 g/station in the east. A similar trend was observed during the Summer, 1992; 4573.6 g in the west compared to 125.2 g collected in the east, or 762.27 g/station and 62.60 g/station, respectively. MB and OP consistently showed the highest abundance of tar by weight while EI and GI consistently showed the lowest abundance of tar by weight. Figure 7 shows a histogram comparison of the abundance and distribution of the tar collected during the Spring and Summer, 1992.

*Analytical Chemistry Results*

A higher number of tar balls were collected than originally anticipated. The study plan proposed to analyze 100 tar balls. In a random selection process, 122 tar ball samples were selected for GC/MS source-fingerprint analysis. Of these 122 samples analyzed by GC/MS, 4 samples were unsuitable for source-fingerprint characterization due to the apparent lack of target constituents. The GC/MS data for each of the remaining 118 samples were classified as to the type of oil residue, source-fingerprinted to differentiate the number of sources represented, treated by cluster plot analysis and statistical analyses.

Source Classification. The classification scheme presented in this study utilized the GC/MS data to characterize the oil present in each sample. Chromatographic data was qualitatively interpreted and classified as follows:

1) Relatively unweathered, high aromatic. Oils classified into this category were identified by a nC-18/phytane ratio of greater than 1 and were highly enriched with target AHs. Oils in this classification are often representative of slightly weathered refined blended heavy fuel oils.

2) Relatively unweathered, high paraffin. Oils classified into this category were identified by a nC-18/phytane ratio of greater than 1 and were enriched with normal paraffins between nC-15 and nC-33 often with the most abundant normal paraffin being nC-19. Oils in this classification have high pour-points and many may be representative of heavy fuel oils.

15
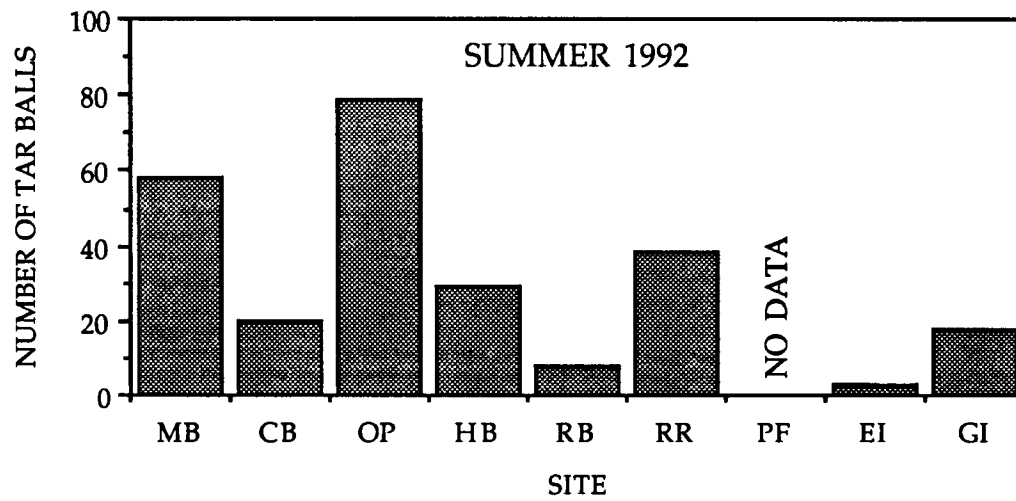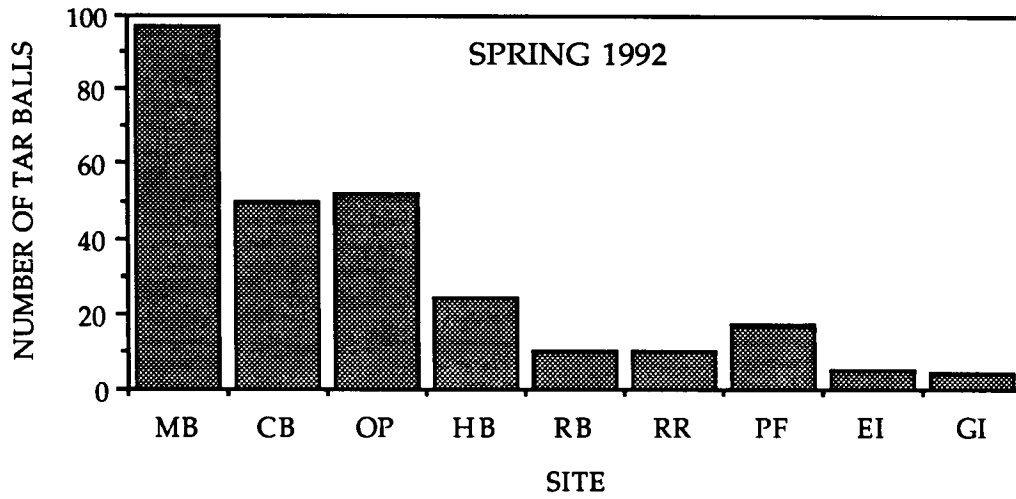
Figure 7. Number of tar balls collected per station by sampling period.
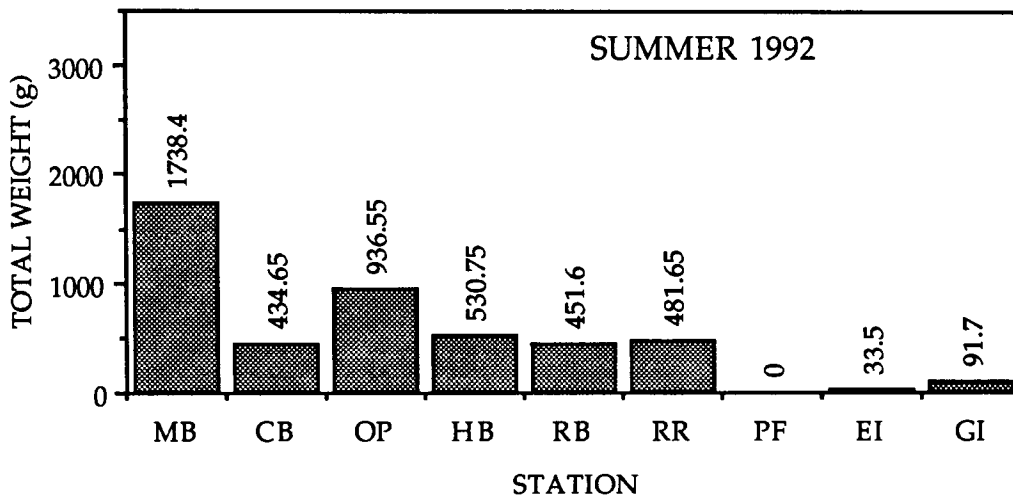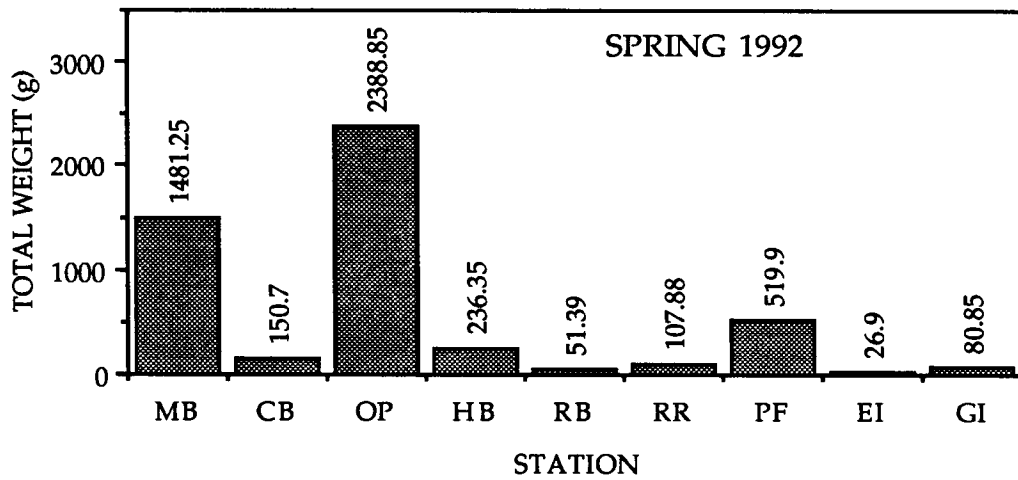
Figure 8.    Comparison of the tar abundance in grams/station by sampling period.

3) Relatively unweathered, bimodal-wax. These tar balls are characterized by a nC-18/phytane ratio greater than 1 and a bimodal distribution of normal alkanes with a pronounced wax component from nC-21 extending to nC-37. Often nC-29 was the most abundant normal alkane. These oils are believed to be representative of crude oil and heavy fuel oil tank washings or sludge discharges.

4) Weathered, high aromatic. Oils classified into this category were identified by a nC-18/phytane ratio of less than 1 and were highly enriched with target AHs. Oils in this classification are often representative of weathered refined heavy fuel oils and some highly weathered crude oils.

5) Weathered, high paraffin. Oils classified into this category were identified by a nC-18/phytane ratio of less than 1 and were enriched with normal paraffins between nC-15 and nC-33. Oils in this classification have high pour-points and many may be derived from heavy, high pour-point fuel oils.

6) Weathered, bimodal unresolved complex mixture (UCM). These tar balls are characterized by a nC-18/phytane ratio less than 1 and a bimodal distribution of the UCM. Oils in this classification are often weathered crude oils.

7) Weathered, bimodal wax. These tar balls are characterized by a nC-18/phytane ratio less than 1 and a bimodal distribution of normal alkanes with a pronounced nC-21 extending to nC-37 wax component; often nC-29 is the most abundant normal alkane detected. These oils are believed to be representative of crude oil and fuel oil tank washing and sludge discharges as noted from the unweathered, bimodal wax.

8) Weathered, bimodal UCM, and wax (trimodal). Oils classified as trimodal are essentially weathered oils characterized by a bimodal UCM with an added heavy wax component. These oils are believed to be representative of crude oil and fuel oil tank washing or sludge discharges.

9) Unclassifiable. Oils that did not fit any of the above classifications. Generally, these oils were so heavily weathered that they could not be classified with any confidence.


Figures 9 and 10 show chromatographic ion plots of oils typically classified as weathered high aromatic, unweathered paraffinic, weathered bimodal UCM, and weathered bimodal wax. Table 3 provides a summary of the GC/MS tar ball classifications for the samples analyzed in the 1992 collection. The most common classification identified was the relatively unweathered, high paraffin which represented 32% of the samples analyzed. The weathered high paraffin samples represented only 2% of the total which is consistent with our assumption that these are high pour-point refined oils which tend to biodegrade relatively slowly. A total

18

of 26% of the samples analyzed contained the bimodal wax component that is generally believed to be related to crude oil tanker washing or sludge discharges resulting from cleaning waxy residues from the sides of storage tanks or cargo holds (Butler et al. 1973). Cleaning bunker fuel tanks and fuel lines may also result in a similar wax signature.

Table 3. Classification comparison for total sample population analyzed.

| | No. of Samples* | % of Total |
|---|---|---|
| Relatively unweathered: | | |
| high aromatic | 6 | 5 |
| high paraffin | 38 | 32 |
| bimodal wax | 7 | 6 |
| | | |
| Weathered: | | |
| high aromatic | 17 | 14 |
| high paraffin | 2 | 2 |
| bimodal UCM | 2 | 2 |
| bimodal wax | 20 | 17 |
| bimodal UCM and wax | 3 | 3 |
| | | |
| Unclassifiable | 23 | 19 |

*n=118
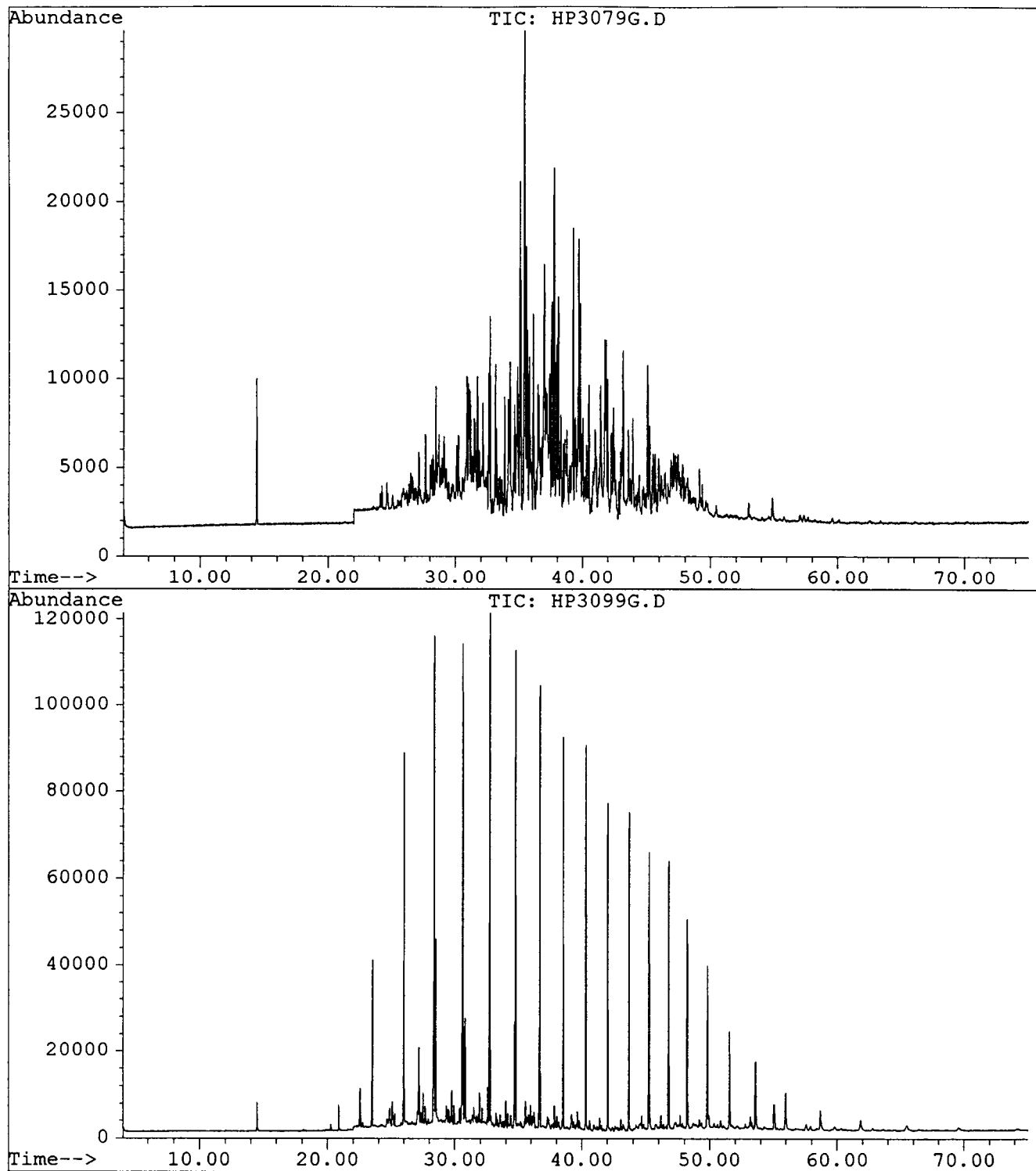
Figure 9.    TIC comparisons from samples classified as a high aromatic (top)
to an unweathered paraffinic oil (bottom).
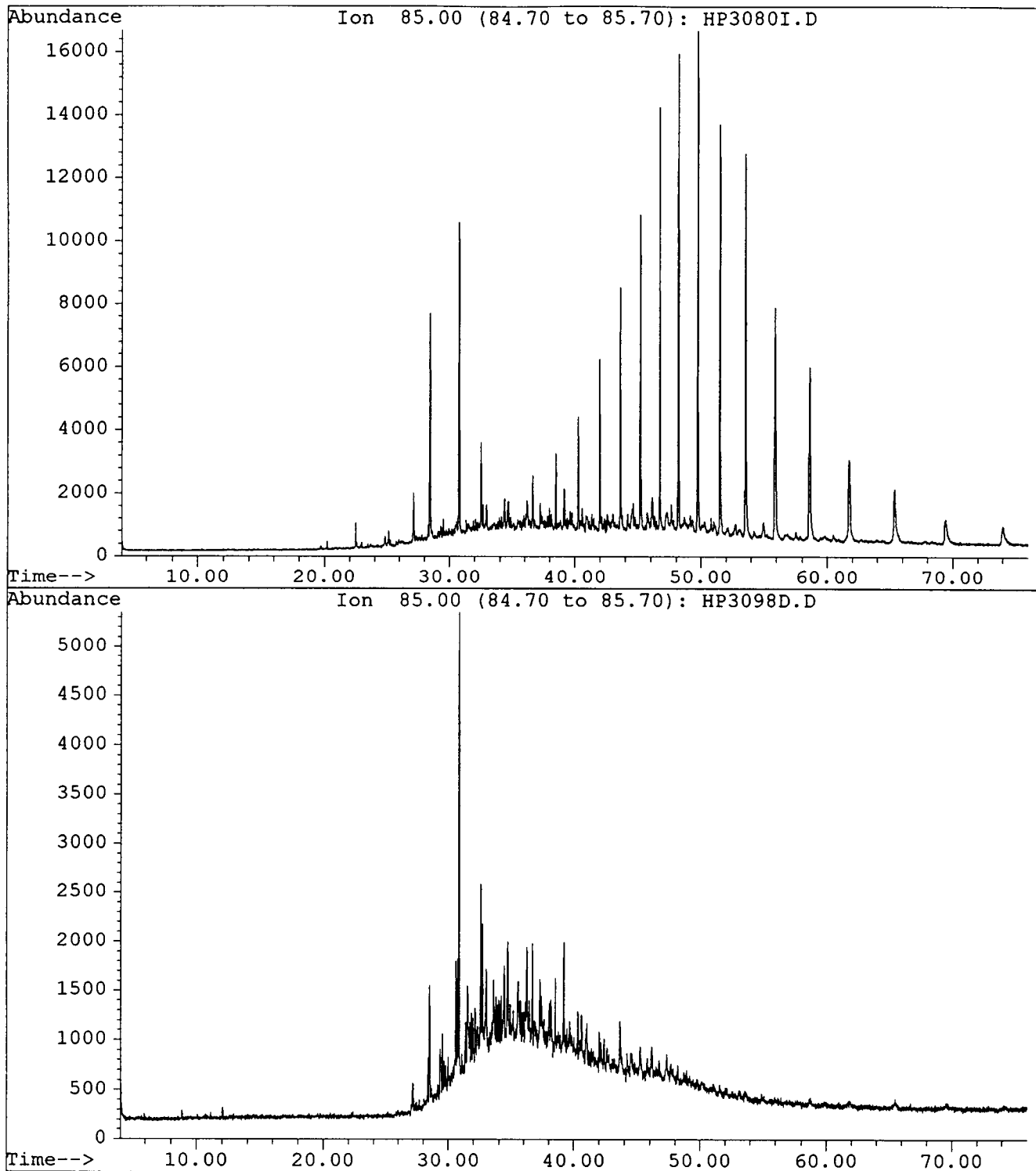
Figure 10.    Comparison of the (m/e) 85 chromatographic profile for oils
classified as weathered bimodal wax (top) and weathered
bimodal UCM (bottom).

