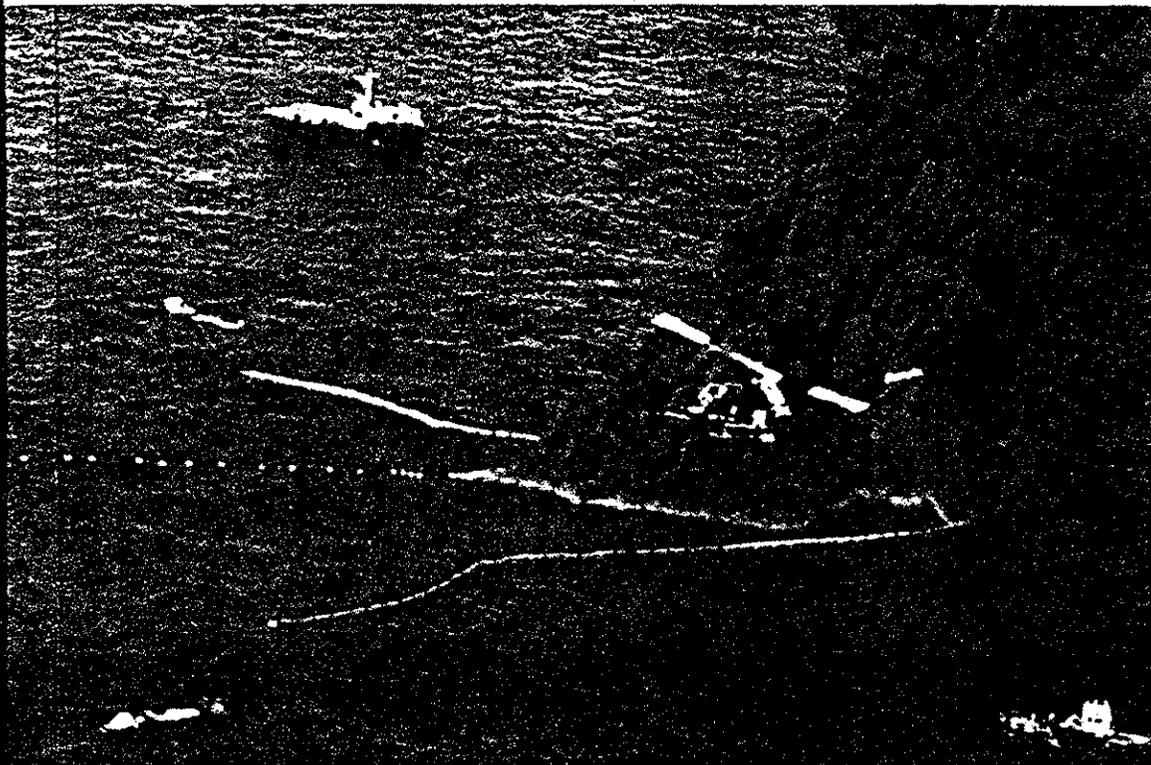


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## STUDY OF THE EFFECTS OF WEATHERING ON THE CHEMICAL COMPOSITION OF A LIGHT CRUDE OIL

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### INTRODUCTION

The weathering of spilled oil in the environment has been the subject of many research efforts in recent years. When crude oil or petroleum distillate products are accidentally released to the marine environment, they are immediately subject to a wide variety of weathering processes [1]. These processes can include: spreading, evaporation, dissolution, dispersion, photochemical oxidation, water-oil emulsification, microbial degradation, adsorption onto suspended particulate materials, sinking and sedimentation. In the short term after an oil spill (hours to days), evaporation is the single most important weathering process and causes considerable changes in chemical composition and physical properties of the spilled oil [2-9]. In the first few days following a spill, the loss caused by evaporation can be up to 75% and 40% of their volume for light crudes and medium crudes respectively. For heavy or residual oils the loss will be only about 5-10% of their volume [10]. The rapid loss of low molecular weight hydrocarbons (such as C1 to C10) can greatly reduce the biological toxicity and restrict possible adverse effects to areas near the spill site. Hence, a thorough understanding of the quantitative relationship between the weathering by evaporation and the chemical composition changes is especially important for studying the behaviour and fate of spilled oil in the environment and taking appropriate means to restore the damaged resources.

Until recently, methods did not exist to quantify the extent of oil weathering. This information is essential to the full understanding of the fate and behaviour of oil in the environment. This data is also useful for spill modelling. The key to acquiring data on oil weathering is the availability of precise and reliable chemical information. Exact quantitation of compounds in the oil can provide this crucial data. There are compounds in oil which do or do not evaporate, degrade, photooxidize, etc. Thus, examination of the ratio of the amount of two compounds, and/or two compound classes, one of which does not undergo some weathering process and one of which does, can provide this key. This method is the only way to measure the extent of a weathering process in the case of actual spills, and therefore, it is the method which can correlate laboratory data to actual spill data.

In the past decade, some laboratory experiments and field studies have been conducted to determine evaporation and measure the loss of hydrocarbons from oil. The variation in the results that have been obtained, appear to be associated with different evaporation models and experimental

techniques. There are a number of parameters which are used to describe the weathering behaviour of oils. For example, the ratio of alkanes/isoprenoids (such as n-C17/pristane and n-C18/phytane) has traditionally been used to evaluate the extent and degree of oil weathering and degradation by many researchers. However, due to the inherent composition of petroleum, and differences from oil to oil as compared with other hazardous materials, some traditional diagnostic ratios are insufficient to describe the weathering process. There have been few studies in which more comprehensive and complete chemistry data are correlated to different weathering degrees.

In this report, a light crude oil (Alberta Sweet Mix Blend, ASMB) was used to study the effect of weathering (the oil was weathered to varying degrees, 0% to 45%, w/w) on the chemical composition and concentration changes of the oil on a laboratory scale by means of evaporation. This oil was chosen as the target oil for the following reasons: (1) the chemical composition of this oil has been extensively characterized and quantified [11]; (2) this oil is often used by other laboratories in Canada and abroad as a reference material for use in the comparison of analytical methods and results. The analyses include not only the toxic constituents polynuclear aromatic hydrocarbons (PAHs) and their alkyl homologues which cause great environment concerns, but also the major oil constituents n-alkanes (n-C8 to n-C40) and isoprenoids which are useful as indicators of the weathering of oil in environment, and minor (but extremely valuable in tracing and evaluating the fate of oil) constituents biomarker compounds (triterpanes and steranes). The main objectives of this study are: (1) to obtain more complete compositional information about ASMB oil at various degrees of weathering; (2) to quantitatively determine the concentrations of all monitored components at different weathering degrees, and therefore to compute, tabulate and compare the composition changes and concentration changes of corresponding compounds; (3) to quantitatively examine the ratios of the amounts of two compounds, and/or two compound classes, one of which does not undergo weathering process and the another does; (4) to quantitatively correlate weathering percentages by evaporation with the concentration changes of the target analytes by mathematical equations. That is, to firmly base the modelling effort on complete analytical data.

The information obtained from this study will be useful for evaluating the weathering behaviour and predicting the composition and concentration changes of oil in the short term following a spill. It will also be valuable for assessing the possible biological effects and the spill damage to the environment and natural resources. This study is undertaken as part of a large effort in the Emergencies Science Division of Environment Canada and the U. S. Minerals Management Service to investigate various counter-measures in responding to oil spills and to investigate the fate and behaviour of oil for both short and long term in the environment. Further studies of the weathering effects on the chemical composition and concentration of various oils of different classes (such as medium and heavy crudes, and petroleum products as well) from different regions and studies of oil biodegradation are being conducted in this laboratory. The information obtained from further weathering studies will be combined with the information presented in this paper and used for field

application and to create oil-weathering models having operational and predictive capability.