21

Source-fingerprinting. The data derived from all 118 individual samples were compared to each other by an exhaustive matrix comparison process which utilized all the chromatographic data and provided separation of the tar balls analyzed by source. This comparison involved visual scrutinization of each ion pattern for all ions analyzed. Through this manual process and previous experience, certain components within the sources where shown to be quite unique and descriptive which lead to a selection of compositional indexes for cluster plot analyses. These relative comparisons were composed of ratios between components such as the alkylated dibenzothiophenes and alkylated phenanthrenes. Each source was assigned an alphabetical identification such as Source A and Source B. The comparisons were completed for each sampling period independently followed by a total sample comparison for a final source assessment.

Source-fingerprinting of the 65 Spring samples analyzed identified 37 different sources; 8 of which were represented by multiple samples of the same oil source and often distributed at different stations. From the 53 Summer samples analyzed, 33 sources were identified; 9 of which were represented by multiple samples of the same source oil. The number of samples identified from an individual source ranged from 1 to 8. When the two sample sets were compared to each other, 5 sources were observed in both the Spring and Summer 1992 samples, therefore a total of 66 sources existed for both sampling periods.

An interesting observation was the wide distribution of several of the correlated tar ball samples identified as being from the same source. Source A, with four samples, was observed at GI, OP, and CB. Other sources noted for their wide distribution are Source B, Source C, and Source G. Three stations, MB, OP, and RR appear to have been significantly impacted by tar balls from one dominate source. Of the 118 samples analyzed, 45% were representative of unrelated sources and reported as a single sourced sample and may be associated with small incidental spills. The remaining 55% of the samples analyzed were originated from the 18 multiple sources and may represent spills of a larger magnitude. The 5 sources which were identified in both sampling periods, represent only 4% of the total and suggest that they may originate from a chronic source or a larger discharge of oil that has been widely distributed in the northern waters of the Gulf of Mexico. Figure 13 shows a histogram comparison of the sources represented by multiple samples in the set of 118 tar balls analyzed. Note the wide distribution of some of the matched sources.

Source E was of particular interest. It appears to be a weathered Middle Eastern crude oil tank sludge discharge. Unknown Source E is compositionaly a high sulfur oil typical of many Middle Eastern production crude oils. Key source-fingerprint and biomarker profiles were very similar to several Middle Eastern oils available as reference oils. Figure 14 shows an extracted ion chromatogram comparison of the triterpane and hopane family (m/e 191) for Source E compared to a blended sample of Kuwait crude oil. Figure 15 shows the same plots but for two

22
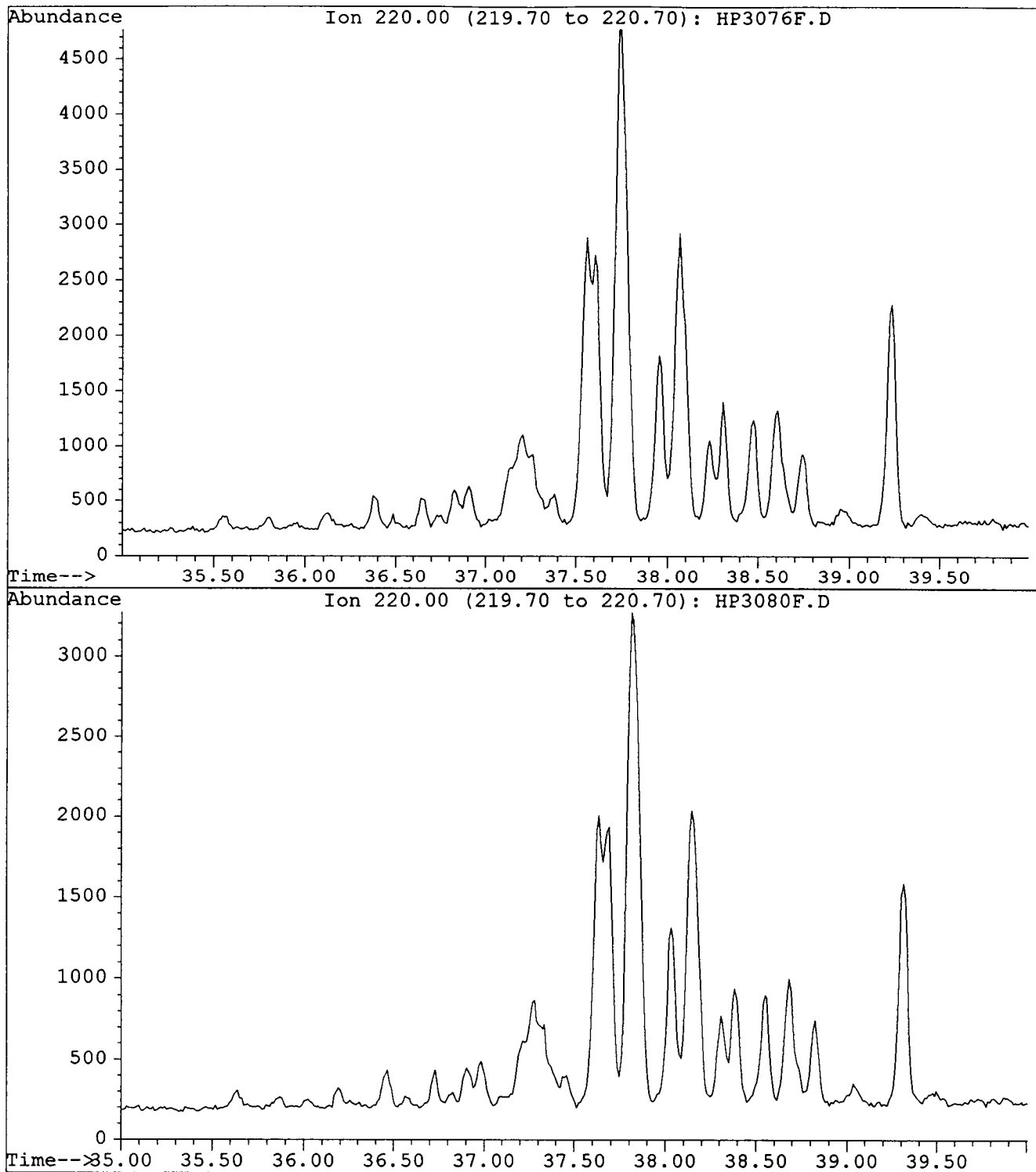
Figure 11.    Chromatographic comparison of the C-3 Phenanthrene
(m/e 220) for two samples identified as positive matches.

23
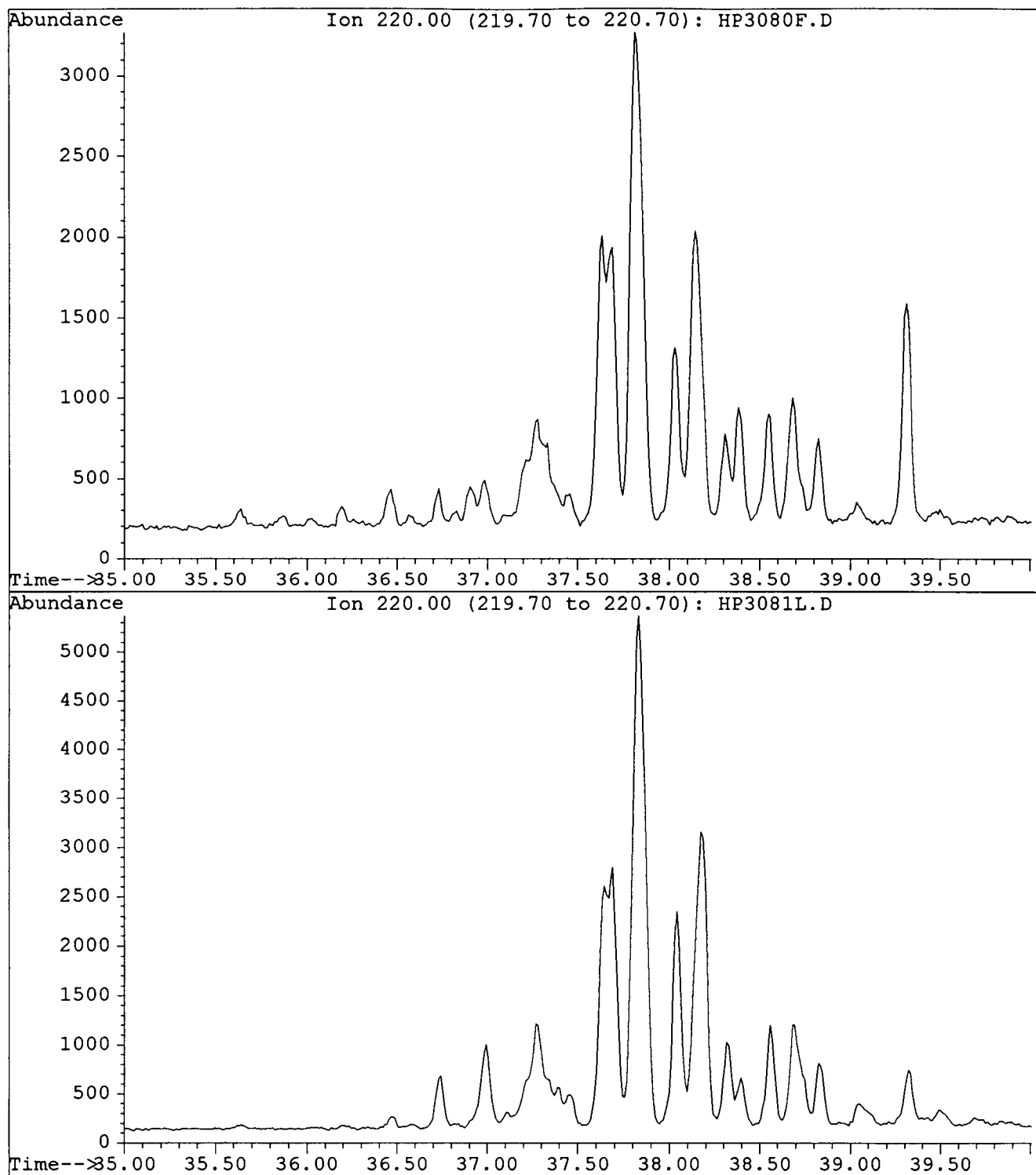
Figure 12.    Chromatographic comparison of the C-3 Phenanthrene
(m/e 220) for two samples classified as a nonmatch.

24

additional Kuwait crude oils, a sample from the Al-Bergan oil field in Southern Kuwait and a sample of oil from the Arabian Gulf oil spill (1991); note the consistency in this fingerprint comparison. Figure 16 shows a similar comparison for additional oils from the Middle East region, namely a Saudi Arabian 'Arabian Light' and Bashara crude oil from Iraq. The Arabian Light sample which is also very similar to source E but distinctively different when compared to the Bashara crude oil. Two additional domestic production oils were also included for comparison, but they are obvious nonmatches. Figure 17 shows the same comparison for North Slope crude oil and a "typical" South Louisiana crude oil. Two samples of tar balls collected at east stations were found to be from the same source as several of the tar balls collected at west stations. Source A was found at GI, in the east, and CB and OP in the west. Source G was found at PF, in the east, and OP in the west.
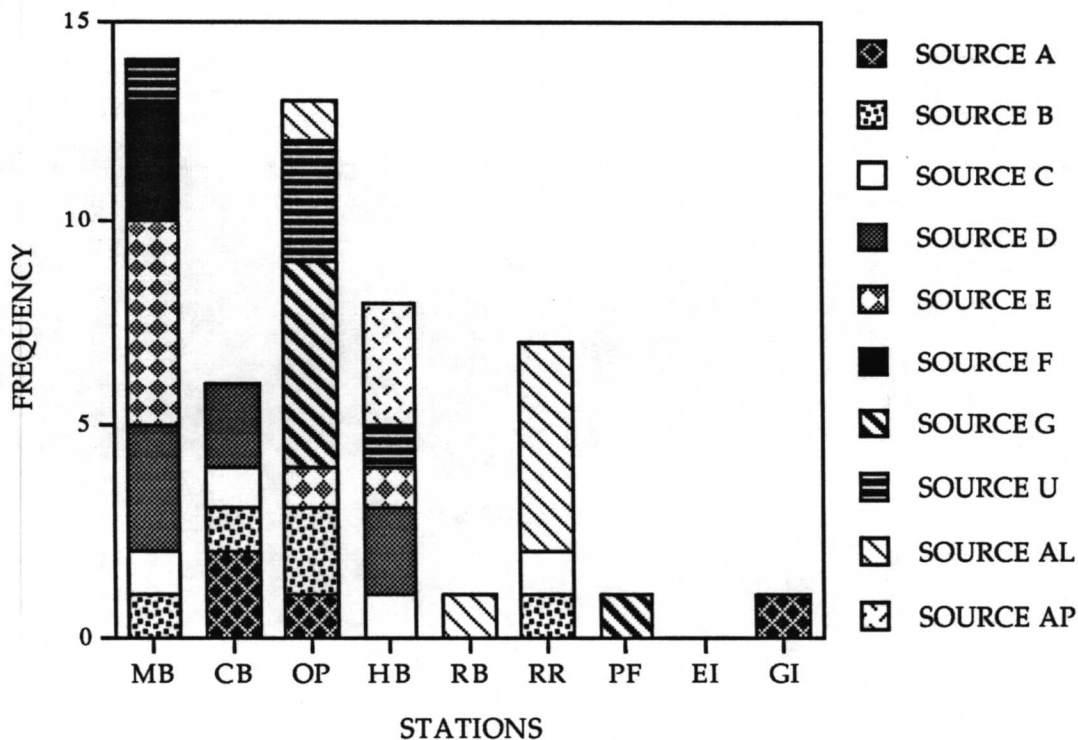


Figure 13.    Station distribution for sources identified with more than three occurring samples.
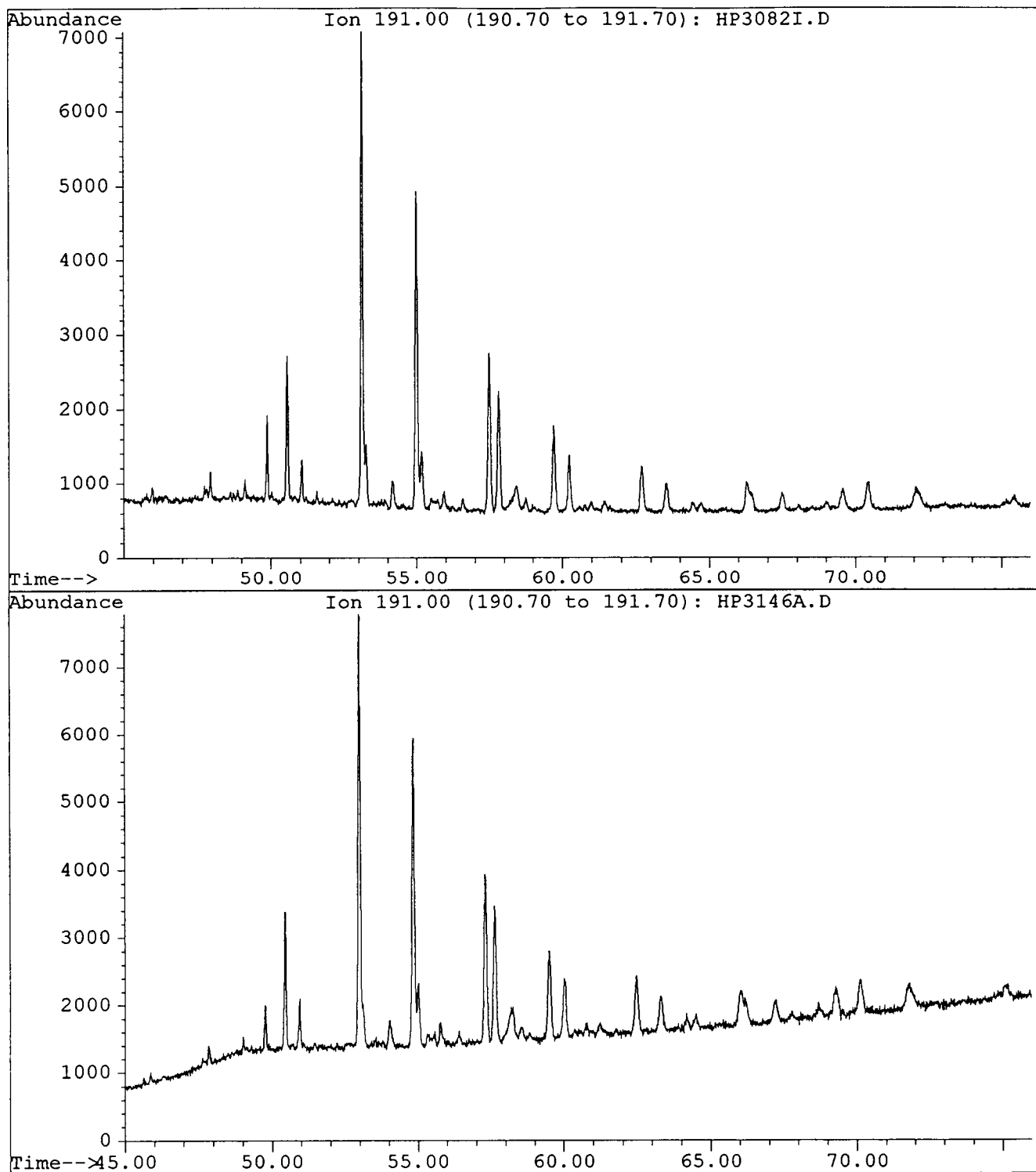
Figure 14. Chromatographic comparison of the triterpanes and hopanes
(m/e 191) profiles for tar ball Source E (top) to a Kuwait crude oil
sample (bottom).