## EXPERIMENTAL

### Materials:

All solvents including n-hexane, benzene, dichloromethane, methanol and acetone were distilled chromatographic-grade and were used without further purification. Silica gel (100-200 mesh, pore size 150 Angstroms, pore 1.2 cm<sup>2</sup>/g, active surface 320 m<sup>2</sup>/g) was purchased from Fisher Scientific (Fair Lawn, New Jersey, USA). Before use, 200-300 grams of silica gel was placed in a 41 mm I.D. x 900 mm length chromatographic column with a coarse-porosity fritted disk. The column was serially rinsed with approximately 3 x 250 mL of acetone, n-hexane and dichloromethane. The silica gel was removed from the column and left in a fumehood overnight and then completely dried in an oven at 40-50 °C. The dried silica gel was then put in a shallow tray, loosely covered with aluminum foil, and activated at 180 °C for 20 hours.

Aliphatic standards (purity > 99%) from n-C<sub>6</sub> to n-C<sub>30</sub> including pristane, phytane and 5- $\alpha$ -androstane were obtained from Aldrich (Wisconsin, USA), Sigma Chemical Company (St. Louis, USA) and Polyscience Corporation (Illinois, USA). PAH standard mixtures were purchased from Ultra Scientific (North Kingstown, RI, USA). The PAH calibration standard (SRM 1491), and deuterated internal and surrogate standards (d14-terphenyl, d10-acenaphthene, d10-phenanthrene, d12-benz(a)anthracene and d12-perylene) were obtained from the National Institute of Standards & Technology (NIST, USA) and Supelco (Bellefonte, PA, USA), respectively. The alkylated PAH compounds and dibenzothiophene (purity > 98%) were obtained from Aldrich.

The biomarker standards (purities > 96%, 0.1 mg/mL) were purchased from Chiron Laboratories A. S. (Trondheim, Norway). Triterpane standards included C<sub>27</sub>, 17 $\alpha$ (H)-22, 29,30-trisnorhopane, C<sub>30</sub>, 17 $\beta$ (H) 21 $\beta$ (H)-hopane, C<sub>30</sub>, 17 $\beta$ (H) 21 $\alpha$ (H)-hopane, and C<sub>28</sub>, 17 $\beta$ (H) 21 $\alpha$ (H)-30-norhopane. Sterane standards were C<sub>21</sub>, 5 $\beta$ (H)-pregnane, C<sub>22</sub>, 20-methyl-5 $\alpha$ (H)-pregnane, C<sub>24</sub>, 5 $\beta$ (H)-cholane, and series of C<sub>27</sub>, C<sub>28</sub> and C<sub>29</sub> (20R  $\alpha\alpha\alpha$ , 20R  $\beta\alpha\alpha$ , 20S  $\alpha\alpha\alpha$ , and 20R  $\alpha\beta\beta$ ) steranes.

The Alberta Sweet Mix Blend crude oil is the standard oil used for dispersant treating tests in the Emergencies Science Division (ESD), Environment Canada. Its density is 0.84 g/mL and it has a sulphur content of 0.55% (w/w).

### Weathered ASMB Oil:

A new oil-evaporation technique applying a lab-scale rotary evaporator was designed and used for this purpose. The oil-weathering system consists of a Wheaton N-10 Spin Vap with a 10 L flask, an integral Haake F3-CH Circulating Water Bath (capacity 14 L), and a Millipore Vacuum Pump. The bath temperature can be controlled to  $\pm 0.5$  ° and the thermo control range is 1 °C to 120 °C. The rotation speed can be continuously varied from 10 to 135 rpm.

Testing with the rotary evaporator at temperatures of 20, 40, 60, and 80 °C indicated that evaporative losses of oil were similar to that under actual environmental conditions (wind speed 30 km/hour, oil slick thickness 1mm) (12).