26
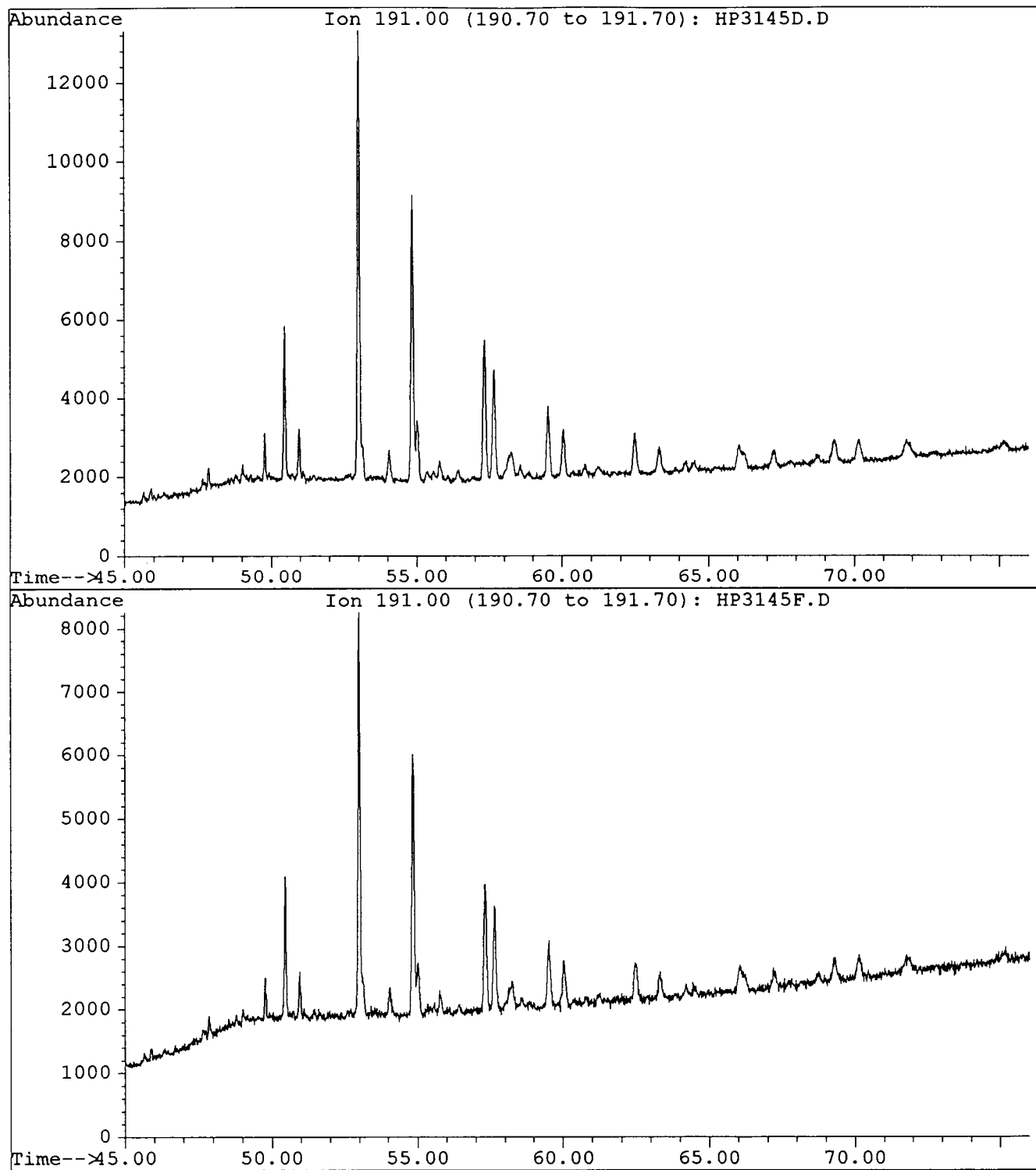
Figure 15.    Chromatographic comparison of the triterpanes and hopanes
(m/e 191) profile for Kuwaiti Al-Bergan crude oil (top) and oil
from the Arabian Gulf oil spill (bottom).

27
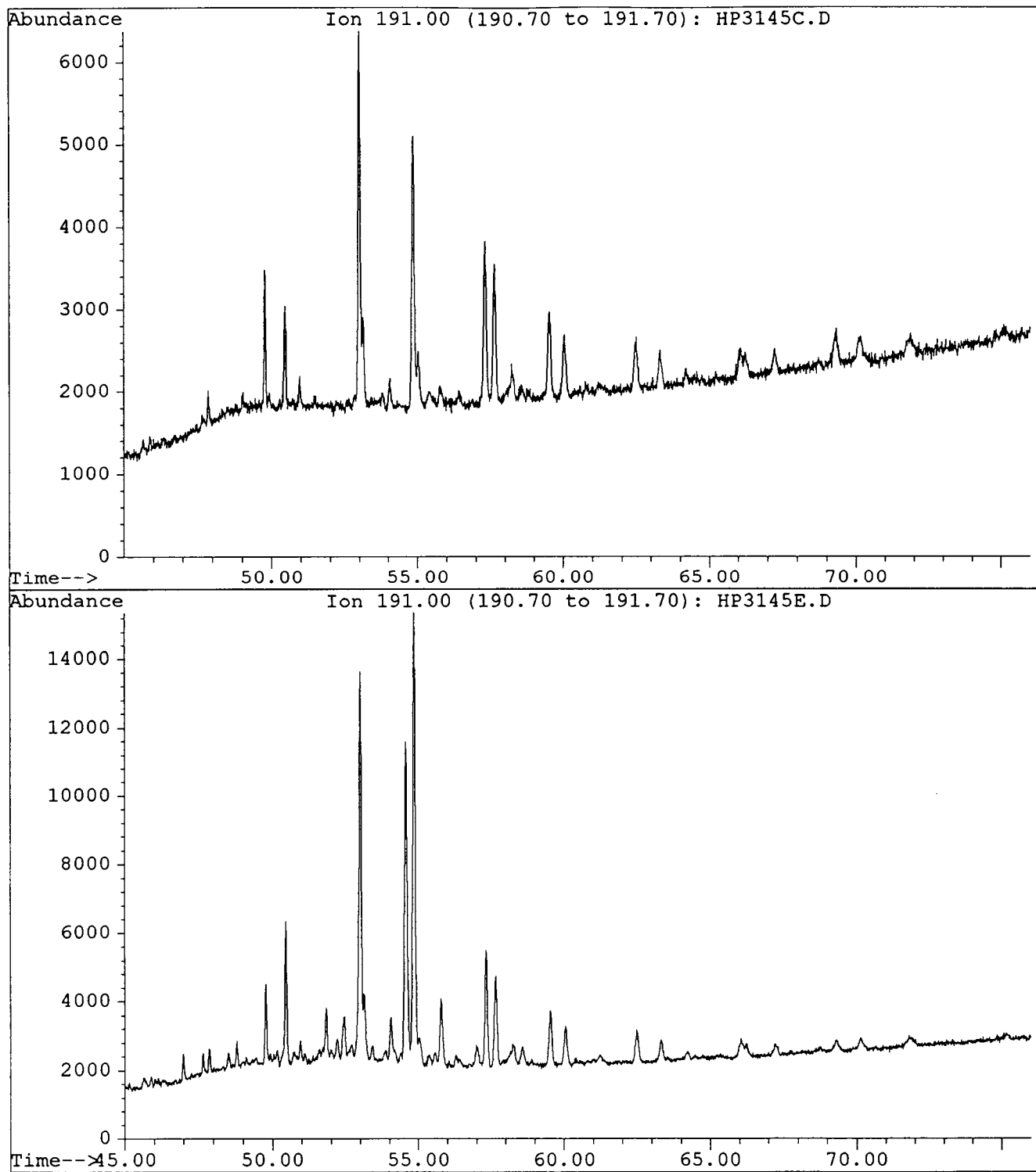
Figure 16. Chromatographic comparison of the triterpanes and hopanes (m/e 191) profile for an Arabian light crude oil (top) and Basrah crude oil (bottom).

28
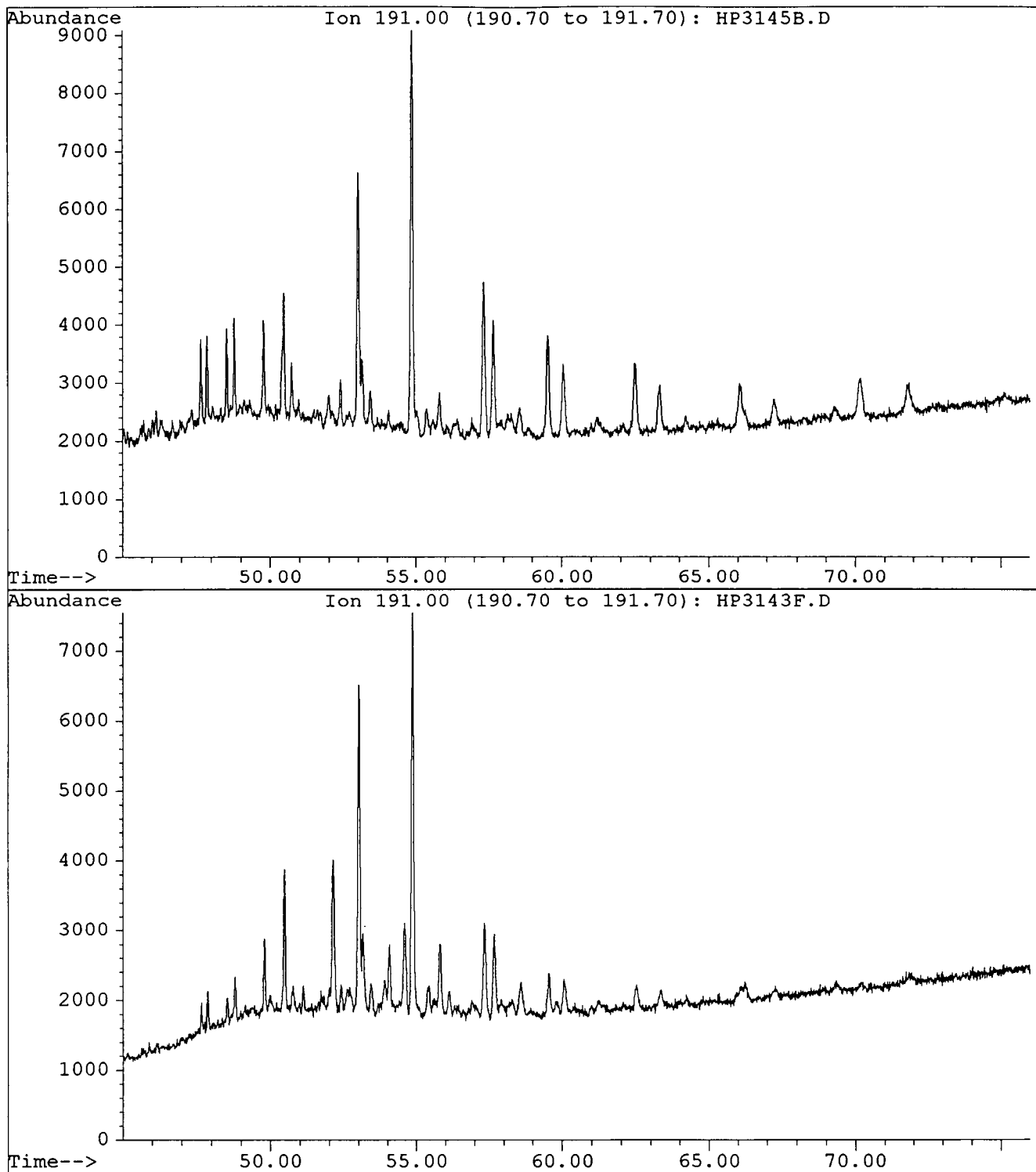
Figure 17. Comparisons of the North Slope crude reference oil (top) to a "typical" South Louisiana OCS production crude oil (bottom).

29
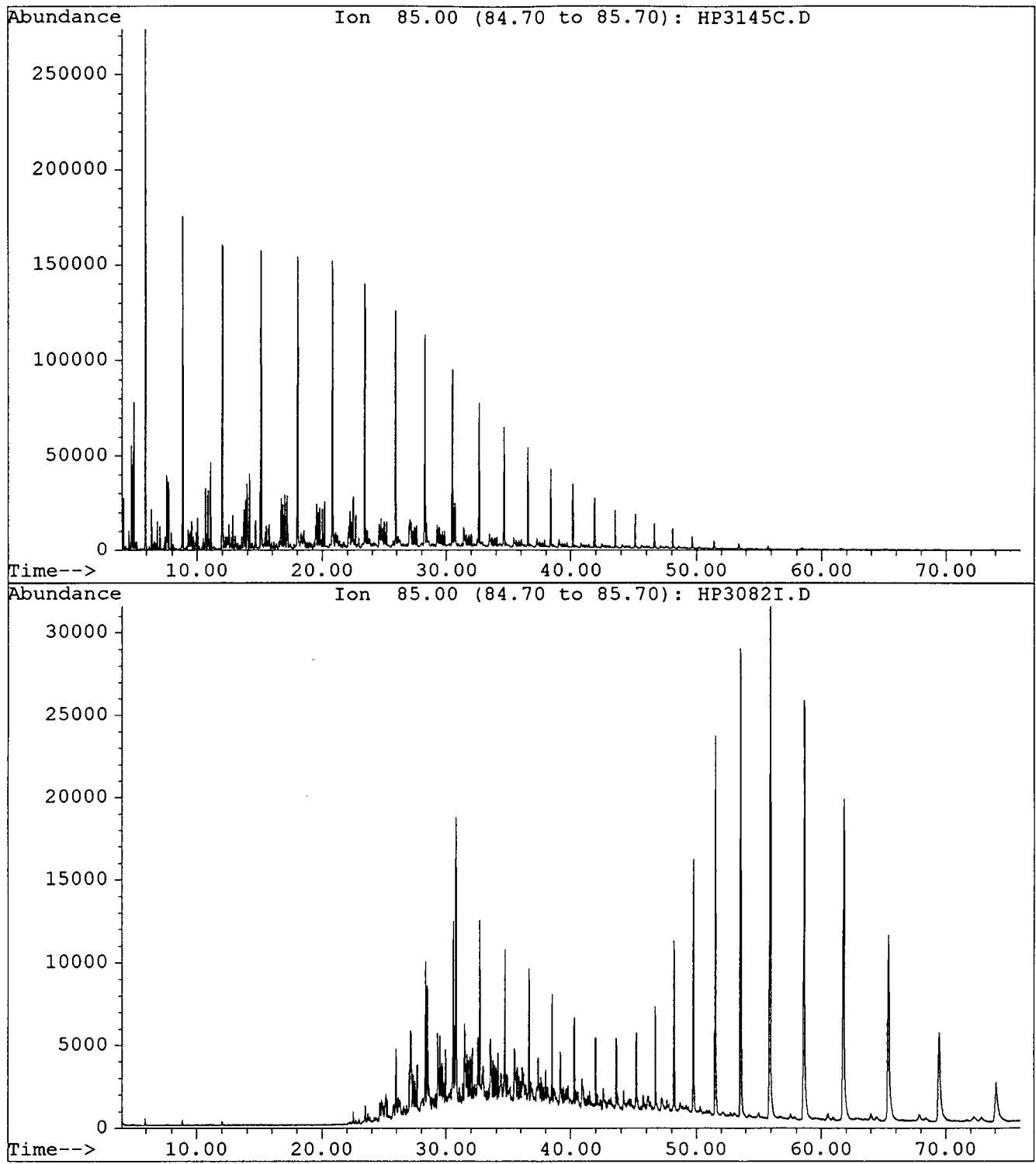
Figure 18. Chromatographic comparison of the normal alkane (top) distribution of an Arabian light crude oil and the unknown Source E suspected as being weathered sludge discharge (bottom).

30

Index Cluster Plots. A set of indexes for each sample were extracted from the GC/MS data for cluster plot and statistical analyses. The indexes selected were relatively uneffected by weathering and included a range of components within the oil to provide a more comprehensive numerical source identification. The goal was to develop a method for aiding in source identification. The indexes selected were the ratio of total C-3 dibenzothiophenes to C-3 phenanthrenes, total C-2 phenathrenes to C-2 chrysenes, and specific isomer ratios of C-3 dibenzothiophenes, C-3 phenanthrenes, methylpyrenes, and methylchrysenes. A ratio table was created tabulating all the samples analyzed and located in Appendix I. As additional information, these results were plotted as a scatter or cluster plot in an attempt to further confirm sources. The cluster plots did not provide a high degree of identification, but were considered a useful screening tool. An explanation for the large number of unresolved groupings was based on a large number of sources represented and the limited numerical spread of the indexes. The resulting cluster plots were often more confusing than enlightening, yielding "inconclusive" results for all cluster index combination plots attempted, such as figure 19. The large number of oil sources in the study population, their similarity in composition, and the various stages of weathering reduced the effectiveness of this approach as a conclusive method, indicating that a simple four component, two dimensional comparison was not adequate. Only by detailed comparison of the chromatographic data could the related samples be identified.

Cluster and Principle Component Analyses. Statistical approaches were also attempted to mathematically assess the GC/MS data for possible source correlations. The techniques utilized were principal component analysis and various cluster analysis techniques. The indexes identified previously were considered the most accurate fingerprinting descriptors for the sample population, comprised of chemical components with reduced weathering rates, and chromatographic uniqueness. This utilization of unique isomers or clusters to create ratio indexes is a common chromatographic technique which reduces the amount of data as well as highlighting natural variation. Ratios can also provide component normalization, reduce intrinsic instrument variability and inherent weathering effects.

The index values were assessed for instrumental variability by utilizing 15 North Slope crude reference oil injections completed during the sample analysis. The ratio groups from the NSC reference oil that did not fall below the 30% variability range were rejected from the statistical data set. The isomer index range was 12% to 23% with the C-3 Dibenzothiophene at 12% variability and C-1 Pyrenes and C-1 Chrysenes at 23%. The other two components with isomer ratio indexes, C-3 Phenanthrenes and Norhopane/Hopane were 15% and 21% respectively.