The following evaporation procedure was used to obtain the weathered ASMB oils with varying weathered percentages from 0% to 45%: (1) Fill bath with distilled water and bring to desired temperature (usually start weathering at 60 °C); (2) weigh sample flask, then add approximately 2 L of ASMB crude oil into the tared roto flask, and take the final weight; (3) place flask on evaporator and run at full speed, 135 rpm. Maintain a flow of air (13 L/min) through the flask by leaving the vacuum release stopcock open; (4) after set periods of time, the sample flask is removed, reweighed and then the percent weathered (wt %) is calculated. A sample of about 5 ml is taken at approximately every ~5% weathering; (5) sampling is continued for about 100 hours (rotovaping time), or until there is little or no change in the % weathered over an 8 hour period. It took 100 hours at 80 °C to get the most weathered sample (45%). In contrast, it only took 30 minutes at 60 °C to obtain 10% weathered oil.

Some advantages of this method are obvious: (1) the weathered percentages of any target oil can be precisely controlled and then directly correlated to compositional changes of the target weathered oil; (2) by plotting weight % lost versus time, it is possible to determine a point at which the evaporation rate is sufficiently slow that the oil may be considered to have achieved the maximum evaporative loss likely to be observed under the conditions of a marine spill; (3) it is also possible, by plotting weight % lost versus viscosity to relate evaporative loss directly to a physical measurement which is easily obtainable in the field.

#### Column Chromatography Fractionation:

The chromatographic column equipped with a Teflon-stopcock (10.5 mm I.D. x 200 mm length) was plugged with Pyrex glass wool at the bottom, and serially rinsed with small volumes of methanol, hexane and dichloromethane, and allowed to dry. The column was dry-packed with 3 grams of activated silica gel with tapping to settle the silica gel, and topped with about 0.5 cm of anhydrous sodium sulphate. The column was conditioned with 20 mL of hexane, and the eluent was discarded. Just prior to exposure of the sodium sulphate layer to air, a 200 µL aliquot of weathered ASMB oil (100 mg/mL in hexane) was quantitatively transferred onto the column using an additional 3 mL of hexane to complete the transfer. All eluents up to this point were discarded. Twelve mL of hexane were used to elute aliphatic hydrocarbons, and 15 mL of 50% of hexane in hexane (v/v) were used to elute aromatic hydrocarbons. Half of the benzene in hexane (v/v) were used to elute aromatic hydrocarbons. Half of the hexane fraction was labelled "F1" and used for analysis of aliphatics, tripteranes and steranes; half of the 50% benzene fraction was labelled "F2" and used for analysis of target PAHs and alkylated PAHs. The remaining half of F1 and F2 were combined into a fraction (labelled as "F3") and used for the determination of total petroleum hydrocarbons. These three fractions were concentrated to a preinjection volume of 0.5 to 1.0 mL under a nitrogen stream in a pre-calibrated centrifuge tube.

#### Capillary Gas Chromatography

The analysis for individual n-alkane, pristane and phytane, and total petroleum hydrocarbons ( $C_{60}$  through  $C_{40}$ ) was performed on a Hewlett Packard (HP) 5890 gas chromatograph equipped with a flame ionization detector (FID) and an HP 7673 autosampler. The column was 30 m x 0.32 mm I.D. x 0.25 µm film DB-5 fused silica capillary column (J&W, Folsom, CA, USA). The carrier gas was helium (2.5 mL/min). The injector and detector temperatures were set at 290 °C and 300 °C, respectively. The temperature was programmed from 50 °C with 2 minutes hold to 300 °C at 6 °C/min, and 16 min hold at 300 °C. A 1-µL aliquot was injected in the splitless mode with a 1 min purge-off.

The analysis of target PAHs, alkylated PAH compounds, and biomarker compounds were performed on a HP 5890 gas chromatograph - 5972 mass spectrometer (GC-MS). System control and data acquisition were achieved by HP G1034C MS ChemStation (DOS series). The MSD was operated in selected ion monitoring (SIM) mode for quantitation of target compounds. The columns used were 30 m x 0.25 mm I.D. x 0.25 µm film HP-5 fused silica columns. The chromatographic conditions were as follows: carrier gas, helium (1.0 mL/min); injection mode, splitless; injector and detector temperature, 290 °C and 300 °C, respectively; temperature program for target PAHs, 90 °C for 1 min, then 25 °C/min to 160 °C, and then 8 °C/min to 290 °C and hold 15 min; temperature program for alkylated PAHs and biomarker compounds, 50 °C for 2 min, then 6 °C/min to 300 °C, hold 16 min.