31
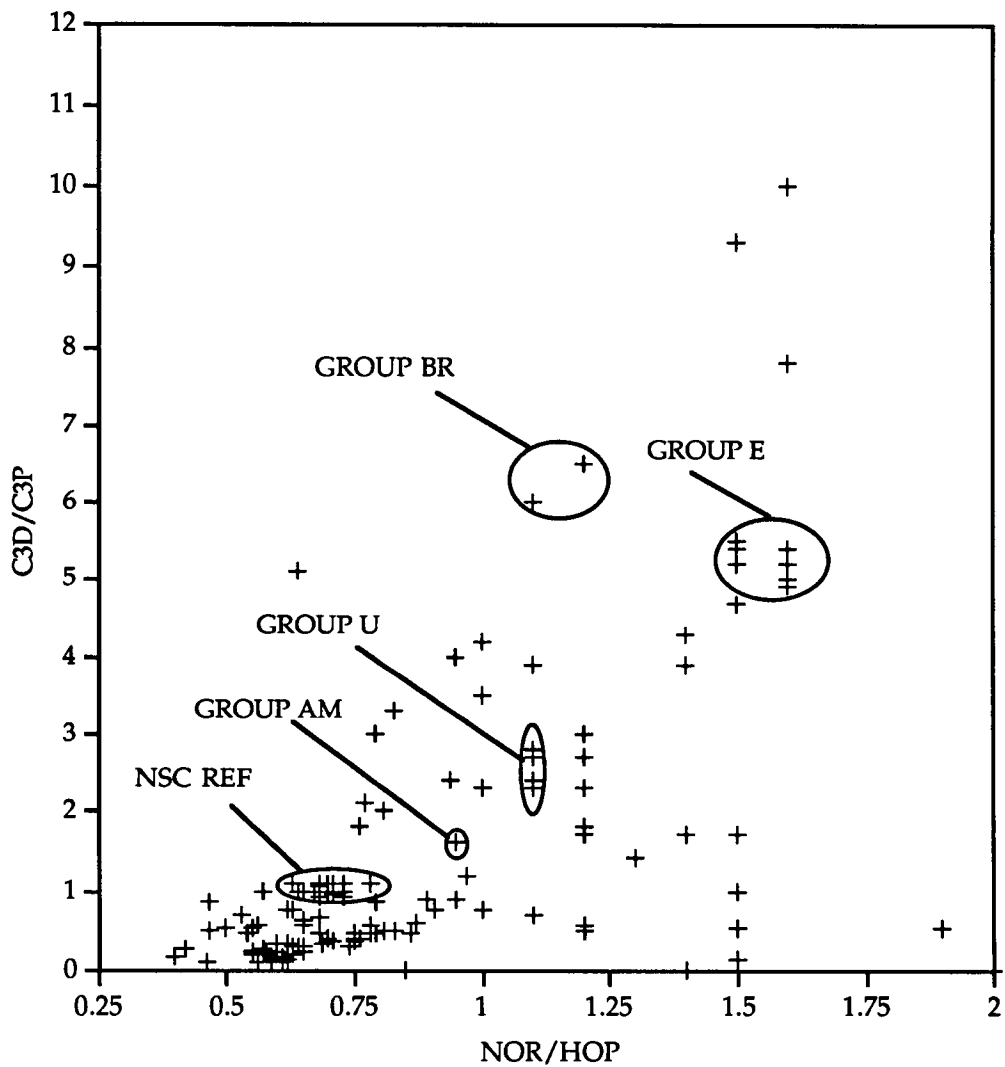
Figure 19. Primary cluster plot of all 118 tar ball samples and 15 NSC reference oils analyzed as a control. Four of the identified sources and the NSC reference oils are highlighted.

The cluster of isomers used for the C-3 Dibenzothiophene/C-3 Phenanthrene were also within acceptable limits at 18%. The outlying index was C-2 Phenanthrenes to C-2 Chrysenes at 66%. At the onset of this project, the intent was to classify the samples analyzed using analytical values that were independent of internal standard corrections, therefore the C-2 Phenanthrene/C-2 Chrysene value were rejected.

For effective utilization of statistics, even experimental statistics, replication of sources must be made and variability established. The replication sample was the NSC reference oil. The error associated in statistical grouping using an unweathered oil was elimination of the slight additional variability that would exist with environmentally weathered samples; although, this error is not expected to be greater than the instrument variability. All statistical methods were capable of clustering the NSC oil, though samples not sourced from NSC oil were occasionally placed within or adjacent to that cluster.

Principle component analysis was completed after logarithemically transforming the indexes into log form. All statistical indexes were used simultaneously with two indexes (norhopane/hopane and C-3 dibenzothiophene/C-3 Phenanthrene) weighted for the final statistical evaluation. The first two principle components described approximately 80% of the variance, which was reflected in the statistical plots utilizing various combinations of 6 principle components. The results indicated only loose clustering for the samples originally source-fingerprinted as similar, but highlighted a sample matched to the NSC reference oil. This correlation was confirmed by detailed source-fingerprinting.

Four cluster analysis techniques were used as an additional assessment of the sample indexes. They included single linkage, average linkage, complete linkage and centroid and differ by the process used to define the original cluster, or nearest two samples. Single linkage defines the distance between two clusters as the minimum distance between an observation from one cluster to another cluster. Average linkage joins clusters with small and like variances within the average distance between pairs of observations. Complete linkage is biased toward clusters with equal diameters and defines the distance between two clusters as the maximum distance between two closely associated points. The centroid procedure tends to incorporate outliers more readily by defining the distance between two clusters as the squared distance between the associated point's means. As in the principle component analysis, the reference oil was identified as a single source and a few of the sources were clustered correctly, but the distance plot was unable to discern distinct clusters. A hierarchical plot of the distance between the clusters for each method is provided in Appendix II along with other statistical results.

The initial attempts for source recognition were not highly successful for various reasons, principally the limited value range of the index values. If additional studies for comparison of unknown sources are required. Further investigation should be applied to the process of classification and regression trees (CART) which

33

could provide more information by utilizing the components as characterization indicators for decisive hierarchical clusters. This may limit the extent of exhaustive source fingerprinting of chromatographic data required, though never eliminate the need for source-fingerprinting.

## CONCLUSIONS

During two sampling periods along the southern coast of Louisiana, 528 tar ball samples were collected from nine stations with insignificant variability between the two sampling periods. Most of the tar ball samples appeared as black, solidified tars. The sand content within the samples was estimated by visual appearance and averaged between 40 to 60%. Only low concentrations of organics and shell fragments were observed incorporated into the tar ball samples.

In comparison to other shoreline studies within the Gulf of Mexico, the concentration of tar balls along the Louisiana coast were low. The range of stranded tar for the wider Gulf of Mexico Region was 0 to 4366.61 g/m (the highest value was reported in Discovery Bay, Jamaica by Jones and Bacon, 1990); during our study, the quantity of tar collected ranged from 0.53 to 47.77 g/m. If the estimated threshold concentration of 100 g/m is considered a good guide in determining the degradation of beaches for tourist purposes (Atwood et al. 1987), the beaches studied were below a level of social-economic concern. Although, any stranded oil on a beach is aesthetically unpleasant, and the presence of oil reduces the value placed on that beach as a resource.

Of the 118 samples analyzed by detailed GC/MS, 32% were indicative of high pour point, heavy oils (most likely bunker or heavy heating oils); closely followed by tanker washings or sludge discharges at 26%. Therefore, greater than 50% of the samples collected can be associated with transportation activities. The persistence of the spilled heavy petroleum oils, enriched with asphaltene and high molecular weight residuum hydrocarbon components was considered greater than for many crude oils and light refined petroleum products. Often, light oils spilled in the marine environment spread very thin on the water's surface and disperse by natural processes, such as storms, never forming tar balls. Heavy oils, which are more viscous and less affected by physical processes, persist longer. Microbial degradation, the ultimate fate of most tar balls in the marine environment, is limited by the available surface area of the petroleum and by the recalcitrant petroleum constituents.

Source-fingerprinting by manual comparison of the available GC/MS data was effective in identifying 66 different sources from a sample population of 118. Cluster plot analyses are effective in screening a large population of GC/MS data to determine which samples may be related. The possible matches would then require conformation by a qualitative comparison of all chromatographic data. Mathematical, or statistical, techniques were limited by the lack of replication and

34

range in index values. The use of statistical principal component analyses may provide a higher degree of separation of suspected sources. More work is required to fully develop a statistical approach to source-fingerprinting.

Several of the sources appear to be derived from the discharge of tanker washings containing crude oil and high molecular weight paraffins. Biomarker signatures typical of Middle East and Alaskan North Slope crudes have been identified in the tar balls analyzed. This is not surprising since approximately 30% and 8%, respectively, of the crude oils transported into the Northern Gulf of Mexico are from these two sources (Rainey, 1990).

## RECOMMENDATIONS

A repeat of this study in the 1994-1995 time period to assess changes in the abundance, distribution, and sources of tar balls on the Louisiana coast.

Comparison of reference oils including many from the Louisiana OCS production zones to the tar balls analyzed in this study. The few geographical associations highlighted in this report were from casual observation only; no systematic effort was made to establish specific sources.

Further develop statistical approaches to synthesis large sets of GC/MS source-fingerprint data. Reanalyze the source index data by these improved methods.

Creation of a classification and regression tree for assessment of larger numbers of samples/sources.

## REFERENCES

Asuquo, F. E. 1991. Tar balls on Ibeno-Okpposo Beach of South-east Nigeria. *Marine Pollution Bulletin.* 22(3):150-151.

Atwood, D. K., F. J. Burton, J. E. Corredor, G. R. Harvey, A. J. Mata-Jimenez, A. Vasquez-Botello and B. A. Wade. 1987. Results of the CARIPOL Petroleum Pollution Monitoring Project in the Wider Caribbean. *Marine Pollution Bulletin.* 18(10):540-548.

Benzhitsky, A. G. 1981. Distribution of tar balls in the surface layer of the Arabian Sea in April-June 1980. *Oceanology.* 21(6):717-720.

Blumer, M., M. Ehrhardt and J. H. Jones. 1973. The environmental fate of stranded crude oil. *Deep-Sea Research.* 20:239-259.

Botello, A. V., C. Gonzalez and G. Diaz. 1991. Pollution by petroleum hydrocarbons in sediments from contimental shelf of Tabasco State, Mexico. *Environmental Contamination & Toxicology.* 47(4):565-571.

Brakstad, F. and O. Grahl-Nielsen. 1988. Identification of weathered oils. *Marine Pollution Bulletin.* 19(7):319-324.

Burns, K. A., J. P. Villeneuve, V. C. Anderlin and S. W. Fowler. 1982. Survey of tar, hydrocarbon and metal pollution in the coastal waters of Oman. *Marine Pollution Bulletin.* 13(7):240-247.

Burton, F. J. 1987. A survey of marine and littoral oil pollution in the Cayman Islands, 1983-1983. *Caribbean Journal of Science.* 23(1):115-121.

Butler, J. N., B. F. Morris and J. Sass. 1973. Pelagic tar from Bermuda and the Sargasso Sea. Bermuda Biological Station Spec. Publ. No. 10.

Butt, J. A., D. F. Duckworth and S. G. Perry. 1986. <u>Characterization of Spilled Oil Samples.</u> John Wiley and Sons, New York.

Carr, A. 1987. Impact of nondegradable marine debris on the ecology and survival outlook of sea turtles. *Marine Pollution Bulletin.* 18(6B):352-356.

Colombo, J. C. , E. Pelletier, C. Brochu and M. Khalil. 1989. Determination of hydrocarbon sources using n-alkane and polyaromatic hydrocarbon distribution indexes. Case Study: Rio de La Plata Estuary, Argentina. *Environmental Science and Technology.* 23:888-894.

Corredor, J. E., J. M. Morell and C. E. Del Castillo. 1990. Persistence of spilled crude oil in tropical intertidal environment. *Marine Pollution Bulletin.* 21(8):388-392.

Davis, N. J., and G. A. Wolfe. 1990. The Mersey Oil Spill, August, 1989. A case of sediments contaminating the oil? *Marine Pollution Bulletin.* 21(10):481-484.

Georges, C. and B. L. Oostdam. 1983. The characteristics and dynamics of tar pollution on the beaches of Trinidad and Tobago. *Marine Pollution Bulletin.* 14(5):170-178.

Getter, C. D., T. G. Ballou and C. B. Koons. 1985. Effects of dispersed oil on mangroves. Synthesis of a seven-year study. *Marine Pollution Bulletin.* 16(8):318-324.

Getter C. D., G. I. Scott and J. Michel. 1981. The effects of oil spills on mangrove forests: a comparison of five oil spill sites in the Gulf of Mexico and

the Caribbean Sea. In Proceedings of the 1981 Oil Spill Conference. API Washington D.C. pp. 535-540.

Geyer, R. A. 1980. Marine Environmental Pollution, Vol. 1. Hydrocarbons. Elsevier Scientific Publishing Co., New York.

Goodwin, N. S., P. J. D. Park and A. P. Rawlinson. 1981. Crude oil biodegradation under simulated and natural conditions. *Advances in Organic Geochemistry.* pp. 650-658.

Gough, M. A. and S. J. Rowland. 1990. Characterization of Unresolved Complex Mixtures of Hydrocarbons in Petroleum. *Nature.* 344:648-650 (12 April).

Grahl-Nelson, O. and T. Lygre. 1990. Identification of samples of oil related to two spills. *Marine Pollution Bulletin.* 21(4):176-183.

Guzman, H. M., J. B. C. Jackson, and E. Weil. 1991. Short-term ecological consequences of a major oil spill on Panamanian subtidal reef corals. *Coral Reefs.* 10:1-12.

Hayes, M. 1978. Coastal Process Field Manual for Oil Spill Assessment. RPI Inc.

Henry, C. B. and E. B. Overton. 1993a. Chemical composition and source-fingerprinting of depositional oil from the Kuwait oil fires. In Proceedings of the 1993 Oil Spill Conference. API Washington, D.C., pp. 407-414.

Henry, C. B. and E. B. Overton. 1993b. Source-fingerprinting and compound specific quantitative analysis of oil contaminated soils and sediments. Unpubl. MS. Louisiana State University, Institute for Environmental Studies.

Henry, C. B. and P. O. Roberts. 1992. LSU response report: St. John Island, U.S.V.I. site visit. Report number IES92-04. Unpubl. MS. Louisiana State University, Institute for Environmental Studies.

Iliffe, T. M. and A. H. Knap. 1979. The fate of stranded pelagic tar on Bermuda beaches. *Marine Pollution Bulletin.* 10:203-205.

Jones, M. A. J. and P. R. Bacon. 1990. Beach tar contamination in Jamaica. *Marine Pollution Bulletin.* 21(7):331-334.

Kennicutt, M. C. II. 1988. The effect of biodegradation on crude oil bulk and molecular composition. *Oil & Chemical Pollution.* 4:89-112.

37

Koons, C. B. and P. H. Monaghan. 1973. Petroleum derived hydrocarbons in Gulf of Mexico waters. Transactions - Gulf Coast Assoc. of Geological Societies. 23:170-181.

Knap, A. H., T. M. Iliffe and J. N. Butler. 1980. Has the amount of tar on the open ocean changed in the past decade? *Marine Pollution Bulletin*. 11:161-164.

Krishnaia, P. R. and L. N. Kanal. 1982. Handbook of Statistics 2, Classification Pattern Recognition and Reduction of Dimensionality. North-Holland Publishing Co., Amsterdam.

Lindstedt, D. M. and J. C. Holmes Jr. 1988. Louisiana's 1987 Beach Cleanup. Louisiana Geological Survey.

Lizarraga-Partida, M. L., F. B. Izquierdo Vicuna and I. W. Chang. 1990. Marine oil degrading bacteria related to oil inputs and surface currents in the western Caribbean Sea. *Oil & Chemical Pollution*. 7:271-281.

Mackay, D and C. D. McAuliffe. 1988. Fate of hydrocarbons discharged at sea. *Oil & Chemical Pollution*. 5:1-20.

Michel, J. , M. O. Hayes, W. J. Sexton, J. C. Gibeaut and C. B. Henry. 1991. Trends in natural removal of the Exxon Valdez oil spill in Prince William Sound from September 1989 to May 1990. In Proceedings of the 1991 Oil Spill Conference, API, Washington D.C. pp. 181-187.

Morris, B. F. 1971. Petroleum: Tar quantities floating in the northwestern Atlantic taken with a new quantitative neuston net. *Science*. 173:430-432.

Overton, E. B., J. McFall, S. W. Mascarella, C. F. Steele, S. A. Antoine, I. R. Politzer and J. L. Laseter. 1981. Identification of petroleum residue sources after a fire and oil spill. In Proceedings of the 1981 Oil Spill Conference. pp. 541-546.

Overton, E. B., L. V. McCarthy, S. W. Marcaella, S. R. Antoine, J. L. Laseter and J. W. Farrington. 1980. Detailed chemical analysis of Ixtoc I crude oil and selected environmental samples from the Researcher and Pierce cruises. In Proceedings of a Symposium on Preliminary results from the September 1979 Researcher/Pierce Itox 1 Cruise, Key Biscayne, FL, June 9-10, 1980. NOAA, Office of Marine Pollution Assessment, Boulder, CO.

Rainey, G. 1990. The risk of oil spills from the transportation of petroleum in the Gulf of Mexico. In, Proceedings of the Eleventh Annual Gulf of Mexico Information Transfer Meeting. pp. 1-12.

Reed, W. E. 1977. Molecular compositions of weathered petroleum and comparison with its possible source. *Geochimica et Cosmochimica Acta.* 41:237-247.

Roberts, P. O. and C. B. Henry. 1992. LSU Response Report. St. Eustatius Refinery Oil Spill Response, Incident no. 89. Unpubl. Louisiana State University, Institute for Environmental Studies.

RPI International. 1987. Natural resource response guide: Marine fish. Ocean Assessements Division, Office of Oceanography & Marine Services, National Ocean Service, National Oceanic & Atmospheric Administration.

Seifert, W. K. and J. M. Moldowan. 1978. Applications of steranes, terpanes and monoaromatics to the maturation, migration and source of crude oils. *Geochima et Cosmochimica Acta.* 42:77-95.

Sergy, G. A., E. Owens and B. Humphrey. 1991. On describing and estimating the fate of stranded oil. In Proceedings from the 1991 Oil Spill Conference. pp. 489-492.

Sleeter, T. D., B. F. Morris and J. N. Butler. 1976. Pelagic tar in the Caribbean and equatorial Atlantic. *Deep Sea Research.* 23:467-474.

Sleeter, T. D., B. F. Morris and J. N. Butler. 1974. Quantitative sampling of pelagic tar in the North Atlantic, 1973. *Deep Sea Research.* 21:773-775.

Smith, G. B. 1975. Pelagic tar in the Norwegian coastal current. *Marine Pollution Bulletin.* 7:70-72.

Smith, S. R. and A. H. Knap. 1985. Significant decrease in the amount of tar stranded on Bermuda. *Marine Pollution Bulletin.* 16(1):19-21.

Thompson, B. 1984. Canonical Correlation Analysis, Uses and Interpretation. Sage Publishing Ltd, England.

Thorndike, R. M. 1978. Correlational Procedures for Research. Gardener Press, Inc., New York.

Urdal, K., N. B. Vogt, S. P. Sporstol, R. G. Lichtenthaler, H. Mostad, K. Kolset, S. Nordenson and K. Esbensen. 1986. Classification of weathered crude oils using multimethod chemical analysis, statistical methods and SIMCA pattern recognition. *Marine Pollution Bulletin.* 17(8):366-373.

Van Vleet, E. S., W. M. Sackett, S. B. Reinhardt and M. E. Mangini. 1984. Distribution, sources and fates of floating oil residues in the Eastern Gulf of Mexico. *Marine Pollution Bulletin.* 15(3):106-110.

Volkman, J. K., R. Alexander, R. I. Kagi and G. W. Woodhouse. 1983. Demethylated hopanes in crude oils and their applications in petroleum geochemistry. *Geochimica et Cosmochimica Acta.* 47:785-794.

Wong, C. S., D. R. Green and W. J. Cretney. 1976. Distribution and source of tar on the Pacific Ocean. *Marine Pollution Bulletin.* 7(6):102-106.

# Appendix I.   Source Indexes

Appendix II. Source Indexes

| FILE NAME | SAMPLE | GRP # | C3DBa/DBb | C3Pa/Pb | C1PYa/PYb | C1CYa/CYb | NOR/HOP | C3D/C3P | C2P/C2C |
|---|---|---|---|---|---|---|---|---|---|
| HP3076B | NSC STD | NA | 2.50 | 1.20 | 0.61 | 2.30 | 0.63 | 1.10 | 11.00 |
| HP3077B | NSC STD | NA | 2.70 | 1.30 | 0.70 | 2.40 | 0.70 | 1.10 | 14.00 |
| HP3078B | NSC STD | NA | 2.30 | 1.30 | 0.62 | 2.40 | 0.68 | 1.10 | 11.00 |
| HP3079B | NSC STD | NA | 2.40 | 1.30 | 0.67 | 2.20 | 0.68 | 1.04 | 12.00 |
| HP3080B | NSC STD | NA | 2.50 | 1.30 | 0.67 | 2.20 | 0.71 | 1.10 | 12.00 |
| HP3081B | NSC STD | NA | 2.40 | 1.20 | 0.64 | 2.00 | 0.71 | 0.96 | 10.00 |
| HP3082B | NSC STD | NA | 2.50 | 1.30 | 0.63 | 2.10 | 0.70 | 1.10 | 14.00 |
| HP3083B | NSC STD | NA | 2.40 | 1.30 | 0.68 | 2.30 | 0.70 | 0.98 | 10.00 |
| HP3096B | NSC STD | NA | 2.70 | 1.30 | 0.67 | 2.30 | 0.67 | 1.00 | 12.00 |
| HP3097B | NSC STD | NA | 2.70 | 1.30 | 0.70 | 2.15 | 0.64 | 0.98 | 15.00 |
| HP3098B | NSC STD | NA | 2.60 | 1.30 | 0.67 | 2.10 | 0.65 | 1.00 | 11.00 |
| HP3099B | NSC STD | NA | 2.60 | 1.30 | 0.62 | 2.10 | 0.73 | 1.10 | 14.00 |
| HP3100B | NSC STD | NA | 2.60 | 1.20 | 0.73 | 2.00 | 0.68 | 0.92 | 11.00 |
| HP3101B | NSC STD | NA | 2.60 | 1.20 | 0.62 | 2.20 | 0.73 | 1.00 | 16.00 |
| HP3105B | NSC STD | NA | 2.90 | 1.40 | 0.58 | 1.90 | 0.78 | 1.10 | 20.00 |
| HP3076D | L2128-034 | A | 2.10 | 1.40 | 1.10 | 2.70 | 0.56 | 0.10 | 7.10 |
| HP3076E | L2128-035 | A | 2.20 | 1.10 | 0.90 | 3.40 | 0.59 | 0.11 | 7.20 |
| HP3078I | L2128-098 | A | 2.60 | 1.50 | 1.20 | 2.30 | 0.60 | 0.32 | 10.00 |
| HP3080J | L2127-060 | B | 2.60 | 1.20 | 1.20 | 2.10 | 0.55 | 0.23 | 49.00 |
| HP3076J | L2128-012 | B | 2.20 | 1.10 | 1.30 | 2.00 | 0.58 | 0.22 | 8.50 |
| HP3078J | L2128-097 | B | 2.60 | 0.93 | 0.64 | 2.10 | 0.55 | 0.18 | 6.60 |
| HP3079J | L2128-152 | B | 2.10 | 1.10 | 1.20 | 2.30 | 0.57 | 0.27 | 8.80 |
| HP3080F | L2127-063 | C | 2.90 | 2.20 | 1.00 | 1.50 | 0.61 | 0.17 | 4.00 |
| HP3079H | L2084-086 | C | 2.50 | 1.90 | 1.20 | 1.50 | 0.60 | 0.21 | 4.40 |
| HP3076F | L2128-016 | C | 3.40 | 2.20 | 0.94 | 1.50 | 0.59 | 0.15 | 4.40 |
| HP3083F | L2128-114 | C | 2.60 | 2.20 | 1.30 | 1.40 | 0.58 | 0.19 | 5.30 |
| HP3079D | L2127-038 | D | 1.45 | 4.30 | 1.10 | 3.20 | 0.75 | 0.45 | 2.40 |
| HP3080D | L2127-042 | D | 1.80 | 5.90 | 1.00 | 2.90 | 0.76 | 0.39 | 1.00 |
| HP3082D | L2127-100 | D | 1.70 | 5.20 | 1.30 | 2.60 | 0.78 | 0.47 | 2.90 |

## Appendix II. Source Indexes

| FILE NAME | SAMPLE | GRP # | C3DBa/DBb | C3Pa/Pb | C1PYa/PYb | C1CYa/CYb | NOR/HOP | C3D/C3P | C2P/C2C |
|---|---|---|---|---|---|---|---|---|---|
| HP3082E | L2127-100D | D | 1.70 | 4.90 | 1.30 | 2.60 | 0.75 | 0.38 | 2.20 |
| HP3078D | L2128-005 | D | 1.80 | 4.40 | 1.45 | 2.70 | 0.75 | 0.36 | 3.40 |
| HP3077D | L2128-025 | D | 1.80 | 5.00 | 1.10 | 2.90 | 0.86 | 0.45 | 3.70 |
| HP3083D | L2128-121 | D | 1.90 | 4.10 | 1.10 | 2.50 | 0.70 | 0.40 | 3.50 |
| HP3083E | L2128-124 | D | 1.90 | 4.70 | 1.90 | 2.50 | 0.81 | 0.48 | 3.60 |
| HP3081K | L2127-062 | E | 1.60 | 3.20 | 0.63 | 2.50 | 1.50 | 4.70 | 14.00 |
| HP3081G | L2127-083 | E | 1.60 | 3.00 | 0.70 | 1.90 | 1.50 | 5.50 | 17.00 |
| HP3081E | L2127-090 | E | 1.50 | 2.60 | 0.50 | 2.10 | 1.60 | 5.40 | 18.00 |
| HP3081H | L2127-092 | E | 1.50 | 3.90 | 0.68 | 2.00 | 1.60 | 5.20 | 19.00 |
| HP3082I | L2127-096 | E | 1.60 | 3.30 | 0.80 | 2.20 | 1.50 | 5.20 | 16.00 |
| HP3077E | L2128-096 | E | 1.60 | 3.20 | 0.83 | 2.10 | 1.50 | 5.40 | 17.00 |
| HP3083H | L2128-109 | E | 1.60 | 3.40 | 0.76 | 2.30 | 1.60 | 4.90 | 20.00 |
| HP3079F | L2127-026 | F=BN | 1.80 | 7.90 | 1.20 | 1.60 | 1.10 | 0.68 | 1.70 |
| HP3082J | L2127-098 | F=BN | 1.80 | 7.90 | 1.20 | 1.80 | 0.91 | 0.76 | 3.00 |
| HP3078E | L2128-059 | G | 1.20 | 9.00 | 1.20 | 1.70 | 0.79 | 0.45 | 0.41 |
| HP3077J | L2128-067 | G | 1.90 | 7.80 | 1.30 | 1.50 | 0.87 | 0.58 | 3.20 |
| HP3077G | L2128-071 | G | 1.90 | 13.00 | 1.40 | 1.70 | 0.71 | 0.35 | 5.80 |
| HP3077H | L2128-081 | G | 1.40 | 8.90 | 1.40 | 1.60 | 1.00 | 0.75 | 0.29 |
| HP3077I | L2128-091 | G | 1.40 | 11.00 | 1.30 | 1.50 | 0.83 | 0.49 | 1.80 |
| HP3083G | L2128-102 | G | 1.20 | 8.10 | 1.60 | 1.40 | 1.20 | 0.49 | 1.00 |
| HP3079E | L2127-034 | H | 2.00 | 7.00 | 1.20 | 1.70 | 0.89 | 0.89 | 5.40 |
| HP3079G | L2127-051 | H | 1.60 | 9.60 | 1.20 | 1.60 | 0.68 | 0.65 | 2.90 |
| HP3079I | L2084-089 | I | 3.70 | 3.20 | 1.30 | 2.10 | 1.30 | 1.40 | 11.00 |
| HP3079K | L2084-146 | J | 1.30 | 3.70 | 1.00 | 59.00 | 0.63 | 0.75 | 0.02 |
| HP3077K | L2128-018 | K | 1.40 | 1.90 | 1.10 | 2.00 | 0.68 | 0.46 | 1.70 |
| HP3076K | L2128-019 | L | 2.20 | 1.00 | 0.59 | 2.20 | 0.50 | 0.54 | 4.30 |
| HP3076I | L2128-028 | M=BQ | 2.10 | 0.84 | 0.95 | 1.90 | 0.62 | 0.14 | 7.80 |
| HP3076H | L2128-036 | N | 1.70 | 3.10 | 0.77 | 1.80 | 1.40 | 3.90 | 6.60 |
| HP3076G | L2128-042 | O | 1.80 | 1.90 | 0.92 | 5.00 | 0.95 | 4.00 | 1.50 |

44

Appendix II.  Source Indexes

| FILE NAME | SAMPLE | GRP # | C3DBa/DBb | C3Pa/Pb | C1PYa/PYb | C1CYa/CYb | NOR/HOP | C3D/C3P | C2P/C2C |
|---|---|---|---|---|---|---|---|---|---|
| HP3078F | L2128-063 | P | 0.00 | 0.00 | 0.00 | 0.00 | 1.40 | 0.00 | 0.00 |
| HP3078G | L2128-066 | Q | 1.60 | 2.20 | 1.30 | 2.00 | 0.73 | 0.93 | 0.64 |
| HP3077F | L2128-070 | R | 2.50 | 2.90 | 1.30 | 1.80 | 0.65 | 0.23 | 1.30 |
| HP3078H | L2128-075 | S | 0.00 | 0.00 | 0.00 | 0.00 | 2.00 | 0.00 | 0.00 |
| HP3078K | L2128-099 | T | 2.80 | 3.50 | 1.10 | 5.00 | 0.61 | 0.09 | 0.03 |
| HP3083I | L2128-122 | U=AQ | 1.90 | 2.40 | 0.67 | 1.80 | 1.20 | 2.30 | 17.00 |
| HP3083K | L2128-129 | V | 1.60 | 4.10 | 1.10 | 1.90 | 0.76 | 1.80 | 3.20 |
| HP3083J | L2128-130 | W | 1.60 | 3.60 | 1.50 | 2.20 | 1.40 | 4.30 | 11.00 |
| HP3082F | L2127-027 | X | 0.00 | 0.00 | 1.30 | 1.90 | 1.50 | 0.00 | 0.00 |
| HP3080K | L2127-040 | Y | 2.50 | 1.20 | 1.00 | 1.30 | 1.50 | 0.13 | 0.80 |
| HP3080E | L2127-050 | Z | 1.50 | 4.60 | 1.40 | 1.20 | 1.20 | 1.80 | 4.10 |
| HP3081D | L2127-061 | AA | 2.20 | 7.00 | 1.20 | 2.10 | 1.20 | 0.57 | 7.50 |
| HP3080I | L2127-064 | AB | 2.00 | 5.20 | 1.30 | 12.00 | 0.76 | 1.80 | 0.21 |
| HP3081I | L2127-064D | AC | 4.30 | 1.60 | 1.50 | 14.00 | 0.77 | 2.10 | 0.19 |
| HP3080H | L2127-066 | AD | 2.00 | 1.60 | 1.30 | 6.40 | 1.10 | 3.90 | 0.05 |
| HP3081F | L2127-070 | AE | 2.70 | 3.20 | 2.00 | 2.70 | 1.90 | 0.53 | 9.00 |
| HP3082G | L2127-070D | AF | 2.90 | 3.80 | 1.00 | 2.30 | 0.65 | 0.62 | 12.00 |
| HP3081L | L2127-072 | AG | 2.10 | 9.60 | 1.60 | 2.10 | 0.47 | 0.87 | 2.40 |
| HP3082H | L2127-073 | AH | 3.90 | 3.00 | 1.50 | 26.00 | 1.50 | 9.30 | 0.02 |
| HP3081J | L2127-074 | AI | 2.00 | 2.10 | 1.20 | 2.80 | 1.00 | 2.30 | 6.50 |
| HP3080G | L2127-076 | AJ | 11.00 | 2.40 | 1.20 | 0.00 | 1.50 | 1.70 | 0.00 |
| HP3082K | L2127-103 | AK | 2.10 | 10.00 | 1.60 | 2.60 | 0.46 | 0.10 | 2.20 |
| HP3099G | L2244-010 | AL | 2.80 | 1.20 | 1.30 | 2.10 | 0.55 | 0.21 | 13.00 |
| HP3098F | L2328-034 | AL | 2.50 | 1.90 | 1.10 | 1.45 | 0.63 | 0.30 | 6.40 |
| HP3098G | L2328-043 | AL | 2.40 | 2.00 | 1.10 | 1.50 | 0.64 | 0.28 | 5.80 |
| HP3098H | L2328-052 | AL | 2.40 | 2.00 | 1.30 | 1.60 | 0.62 | 0.34 | 5.20 |
| HP3098J | L2328-058 | AL | 2.60 | 1.90 | 0.95 | 1.50 | 0.69 | 0.32 | 7.10 |
| HP3099J | L2328-059 | AL | 2.40 | 1.90 | 1.10 | 1.50 | 0.65 | 0.29 | 7.30 |
| HP3096F | L2328-073 | AL | 2.30 | 2.30 | 1.00 | 2.40 | 0.60 | 0.23 | 0.43 |

Appendix II. Source Indexes

| FILE NAME | SAMPLE | GRP # | C3DBa/DBb | C3Pa/Pb | C1PYa/PYb | C1CYa/CYb | NOR/HOP | C3D/C3P | C2P/C2C |
|---|---|---|---|---|---|---|---|---|---|
| HP3098D | L2244-135 | AM | 1.90 | 3.60 | 1.00 | 2.20 | 0.95 | 1.60 | 8.20 |
| HP3100D | L2244-161 | AM | 1.90 | 3.10 | 1.50 | 2.40 | 0.95 | 1.60 | 9.50 |
| HP3099E | L2244-015 | AN | 1.70 | 2.00 | 1.05 | 6.40 | 1.60 | 10.00 | 5.20 |
| HP3096E | L2328-093 | AN | 1.60 | 1.90 | 0.70 | 7.70 | 1.60 | 7.80 | 2.10 |
| HP3097I | L2244-132 | AO | 1.70 | 1.50 | 1.20 | 1.90 | 0.94 | 2.40 | 6.60 |
| HP3099I | L2244-143 | AO | 1.70 | 1.40 | 1.30 | 2.00 | 0.79 | 3.00 | 10.00 |
| HP3097G | L2244-115 | AP | 2.20 | 1.90 | 1.10 | 1.10 | 0.81 | 2.00 | 15.00 |
| HP3097H | L2244-118 | AP | 2.30 | 2.60 | 1.40 | 2.00 | 1.20 | 2.70 | 12.00 |
| HP3098E | L2244-137 | AP | 2.40 | 3.80 | 2.00 | 1.90 | 1.00 | 3.50 | 13.00 |
| HP3099F | L2244-004 | AQ=U | 2.30 | 3.10 | 1.60 | 1.50 | 1.10 | 2.80 | 14.00 |
| HP3101G | L2244-034 | AQ=U | 2.30 | 2.90 | 1.30 | 1.70 | 1.10 | 2.70 | 15.00 |
| HP3100G | L2244-148 | AQ=U | 2.00 | 2.50 | 1.00 | 1.60 | 1.10 | 2.40 | 13.00 |
| HP3100I | L2244-168 | AQ=U | 1.90 | 2.20 | 0.65 | 1.60 | 1.10 | 2.30 | 12.00 |
| HP3097J | L2244-101 | AR | 1.70 | 1.30 | 2.00 | 2.00 | 0.55 | 0.54 | 1.10 |
| HP3100F | L2244-147 | AR | 2.10 | 2.60 | 1.30 | 1.70 | 0.40 | 0.15 | 1.60 |
| HP3101F | L2244-035 | AS | 1.40 | 2.70 | 1.10 | 3.00 | 1.60 | 5.00 | 12.00 |
| HP3101D | L2244-038 | AS | 1.60 | 2.80 | 1.60 | 0.00 | 0.64 | 5.10 | 43.00 |
| HP3105D | L2244-066 | AS | 2.20 | 2.20 | 0.00 | 1.10 | 0.83 | 3.30 | 7.40 |
| HP3097F | L2244-091 | AT | 1.90 | 2.90 | 1.10 | 3.10 | 0.78 | 0.57 | 3.60 |
| HP3098K | L2328-038 | AU | 1.90 | 1.40 | 1.40 | 1.90 | 0.56 | 0.57 | 7.00 |
| HP3096G | L2328-078 | AV | 2.40 | 1.60 | 1.30 | 9.80 | 0.53 | 0.68 | 1.50 |
| HP3098I | L2328-055 | AW | 2.50 | 4.40 | 2.20 | 1.80 | 0.79 | 0.84 | 5.60 |
| HP3097E | L2244-098 | AX | 2.20 | 2.20 | 1.00 | 2.30 | 0.42 | 0.26 | 11.00 |
| HP3097K | L2244-093 | AY | 1.80 | 2.20 | 1.00 | 1.90 | 1.50 | 1.00 | 1.80 |
| HP3096I | L2328-084 | AZ | 1.90 | 4.60 | 1.25 | 1.30 | 1.50 | 0.52 | 5.00 |
| HP3096D | L2328-003 | BA | 0.00 | 0.00 | 0.00 | 0.00 | 0.85 | 0.00 | 0.00 |
| HP3096J | L2328-081 | BB | 1.70 | 1.10 | 1.20 | 1.50 | 0.54 | 0.45 | 0.73 |
| HP3099D | L2244-029 | BC | 2.40 | 4.40 | 3.00 | 2.60 | 0.63 | 1.10 | 17.00 |
| HP3096H | L2328-097 | BD | 3.20 | 1.15 | 1.60 | 3.30 | 0.59 | 0.12 | 16.00 |