#### QUANTITATION

The concentrations of individual n-alkanes, selected isoprenoids such as pristane and phytane, and total petroleum hydrocarbons were determined by high resolution capillary GC/FID. Prior to sample analysis, the instrument was calibrated using a standard solution, which was composed of  $C_6$  through  $C_{30}$  n-alkanes, pristane and phytane, and 5- $\alpha$ -androstane as the internal standard. A 5-point calibration was established demonstrating the linear range of the analysis. The relative response factor (RRF) for each hydrocarbon component was calculated relative to the internal standard.

Quantitation of target PAHs and alkylated PAH homologues was performed on GC/MS in SIM mode with RRFs for each compound determined during instrument calibration. The ions monitored were 128, 142, 156, 170, and 184 for alkyl homologues of naphthalene; 178, 192, 206, 220, and 234 for phenanthrene alkyl series; 184, 198, 212, and 226 for dibenzothiophene alkyl series; 166, 180, 194 and 208 for fluorene alkyl series; and 228, 242, 256, and 270 for chrysene alkyl series. The RRF for target PAH compounds were calculated from authentic standards. PAH alkyl homologues were quantified by using the straight baseline integration of each level of alkylation. Although the alkylated homologue groups can be quantified using the RRF of the respective unsubstituted parent PAH compounds, it is preferable to obtain the RRFs directly from alkylated PAH standards, if they are commercially available. It has been found that 30% to 150% of errors may be introduced if alkylated

naphthalene homologues are quantified using the RRF obtained from the parent naphthalene [11]. In this work, the RRFs obtained from 1-methyl-naphthalene, 2-methyl-naphthalene, 2,6-dimethyl-naphthalene, 2,3,5-trimethyl-naphthalene, and 1-methyl-phenanthrene were used for quantitation of 1-methyl-naphthalene, 2-methyl-naphthalene, C<sub>2</sub>-naphthalene, C<sub>3</sub>-naphthalene, and C<sub>1</sub>-phenanthrene in oil, respectively. The RRFs of 2,3,5-trimethyl-naphthalene and 1-methyl-phenanthrene were used for quantification of C<sub>2</sub>-naphthalene, and C<sub>2</sub>, C<sub>3</sub>, and C<sub>1</sub>-phenanthrenes respectively. The selection criteria for the integration and reporting of each alkylated homologue were based primarily on pattern recognition and the presence of selected confirmation ions.

The average RRF for the biomarker compound C<sub>30</sub> 17β(H) 21α(H)-hopane was determined relative to the internal standard C<sub>30</sub> 17β(H) 21β(H)-hopane. The average RRF for C<sub>30</sub> 17β(H) 21α(H)-hopane (m/z 191) was used for quantitation of C<sub>30</sub> 17α(H) 21β(H)-hopane and other triterpanes in the oil sample. For quantitation of steranes, the RRF of C<sub>29</sub> 20R ααα-ethylcholesterane monitored at m/z 217 was determined relative to C<sub>30</sub> 17β(H) 21β(H)-hopane monitored at m/z 191, and then the average RRF of C<sub>29</sub> 20R ααα-ethylcholesterane was used for estimation of sterane compounds in the oil.