46

Appendix II. Source Indexes

| FILE NAME | SAMPLE | GRP # | C3DBa/DBb | C3Pa/Pb | C1PYa/PYb | C1CYa/CYb | NOR/HOP | C3D/C3P | C2P/C2C |
|---|---|---|---|---|---|---|---|---|---|
| HP3099K | L2328-069 | BE | 1.30 | 3.50 | 0.97 | 2.00 | 1.20 | 3.00 | 0.15 |
| HP3099H | L2244-025 | BF | 1.70 | 8.70 | 1.40 | 1.50 | 0.74 | 0.29 | 5.00 |
| HP3100E | L2244-185 | BG | 1.80 | 3.70 | 1.50 | 1.60 | 0.57 | 1.00 | 6.60 |
| HP3100H | L2244-165 | BH | 2.50 | 0.97 | 0.65 | 2.10 | 0.55 | 0.19 | 7.00 |
| HP3100J | L2244-172 | BI | 1.50 | 7.00 | 1.20 | 1.40 | 0.95 | 0.90 | 3.30 |
| HP3100K | L2244-178 | BJ | 1.40 | 1.30 | 1.30 | 1.50 | 0.97 | 1.20 | 0.48 |
| HP3100L | L2244-156 | BK | 1.40 | 1.10 | 1.10 | 1.40 | 0.47 | 0.48 | 1.40 |
| HP3097D | L2244-109 | BL | 1.70 | 4.60 | 0.76 | 1.80 | 1.00 | 4.20 | 33.00 |
| HP3101H | L2244-043 | BM | 2.00 | 7.50 | 1.50 | 7.40 | 1.40 | 1.70 | 1.00 |
| HP3101I | L2244-044 | BN=F | 1.80 | 4.80 | 1.30 | 1.90 | 1.20 | 1.70 | 2.60 |
| HP3101K | L2328-031 | BO | 2.05 | 2.10 | 1.30 | 2.20 | 0.62 | 0.75 | 2.40 |
| HP3096K | L2328-072x | BP | 4.10 | 12.00 | 1.30 | 2.00 | 0.65 | 0.55 | 20.00 |
| HP3105E | L2244-075 | BQ=M | 2.40 | 0.76 | 1.60 | 1.90 | 0.63 | 0.18 | 9.40 |
| HP3105F | L2244-062 | BR | 1.00 | 1.20 | 1.80 | 2.90 | 1.10 | 6.00 | 9.40 |
| HP3105G | L2244-073 | BR | 1.60 | 1.40 | 1.50 | 0.00 | 1.20 | 6.50 | 0.00 |
| HP3105I | L2244-083 | BS | 1.60 | 1.20 | 0.81 | 1.60 | 0.71 | 0.97 | 3.00 |

# Appendix II. Principle Component Analyses

This appendix contains the following statistical information:

- Program and data utilized for SAS/STAT analyses.

- Principle component statistical analysis results.

- Principle component plots for the following components:

    Prin1*Prin2
    Prin1*Prin3
    Prin1*Prin4
    Prin2*Prin3
    Prin2*Prin4

- Distance between clusters plotted in the following forms:

    Single linkage clusters
    Average linkage clusters
    Centroid clusters

```
options ps=66 ls=77 pageno=1;
data one;
length sample $10 groupno $3 id $14;
input filename$ sample$ groupno$ c3db c3p c1py c1chy norhop c3dc3p;
id=trim(sample)||" "||groupno;
y1=log(c3db);
y2=log(c3p);
y3=log(c1py);
y4=log(c1chy);
y5=log(3*norhop);
y6=log(2*c3dc3p);
cards;
```

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| HP3076B | NSC-STD | * | 2.50 | 1.20 | 0.61 | 2.30 | 0.63 | 1.10 |
| HP3077B | NSC-STD | * | 2.70 | 1.30 | 0.70 | 2.40 | 0.70 | 1.10 |
| HP3078B | NSC-STD | * | 2.30 | 1.30 | 0.62 | 2.40 | 0.68 | 1.10 |
| HP3079B | NSC-STD | * | 2.40 | 1.30 | 0.67 | 2.20 | 0.68 | 1.04 |
| HP3080B | NSC-STD | * | 2.50 | 1.30 | 0.67 | 2.20 | 0.71 | 1.10 |
| HP3081B | NSC-STD | * | 2.40 | 1.20 | 0.64 | 2.00 | 0.71 | 0.96 |
| HP3082B | NSC-STD | * | 2.50 | 1.30 | 0.63 | 2.10 | 0.70 | 1.10 |
| HP3083B | NSC-STD | * | 2.40 | 1.30 | 0.68 | 2.30 | 0.70 | 0.98 |
| HP3096B | NSC-STD | * | 2.70 | 1.30 | 0.67 | 2.30 | 0.67 | 1.00 |
| HP3097B | NSC-STD | * | 2.70 | 1.30 | 0.70 | 2.15 | 0.64 | 0.98 |
| HP3098B | NSC-STD | * | 2.60 | 1.30 | 0.67 | 2.10 | 0.65 | 1.00 |
| HP3099B | NSC-STD | * | 2.60 | 1.30 | 0.62 | 2.10 | 0.73 | 1.10 |
| HP3100B | NSC-STD | * | 2.60 | 1.20 | 0.73 | 2.00 | 0.68 | 0.92 |
| HP3101B | NSC-STD | * | 2.60 | 1.20 | 0.62 | 2.20 | 0.73 | 1.00 |
| HP3105B | NSC-STD | * | 2.90 | 1.40 | 0.58 | 1.90 | 0.78 | 1.10 |
| HP3076D | L2128-034 | A | 2.10 | 1.40 | 1.10 | 2.70 | 0.56 | 0.10 |
| HP3076E | L2128-035 | A | 2.20 | 1.10 | 0.90 | 3.40 | 0.59 | 0.11 |
| HP3078I | L2128-098 | A | 2.60 | 1.50 | 1.20 | 2.30 | 0.60 | 0.32 |
| HP3078J | L2127-060 | B | 2.60 | 1.20 | 1.20 | 2.10 | 0.55 | 0.23 |
| HP3076J | L2128-012 | B | 2.20 | 1.10 | 1.30 | 2.00 | 0.58 | 0.22 |
| HP3078J | L2128-097 | B | 2.60 | 0.93 | 0.64 | 2.10 | 0.55 | 0.18 |
| HP3079J | L2128-152 | B | 2.10 | 1.10 | 1.20 | 2.30 | 0.57 | 0.27 |
| HP3079H | L2084-086 | C | 2.50 | 1.90 | 1.20 | 1.50 | 0.60 | 0.21 |
| HP3080F | L2127-063 | C | 2.90 | 2.20 | 1.00 | 1.50 | 0.61 | 0.17 |
| HP3076F | L2128-016 | C | 3.40 | 2.20 | 0.94 | 1.50 | 0.59 | 0.15 |
| HP3083F | L2128-114 | C | 2.60 | 2.20 | 1.30 | 1.40 | 0.58 | 0.19 |
| HP3079D | L2127-038 | D | 1.45 | 4.30 | 1.10 | 3.20 | 0.75 | 0.45 |
| HP3080D | L2127-042 | D | 1.80 | 5.90 | 1.00 | 2.90 | 0.76 | 0.39 |
| HP3082D | L2127-100 | D | 1.70 | 5.20 | 1.30 | 2.60 | 0.78 | 0.47 |
| HP3082E | L2127-100D | D | 1.70 | 4.90 | 1.30 | 2.60 | 0.75 | 0.38 |
| HP3078D | L2128-005 | D | 1.80 | 4.40 | 1.45 | 2.70 | 0.75 | 0.36 |
| HP3077D | L2128-025 | D | 1.80 | 5.00 | 1.10 | 2.90 | 0.86 | 0.45 |
| HP3083D | L2128-121 | D | 1.90 | 4.10 | 1.10 | 2.50 | 0.70 | 0.40 |
| HP3083E | L2128-124 | D | 1.90 | 4.70 | 1.90 | 2.50 | 0.81 | 0.48 |
| HP3081K | L2127-062 | E | 1.60 | 3.20 | 0.63 | 2.50 | 1.50 | 4.70 |
| HP3081G | L2127-083 | E | 1.60 | 3.00 | 0.70 | 1.90 | 1.50 | 5.50 |
| HP3081E | L2127-090 | E | 1.50 | 2.60 | 0.50 | 2.10 | 1.60 | 5.40 |
| HP3081H | L2127-092 | E | 1.50 | 3.90 | 0.68 | 2.00 | 1.60 | 5.20 |
| HP3082I | L2127-096 | E | 1.60 | 3.30 | 0.80 | 2.20 | 1.50 | 5.20 |
| HP3077E | L2128-096 | E | 1.60 | 3.20 | 0.83 | 2.10 | 1.50 | 5.40 |
| HP3083H | L2128-109 | E | 1.60 | 3.40 | 0.76 | 2.30 | 1.60 | 4.90 |
| HP3079F | L2127-026 | F | 1.80 | 7.90 | 1.20 | 1.60 | 1.10 | 0.68 |
| HP3082J | L2127-098 | F | 1.80 | 7.90 | 1.20 | 1.80 | 0.91 | 0.76 |
| HP3078E | L2128-059 | G | 1.20 | 9.00 | 1.20 | 1.70 | 0.79 | 0.45 |
| HP3077J | L2128-067 | G | 1.90 | 7.80 | 1.30 | 1.50 | 0.87 | 0.58 |
| HP3077G | L2128-071 | G | 1.90 | 13.00 | 1.40 | 1.70 | 0.71 | 0.35 |
| HP3077H | L2128-081 | G | 1.40 | 8.90 | 1.40 | 1.60 | 1.00 | 0.75 |

51

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| HP3077I | L2128-091 | G | 1.40 | 11.00 | 1.30 | 1.50 | 0.83 | 0.49 |
| HP3083G | L2128-102 | G | 1.20 | 8.10 | 1.60 | 1.40 | 1.20 | 0.49 |
| HP3079E | L2127-034 | H | 2.00 | 7.00 | 1.20 | 1.70 | 0.89 | 0.89 |
| HP3079G | L2127-051 | H | 1.60 | 9.60 | 1.20 | 1.60 | 0.68 | 0.65 |
| HP3079I | L2084-089 | I | 3.70 | 3.20 | 1.30 | 2.10 | 1.30 | 1.40 |
| HP3079K | L2084-146 | J | 1.30 | 3.70 | 1.00 | 59.00 | 0.63 | 0.75 |
| HP3077K | L2128-018 | K | 1.40 | 1.90 | 1.10 | 2.00 | 0.68 | 0.46 |
| HP3076K | L2128-019 | L | 2.20 | 1.00 | 0.59 | 2.20 | 0.50 | 0.54 |
| HP3076I | L2128-028 | M | 2.10 | 0.84 | 0.95 | 1.90 | 0.62 | 0.14 |
| HP3076H | L2128-036 | N | 1.70 | 3.10 | 0.77 | 1.80 | 1.40 | 3.90 |
| HP3076G | L2128-042 | O | 1.80 | 1.90 | 0.92 | 5.00 | 0.95 | 4.00 |
| HP3078F | L2128-063 | P | 0.00 | 0.00 | 0.00 | 0.00 | 1.40 | 0.00 |
| HP3078G | L2128-066 | Q | 1.60 | 2.20 | 1.30 | 2.00 | 0.73 | 0.93 |
| HP3077F | L2128-070 | R | 2.50 | 2.90 | 1.30 | 1.80 | 0.65 | 0.23 |
| HP3078H | L2128-075 | S | 0.00 | 0.00 | 0.00 | 0.00 | 2.00 | 0.00 |
| HP3078K | L2128-099 | T | 2.80 | 3.50 | 1.10 | 5.00 | 0.61 | 0.09 |
| HP3083I | L2128-122 | U | 1.90 | 2.40 | 0.67 | 1.80 | 1.20 | 2.30 |
| HP3083K | L2128-129 | V | 1.60 | 4.10 | 1.10 | 1.90 | 0.76 | 1.80 |
| HP3083J | L2128-130 | W | 1.60 | 3.60 | 1.50 | 2.20 | 1.40 | 4.30 |
| HP3082F | L2127-027 | X | 0.00 | 0.00 | 1.30 | 1.90 | 1.50 | 0.00 |
| HP3080K | L2127-040 | Y | 2.50 | 1.20 | 1.00 | 1.30 | 1.50 | 0.13 |
| HP3080E | L2127-050 | Z | 1.50 | 4.60 | 1.40 | 1.20 | 1.20 | 1.80 |
| HP3081D | L2127-061 | a | 2.20 | 7.00 | 1.20 | 2.10 | 1.20 | 0.57 |
| HP3080I | L2127-064 | b | 2.00 | 5.20 | 1.30 | 12.00 | 0.76 | 1.80 |
| HP3081I | L2127-064D | c | 4.30 | 1.60 | 1.50 | 14.00 | 0.77 | 2.10 |
| HP3080H | L2127-066 | d | 2.00 | 1.60 | 1.30 | 6.40 | 1.10 | 3.90 |
| HP3081F | L2127-070 | e | 2.70 | 3.20 | 2.00 | 2.70 | 1.90 | 0.53 |
| HP3082G | L2127-070D | f | 2.90 | 3.80 | 1.00 | 2.30 | 0.65 | 0.62 |
| HP3081L | L2127-072 | g | 2.10 | 9.60 | 1.60 | 2.10 | 0.47 | 0.87 |
| HP3082H | L2127-073 | h | 3.90 | 3.00 | 1.50 | 26.00 | 1.50 | 9.30 |
| HP3081J | L2127-074 | i | 2.00 | 2.10 | 1.20 | 2.80 | 1.00 | 2.30 |
| HP3080G | L2127-076 | j | 11.00 | 2.40 | 1.20 | 0.00 | 1.50 | 1.70 |
| HP3082K | L2127-103 | k | 2.10 | 10.00 | 1.60 | 2.60 | 0.46 | 0.10 |
| HP3099G | L2244-010 | l | 2.80 | 1.20 | 1.30 | 2.10 | 0.55 | 0.21 |
| HP3098F | L2328-034 | l | 2.50 | 1.90 | 1.10 | 1.45 | 0.63 | 0.30 |
| HP3098G | L2328-043 | l | 2.40 | 2.00 | 1.10 | 1.50 | 0.64 | 0.28 |
| HP3098H | L2328-052 | l | 2.40 | 2.00 | 1.30 | 1.60 | 0.62 | 0.34 |
| HP3098J | L2328-058 | l | 2.60 | 1.90 | 0.95 | 1.50 | 0.69 | 0.32 |
| HP3099J | L2328-059 | l | 2.40 | 1.90 | 1.10 | 1.50 | 0.65 | 0.29 |
| HP3096F | L2328-073 | l | 2.30 | 2.30 | 1.00 | 2.40 | 0.60 | 0.23 |
| HP3098D | L2244-135 | m | 1.90 | 3.60 | 1.00 | 2.20 | 0.95 | 1.60 |
| HP3100D | L2244-161 | m | 1.90 | 3.10 | 1.50 | 2.40 | 0.95 | 1.60 |
| HP3099E | L2244-015 | n | 1.70 | 2.00 | 1.05 | 6.40 | 1.60 | 10.00 |
| HP3096E | L2328-093 | n | 1.60 | 1.90 | 0.70 | 7.70 | 1.60 | 7.80 |
| HP3097I | L2244-132 | o | 1.70 | 1.50 | 1.20 | 1.90 | 0.94 | 2.40 |
| HP3099I | L2244-143 | o | 1.70 | 1.40 | 1.30 | 2.00 | 0.79 | 3.00 |
| HP3097G | L2244-115 | p | 2.20 | 1.90 | 1.10 | 1.10 | 0.81 | 2.00 |
| HP3097H | L2244-118 | p | 2.30 | 2.60 | 1.40 | 2.00 | 1.20 | 2.70 |
| HP3098E | L2244-137 | p | 2.40 | 3.80 | 2.00 | 1.90 | 1.00 | 3.50 |
| HP3099F | L2244-004 | U | 2.30 | 3.10 | 1.60 | 1.50 | 1.10 | 2.80 |
| HP3101G | L2244-034 | U | 2.30 | 2.90 | 1.30 | 1.70 | 1.10 | 2.70 |
| HP3100G | L2244-148 | U | 2.00 | 2.50 | 1.00 | 1.60 | 1.10 | 2.40 |
| HP3100I | L2244-168 | U | 1.90 | 2.20 | 0.65 | 1.60 | 1.10 | 2.30 |
| HP3097J | L2244-101 | q | 1.70 | 1.30 | 2.00 | 2.00 | 0.55 | 0.54 |
| HP3100F | L2244-147 | q | 2.10 | 2.60 | 1.30 | 1.70 | 0.40 | 0.15 |
| HP3101F | L2244-035 | r | 1.40 | 2.70 | 1.10 | 3.00 | 1.60 | 5.00 |
| HP3101D | L2244-038 | r | 1.60 | 2.80 | 1.60 | 0.00 | 0.64 | 5.10 |
| HP3105D | L2244-066 | r | 2.20 | 2.20 | 0.00 | 1.10 | 0.83 | 3.30 |
| HP3097F | L2244-091 | s | 1.90 | 2.90 | 1.10 | 3.10 | 0.78 | 0.57 |
| HP3098K | L2328-038 | t | 1.90 | 1.40 | 1.40 | 1.90 | 0.56 | 0.57 |

```
HP3096G  L2328-078      u      2.40     1.60     1.30     9.80     0.53     0.68
HP3098I  L2328-055      v      2.50     4.40     2.20     1.80     0.79     0.84
HP3097E  L2244-098      w      2.20     2.20     1.00     2.30     0.42     0.26
HP3097K  L2244-093      x      1.80     2.20     1.00     1.90     1.50     1.00
HP3096I  L2328-084      y      1.90     4.60     1.25     1.30     1.50     0.52
HP3096D  L2328-003      z      0.00     0.00     0.00     0.00     0.85     0.00
HP3096J  L2328-081      1      1.70     1.10     1.20     1.50     0.54     0.45
HP3099D  L2244-029      2      2.40     4.40     3.00     2.60     0.63     1.10
HP3096H  L2328-097      3      3.20     1.15     1.60     3.30     0.59     0.12
HP3099K  L2328-069      4      1.30     3.50     0.97     2.00     1.20     3.00
HP3099H  L2244-025      5      1.70     8.70     1.40     1.50     0.74     0.29
HP3100E  L2244-185      6      1.80     3.70     1.50     1.60     0.57     1.00
HP3100H  L2244-165      7      2.50     0.97     0.65     2.10     0.55     0.19
HP3100J  L2244-172      8      1.50     7.00     1.20     1.40     0.95     0.90
HP3100K  L2244-178      9      1.40     1.30     1.30     1.50     0.97     1.20
HP3100L  L2244-156      !      1.40     1.10     1.10     1.40     0.47    ·0.48
HP3097D  L2244-109      @      1.70     4.60     0.76     1.80     1.00     4.20
HP3101H  L2244-043      #      2.00     7.50     1.50     7.40     1.40     1.70
HP3101I  L2244-044      $      1.80     4.80     1.30     1.90     1.20     1.70
HP3101K  L2328-031      &      2.05     2.10     1.30     2.20     0.62     0.75
HP3096K  L2328-072x     ^      4.10    12.00     1.30     2.00     0.65     0.55
HP3105E  L2244-075      +      2.40     0.76     1.60     1.90     0.63     0.18
HP3105F  L2244-062      %      1.00     1.20     1.80     2.90     1.10     6.00
HP3105G  L2244-073      %      1.60     1.40     1.50     0.00     1.20     6.50
HP3105G  L2244-082      ?      1.60     1.20     0.81     1.60     0.71     0.97
;

proc princomp data=one cov out=two;
 var y1-y6;
run;

proc plot data=two;
 plot prin1*(prin2 prin3 prin4)=groupno
      prin2*(prin3 prin4)=groupno
      prin3*prin4=groupno;
run;
quit;


proc cluster data=one method=average noprint outtree=tree;
 id id;
 var y1-y6;
 copy filename;
run;

proc tree data=tree;
run;

data depths;
 set tree;
 if _height_>0 then output;
run;

proc sort data=depths;
 by _height_;
run;


data depths;
 set depths;
```