## RESULTS AND DISCUSSION

### Composition and Concentration Changes of Aliphatics

Figures 1A through 1D show the gas chromatographic profiles of aliphatic compounds (F1) of ASMB oil at varying different weathered percentages (0%, 29.8%, 34.5%, and 44.5%). Figures 2A through 2C show the representative GC/MS chromatograms (0%, 29.8%, and 44.5%) of the m/z 85 fragment (one of the characteristic fragments for n-alkanes) of saturated hydrocarbons (F1). A significant advantage of using highly selective SIM mode is that it provides clean traces (compared to GC/FID chromatograms) and detailed compositional information about n-alkanes in oil with minimum interferences from other aliphatic hydrocarbons. Another prominent feature is that the five important isoprenoids in the C<sub>15</sub>-C<sub>19</sub> range—i-C<sub>15</sub>, i-C<sub>16</sub>, i-C<sub>18</sub>, i-C<sub>19</sub> (pristane), i-C<sub>20</sub> (phytane)—are very distinguishable. These chromatograms are not particularly useful for determining the source of the spill, but they give clear information on the degree of weathering or freshness of the samples, which are indicated by the distribution of n-alkane m/z 85 fragments and the hump in the bottom of the chromatograms.

Figures 1 and 2 demonstrate a number of chemical changes that occurred during the evaporation process: (1) the first major change in the oil is the loss of the relatively volatile low molecular weight (MW) aliphatics through evaporation; (2) build-up of less volatile high MW aliphatic components; (3) significant increase of the "hump" (which appears as the area between the lower baseline and the curve defining the base of resolvable peaks) representing the GC unresolved hydrocarbons.

Table 1 summarizes quantitation results of n-alkanes from n-C8 to n-C40 plus pristane and phytane in the weathered ASMB oils. In order to quantitatively

compare the n-alkane concentration changes on the same basis, the ratios of n-alkanes relative to n-C30 are calculated and tabulated in Table 2. n-C30 is chosen as reference because it is well-resolved, highly degradation-resistant, and has relatively high abundance. Figures 3A through 3F depict graphically the n-alkane distribution as determined by using the integrated peak areas by GC/FID and internal standard method. For comparison purpose, the same concentration scale is applied to Figures 3A to 3F. Figure 4 plots the ratios of n-alkanes relative to n-C30 in weathered oil samples versus carbon numbers.

For the source ASMB oil, the most abundant n-alkanes are around n-C8 to n-C17, and the abundance of n-alkanes gradually decrease as the carbon number increases. As the weathered percentages increase, the most abundant aliphatic components shift to higher carbon number n-alkanes. For example, the n-alkane of the highest concentration before n-C16 are n-C9 for 0% weathered oil (4.8 mg/g oil) and n-C16 for 44.5% weathered oil (5.7 mg/g oil), respectively. It is noted that even the ASMB oil was weathered from 0% to 45%, the sum of n-alkanes for six weathered ASMB oil samples was not changed much (in the range of 70-76 mg/g oil). This can be explained as the result of the combination of two opposite effects: one is the loss of low MW aliphatic components, and another is the buildup of high MW aliphatic components by evaporation. Due to the very similar volatilities, the ratios of n-C17/pristane, n-C18/phytane, and pristane/phytane are virtually unaltered (see Table 1). The values of carbon preference index (CPI), defined as the sum of odd n-alkanes over the sum of even n-alkanes, are found to be around 1.0 for all samples, which is a characteristic indication of petroleum. It can be clearly seen from Figure 4 that from n-C20 to n-C22, all data points from six weathered oils converge, indicating that relative to n-C30, the high MW n-alkanes (e.g. >C22) are virtually undegradable by evaporation. The variability in Fraction 1 is primarily in proportion of low MW aliphatics which are most susceptible to evaporation.

Based on the quantitation results, a mathematical equation has been developed to quantitatively describe the correlation of oil component concentrations to the weathered percentages by evaporation as follows:

$$C_{\text{conv}} = C_{\text{det}} (1-P) \quad (1)$$

where: C<sub>conv</sub> - defined as converted concentrations of oil components in weathered samples, which is equivalent to the concentrations in the source oil;

C<sub>det</sub> - concentrations of oil components in weathered samples determined from GC analyses;

P - weathered percentages of oil by weight (%).

Table 4 lists the converted concentration values of n-alkanes in weathered ASMB oil samples obtained from Equation 1. Figure 5 compares plots of C<sub>det</sub> (5A, top) and C<sub>conv</sub> (5B, bottom) of several selected n-alkanes (n-C10, n-C12, n-C16, n-C20, n-C25, and n-C30) versus weathered percentages.