Principal Component Analysis

124 Observations
  6 Variables

## Simple Statistics

|      | Y1 | Y2 | Y3 |
|------|-----|-----|-----|
| Mean | 0.7153643843 | 0.9543289886 | 0.0790842556 |
| Std  | 0.2620568461 | 0.6890603804 | 0.3341835144 |

|      | Y4 | Y5 | Y6 |
|------|-----|-----|-----|
| Mean | 0.8291242379 | 0.8978117558 | 0.504227747 |
| Std  | 0.5639795715 | 0.3576365060 | 1.126553344 |

## Covariance Matrix

|    | Y1 | Y2 | Y3 |
|----|-----|-----|-----|
| Y1 | 0.068673791 | -0.056252784 | -0.004929400 |
| Y2 | -0.056252784 | 0.474804208 | 0.090371189 |
| Y3 | -0.004929400 | 0.090371189 | 0.111678621 |
| Y4 | 0.013903911 | -0.008604433 | 0.009338240 |
| Y5 | -0.030898977 | 0.069876340 | -0.006371521 |
| Y6 | -0.092112447 | 0.068883490 | -0.066154413 |

|    | Y4 | Y5 | Y6 |
|----|-----|-----|-----|
| Y1 | 0.013903911 | -0.030898977 | -0.092112447 |
| Y2 | -0.008604433 | 0.069876340 | 0.068883490 |
| Y3 | 0.009338240 | -0.006371521 | -0.066154413 |
| Y4 | 0.318072957 | 0.015020794 | 0.142660778 |
| Y5 | 0.015020794 | 0.127903870 | 0.286333738 |
| Y6 | 0.142660778 | 0.286333738 | 1.269122437 |

Total Variance = 2.3702558844

## Eigenvalues of the Covariance Matrix

|       | Eigenvalue | Difference | Proportion | Cumulative |
|-------|-----------|-----------|-----------|-----------|
| PRIN1 | 1.37374 | 0.868631 | 0.579575 | 0.57958 |
| PRIN2 | 0.50511 | 0.202549 | 0.213104 | 0.79268 |
| PRIN3 | 0.30256 | 0.219493 | 0.127650 | 0.92033 |
| PRIN4 | 0.08307 | 0.028983 | 0.035047 | 0.95538 |
| PRIN5 | 0.05409 | 0.002406 | 0.022819 | 0.97820 |
| PRIN6 | 0.05168 | . | 0.021804 | 1.00000 |

54

Principal Component Analysis

Eigenvectors

|    | PRIN1 | PRIN2 | PRIN3 | PRIN4 | PRIN5 | PRIN6 |
|----|-------|-------|-------|-------|-------|-------|
| Y1 | -.075260 | -.115013 | 0.087954 | 0.001617 | 0.806593 | 0.568134 |
| Y2 | 0.090148 | 0.949434 | 0.087021 | -.231304 | 0.165675 | -.043881 |
| Y3 | -.043582 | 0.231784 | 0.127126 | 0.962370 | -.016562 | 0.042244 |
| Y4 | 0.130412 | -.107090 | 0.974751 | -.098829 | -.107767 | -.002028 |
| Y5 | 0.228572 | 0.102788 | -.080485 | -.048279 | -.524465 | 0.808280 |
| Y6 | 0.956586 | -.097924 | -.109146 | 0.090780 | 0.187102 | -.142101 |

Plot of PRIN1*PRIN2.  Symbol is value of GROUPNO.

```
      3.0 +
          |
          |               n    h
      2.5 +            n
          |
          |
          |
      2.0 +            %        E   E   E
          |                      rEEE
          |                            W
          |            d O          N    @
      1.5 +                        4   p
 PRIN1    |            o        pU  U
          |                  U
      1.0 +        c    o   i  U        b         ♯
          |                       V  $Z
          |          p         mm
          |                   I
      0.5 +
          |          9      x J
          |      *  **              2      8
          |      **        Q      6      H
      0.0 +      **?              v      F gG
          |                              F
          |        u      &       e      a   H
          |              s   f      y    G
          |                              G^ G
     -0.5 +      t              D DDD      G
          |  L    q   K              D
          |                   D   D
          |    1                D              G
     -1.0 +        l l              5
          |      A  l
          |  B     ll
          |        w l    R
          |  B
     -1.5 +  Bl      C
          | B7        C
          |  +         C
          |    Y      C  q
          | M
     -2.0 +  A 3             k
          |    A        T
          |
          |
     -2.5 +
          ---+--------+--------+--------+--------+--------+--------+--------+--
           -1.5     -1.0     -0.5      0.0      0.5      1.0      1.5      2.0
                                      PRIN2
```

NOTE: 8 obs had missing values.  10 obs hidden.

56

Plot of PRIN1*PRIN3.  Symbol is value of GROUPNO.

```
      3.0 +
          |
          |                         n                    h
      2.5 +                        n
          |
          |
      2.0 +          EEE    %
          |            EE   r
          |            W
          |          N           O  d
      1.5 +          4p
PRIN1     |          UUop
          |          U
      1.0 +          U  o      i              #     b c
          |       z     V
          |     p       mm
          |            I
      0.5 +
          |        9  x                              J
          |        8 ****    2
          |        6H**
      0.0 +     ?  **v  g
          |        F
          |        H  a  e              u
          |      y G  f  s
          |       G G    ^
     -0.5 +         G    DDD
          |         K     D
          |              DD
          |       !1   G  D
     -1.0 +        115
          |         1    A
          |         1    B
          |         R wl
          |           B
     -1.5 +       C  B1
          |       C  B
          |       C  +
          |     Y  C q
          |        M
     -2.0 +            A3
          |          A      T
          |
          |
     -2.5 +
          ---+-------------+-------------+-------------+-------------+-------------+--
            -1             0             1             2             3             4
                                      PRIN3
```
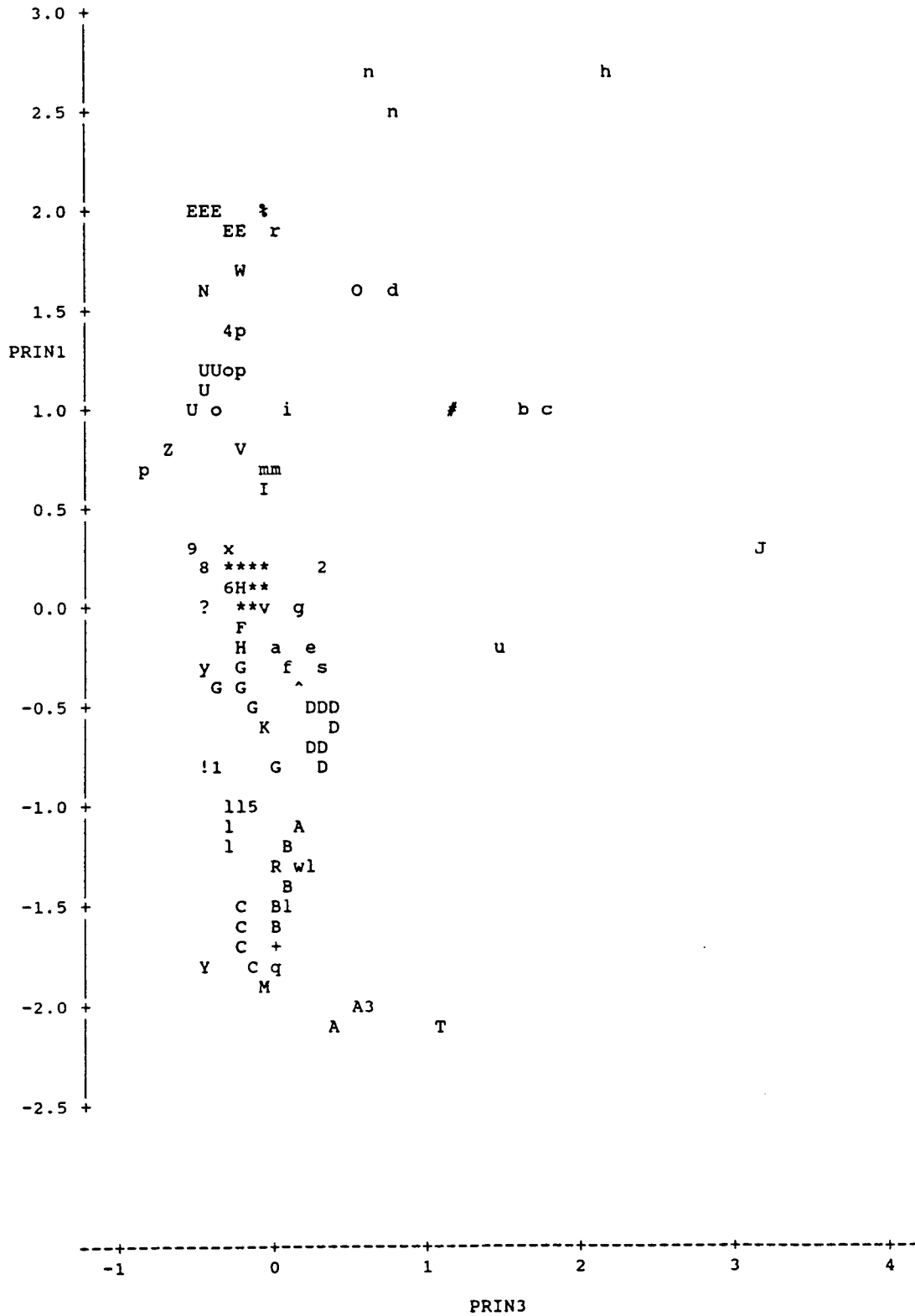
NOTE: 8 obs had missing values.  23 obs hidden.

Plot of PRIN1*PRIN4.  Symbol is value of GROUPNO.

```
PRIN1 |
  3.0 +
      |
      |                              n    h
  2.5 +            n
      |
      |
      |
  2.0 +      E    E   E    E                              %
      |        E    E   E              r
      |                                     W
      |          @  N       O           d
  1.5 +                 4                      p
      |
      |          U                  U  p  oU
  1.0 +          U         b  /  U      i   c
      |                  V   $   z
      |             m         p  m
      |                    I
  0.5 +
      |      J              x              9
      |       *  *** *    8                       2
      |        *  *    H          Q 6
  0.0 +        *   * *F ?G    g            v
      |          F
      |          Ha          u  &      e
      |          f  G  y
      |          ^G         G
 -0.5 +          DD    D          D  t
      |   D                K              q
      |          D  D
      |          G         D    ! 1
 -1.0 +              1         1
      |                 1   A
      |                 11    B
      |          1 w       R
      |                       B
 -1.5 +                  C   1B
      |   B7            C
      |           C
      |         C    Y  q
      |              M
 -2.0 +         A  k           3
      |      T       A
      |
 -2.5 +
      ---+--------+--------+--------+--------+--------+--------+--------+--
       -0.75   -0.50   -0.25    0.00    0.25    0.50    0.75    1.00

                              PRIN4
```
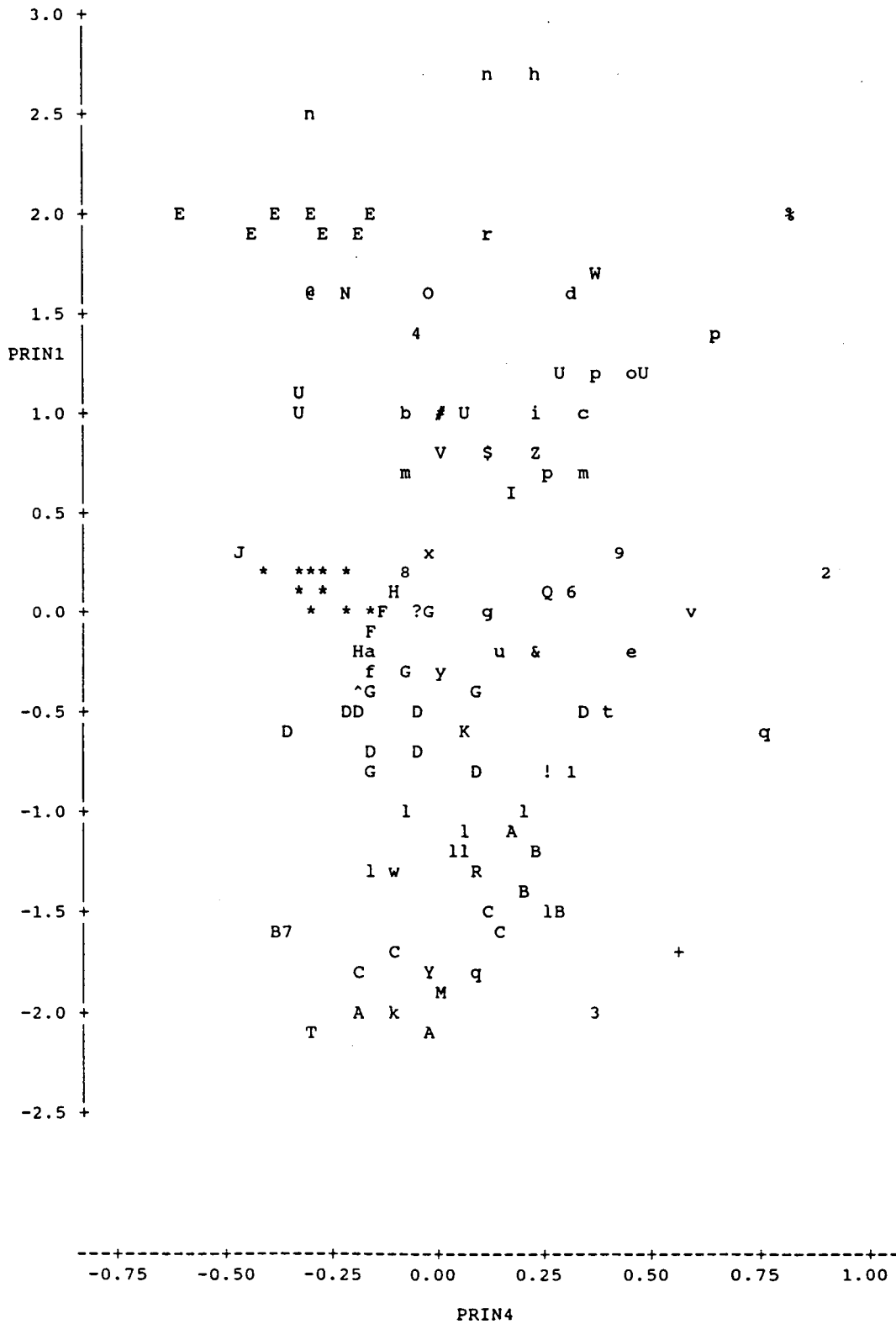
NOTE: 8 obs had missing values.  10 obs hidden.

Plot of PRIN2*PRIN3.   Symbol is value of GROUPNO.

```
PRIN2 |
      |
 1.75 +              G
      |
      |            G              k
 1.50 +                    ^
      |          G  G
      |             G
 1.25 +               g
      |           F
      |            F
      |         8      a
 1.00 +            H              #
      |
      |                  D                       :
 0.75 +       y       DD
      |     Z      v     D
      |          $       D
      |                  D
 0.50 +                D
      |        6       e              b
      |      @  V            T
      |        W    f
 0.25 +        4  mR
      |      E    Im
      |       E        s
      |      NEE
 0.00 +        C                              J
      |    E   CC r  l
      |       1CQ   w
      |      U l  K&
-0.25 +      E l   i
      |   p  U              h
      |
      |            A  A
-0.50 +     Y   tq      n
      |    9 o        O
      |       o    B    3 d        u
      |      1    B
-0.75 +    !   % B    A          c
      |      ****
      |       * *
      |       *M7
-1.00 +        B
      |       L
      |
      |
-1.25 +
      |
      ---+-----------+-----------+-----------+-----------+-----------+-----------+--
        -1           0           1           2           3           4
```

PRIN3

NOTE: 8 obs had missing values.   27 obs hidden.

59

Plot of PRIN2*PRIN4.  Symbol is value of GROUPNO.

PRIN2 |
 1.75 +
      |                          G
      |                          G
 1.50 +                           k
      |                          ^
      |                   G      5       G
      |                    H        G
 1.25 +                                g
      |                      F   G
      |                       F
      |                     a    8
 1.00 +                        H
      |                          #
      |              D
 0.75 +                     D  y        Z       D          v
      |                 D
      |                                D$      Z              v              2
 0.50 +               D
      |                D
      |                   b                6      e
      |        T            V                      W              p
 0.25 +            f
      |                 m4      R
      |      E               q   I      m    U
      |         E        s
      |        NEE                       U
 0.00 +     JE                      C        p
      |          E   Cl C      U  r
      |              w   x l   C  1 Q
      |         U            K      &
-0.25 +  E                  1          i
      |         U                    hp
      |
      |                 A        A
-0.50 +              Y     n        t        q
      |              O            o  9
      |        n              u B l d 3   o
      |                            B1
-0.75 +           A    ?      B! c              %
      |       *  ** *
      |         **      *
      |       7*      M              +
-1.00 +       B
      |       L
      |
-1.25 +
      |
      ---+--------+--------+--------+--------+--------+--------+--------+--
      -0.75    -0.50    -0.25     0.00     0.25     0.50     0.75     1.00
                                  PRIN4
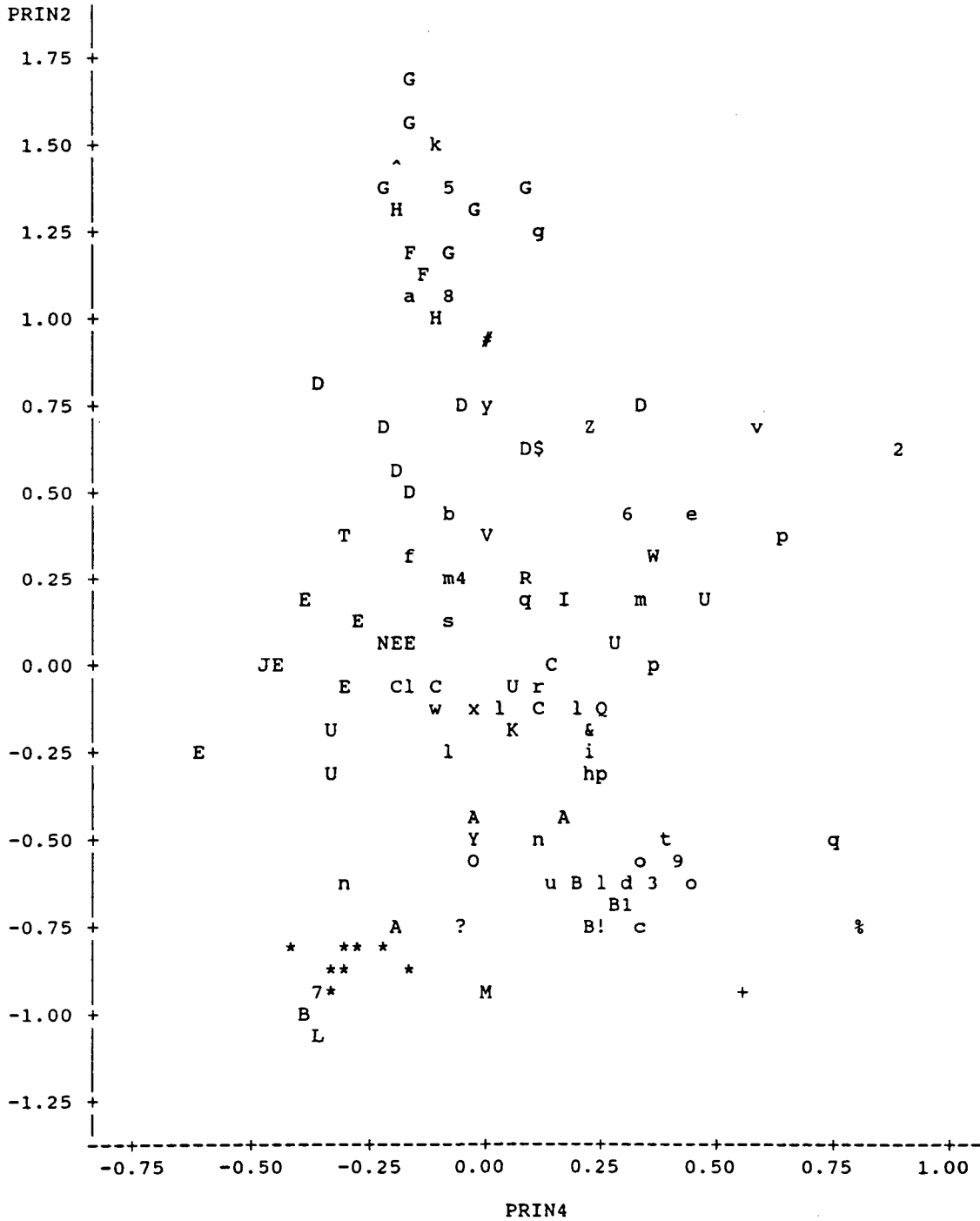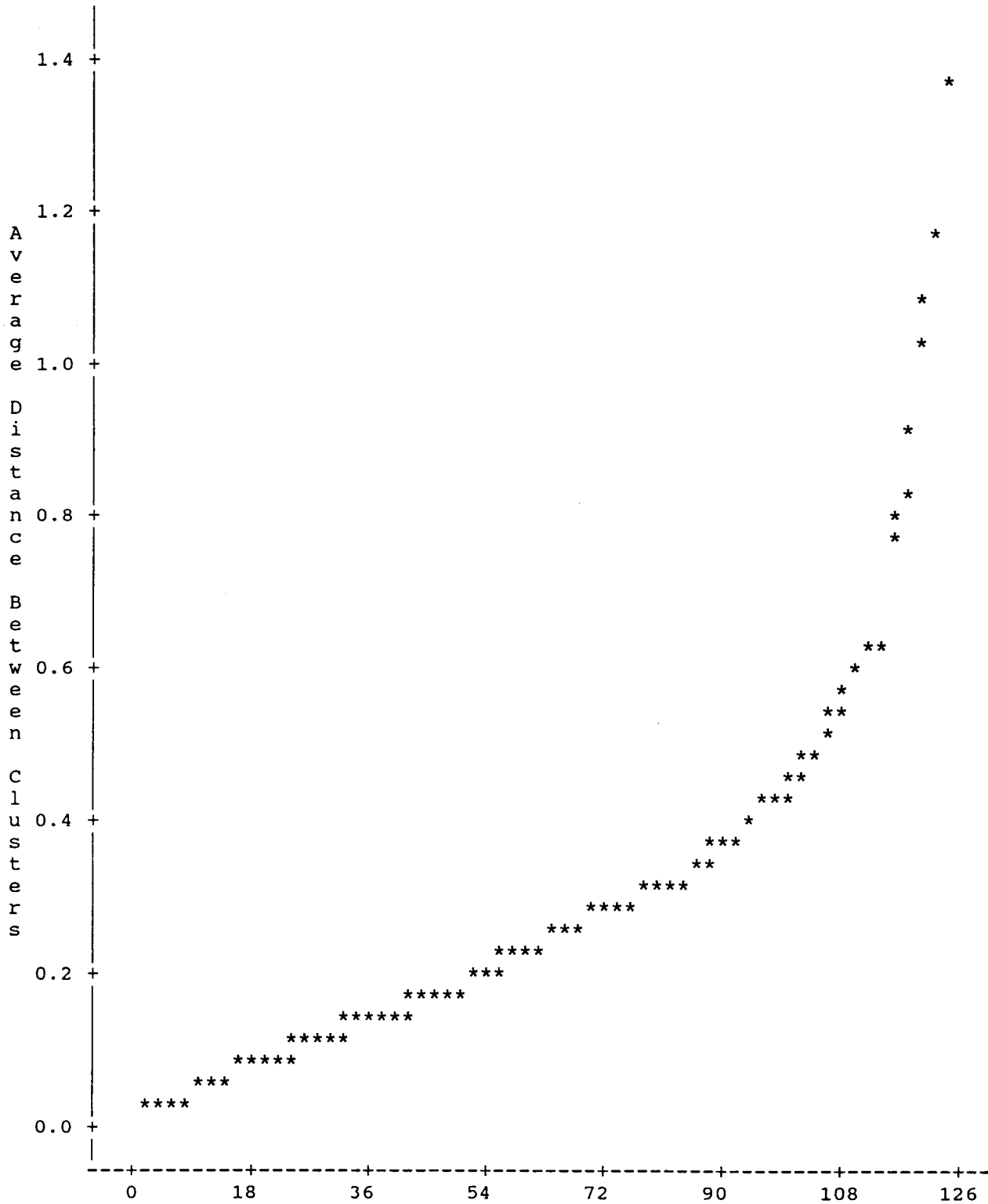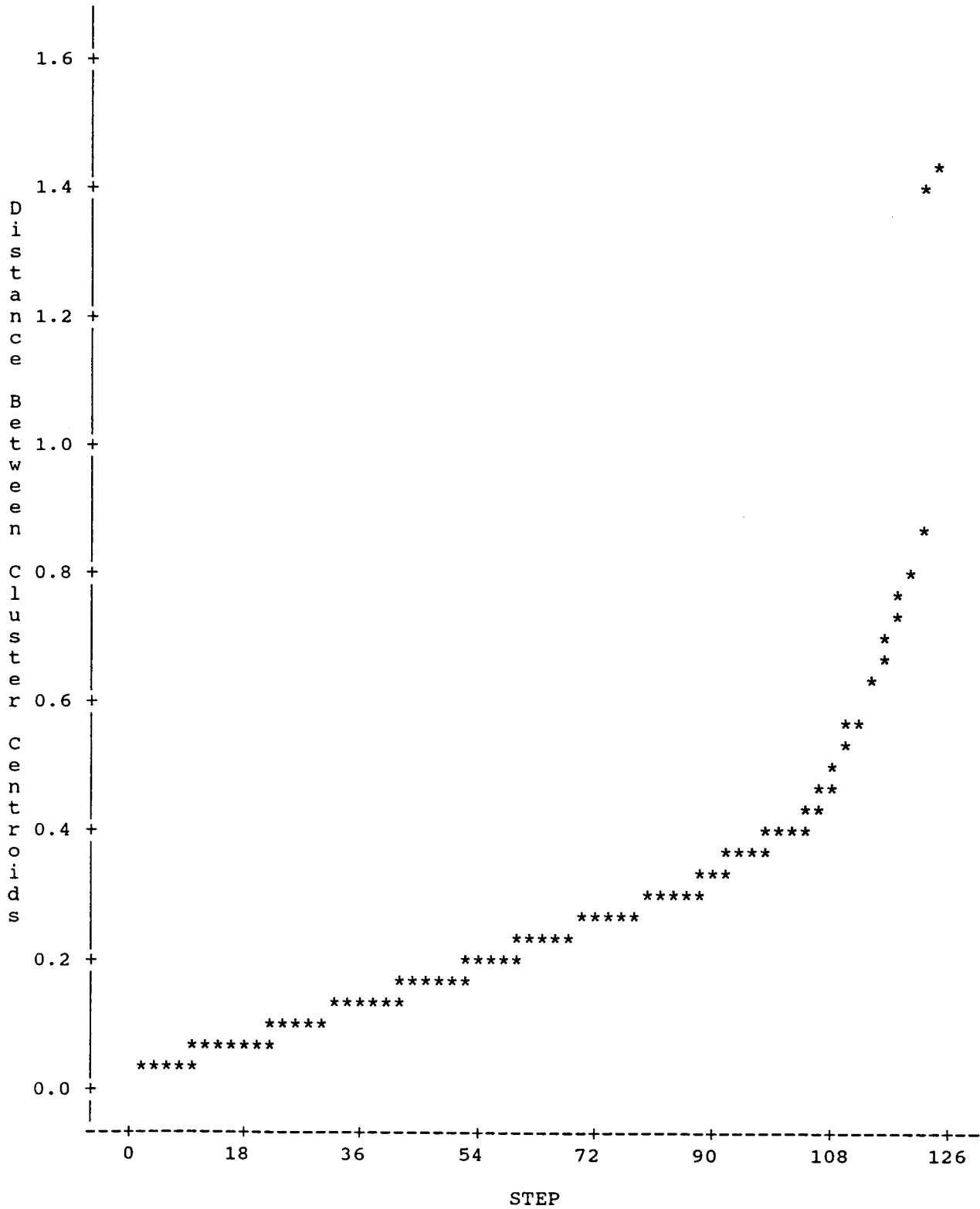
NOTE: 8 obs had missing values.  11 obs hidden.

Plot of _HEIGHT_*STEP.   Symbol used is '*'.
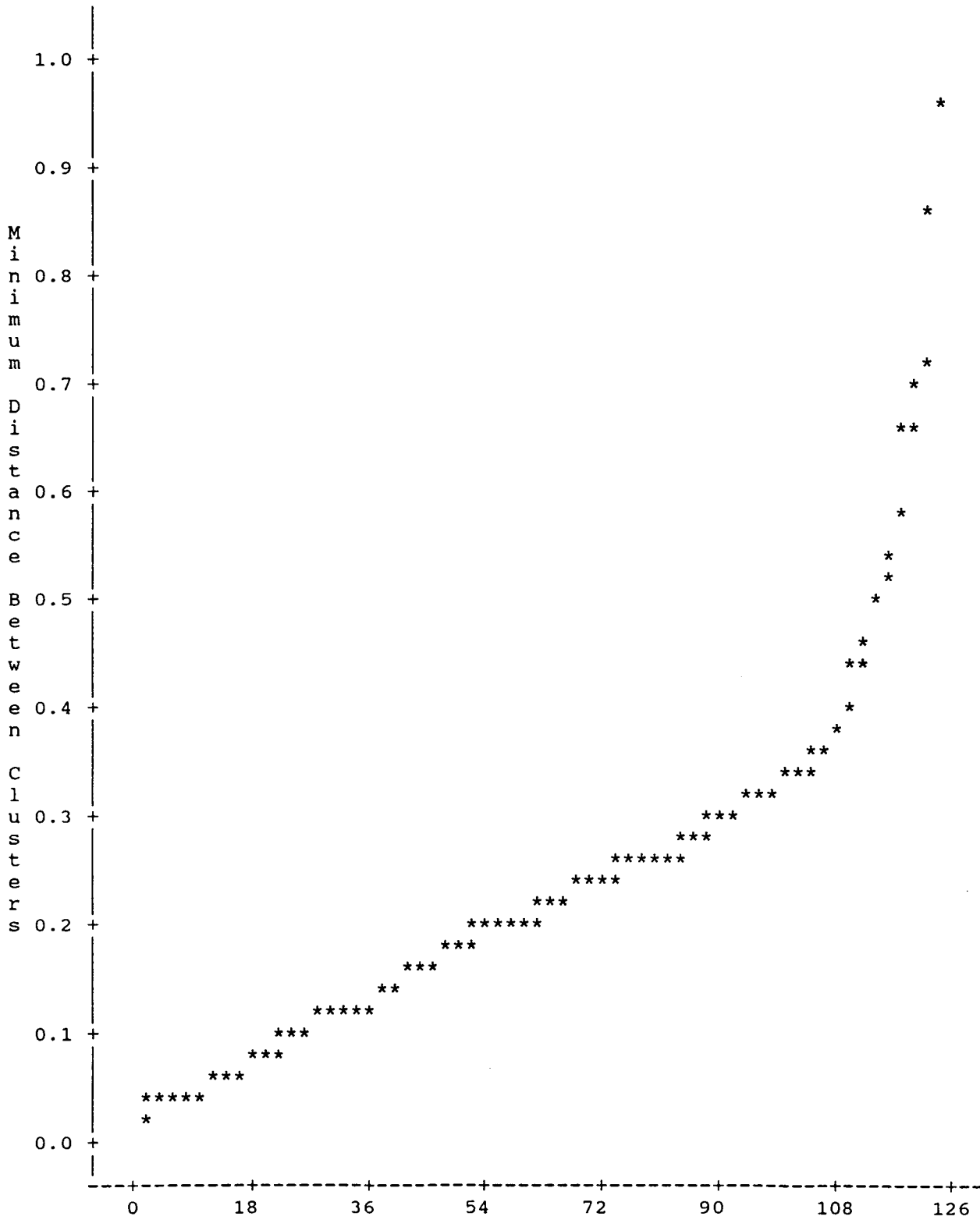
Plot of _HEIGHT_*STEP.  Symbol used is '*'.

Plot of _HEIGHT_*STEP.  Symbol used is '*'.

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally-owned public lands and natural resources. This includes fostering sound use of our land and water resources; protecting our fish, wildlife, and biological diversity; preserving the environmental and cultural values of our national parks and historical places; and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to ensure that their development is in the best interests of all our people by encouraging stewardship and citizen participation in their care. The Department also has a major responsibility for American Indian reservation communities and for people who live in island territories under U.S. administration.