There are two opposing factors which affect the concentration changes

of oil components during the evaporation process. The first factor is evaporation, which results in the concentration decrease of oil components; the second is volume reduction by evaporation, which results in the concentration increase of oil components. The importance of Equation 1 is that it eliminates the effect of volume reduction and focuses the effect of evaporation on the oil component concentration changes. Thus, the composition and concentration changes are compared on an equal basis. Figure 5A reflects the combined effects of evaporation and volume reduction of oil aliphatics, while Figure 5B directly reflects the effect of the single factor evaporation on the composition changes, based on the assumption that the oil volume was not altered during the weathering process. For example, the plots of the measured concentration of n-C16, n-C20, n-C25, and n-C30 versus weathered percentage are all upward, as shown in Figure 5A; however, after the effect of the volume reduction is eliminated, the plot of n-C16 becomes downward and the plots of n-C20, n-C25, and n-C30 are parallel to the x-axis, indicating that the concentration of n-C16 is actually decreased, while the mass of n-C20, n-C25, and n-C30 are almost unchanged. Table 3 and Figure 5B clearly demonstrated that: (1) from C8 to C22, the evaporation rate is a function of carbon chain length with shorter chain n-alkanes decreasing in concentration more rapidly than longer n-alkanes; (2) n-alkanes with carbon number greater than 22 virtually are not lost by evaporation; (3) n-C8, n-C9, and n-C10 to n-C12 are completely lost as the weathered percentages approach 30%, 35% and 45%, respectively; (4) pristane and phytane show small evaporative loss as well, in approximately the same rates as n-C17 and n-C18. Some studies by other researchers [13-18] and the study on various oils with varying natures recently conducted in our laboratory [19] have shown that microorganisms are readily capable of preferentially metabolizing alkanes. Therefore, if the ratios of n-C17/pristane, n-C18/phytane, and pristane/phytane show some dramatic changes, it is often an indication of involvement of biodegradation.

Based on the findings discussed above, a weathering index (WI) by evaporation (Equation 2), defined as the concentration sum of n-C8, n-C10, n-C12, and n-C14 divided by the sum of n-C22, n-C24, n-C26, and n-C28, is introduced to describe the weathering behaviour of oil and to evaluate the weathering degrees of real samples.

$$WI = (n-C8 + n-C10 + n-C12 + n-C14) / (n-C22 + n-C24 + n-C26 + n-C28) \quad (2)$$

Clearly, the value of WI is sensitive to the changes of weathering degree. As the weathered percentages increase, the value of the numerator significantly decreases and the denominator, in contrast, grows larger. A significant feature of using Equation 2 is that the selected eight n-alkanes are well-resolved and have relatively high abundances, and therefore the ratio can be accurately determined. The values determined according to Equation 2 are 2.70, 2.23, 1.70, 1.23, 0.88, and 0.27 for the six standard weathered samples, respectively. For samples in which the low-boiling saturated hydrocarbons n-C8 to n-C14 are completely lost, the weathering index approaches zero. If the weathering indices are drawn against the weathered percentages, a straight line is obtained (see

Figure 6). Figure 6 can be used to estimate the weathering extent and degree of real field-collected oil samples through the preferential depletion of n-C8 to n-C14 relative to virtually undepleted n-C22 to n-C28. For example, Equation 2 has been successfully used to estimate the weathering degrees of residues from the Newfoundland Offshore Burn Experiment [20].

#### Composition and Concentration Changes of Aromatics

Figures 7A, 7B, and 7C show the GC/MS SIM chromatograms of the aromatic compounds (F2) of ASMB oil samples at 0%, 29.8%, and 45% weathered. Table 4 summarizes the quantitation results of alkylated PAH homologues in 6 weathered ASMB oils. For comparison purposes, the converted PAH data obtained by using Equation 1 are also shown in Table 4 (right side). Figures 8A through 8F depict graphically the target alkylated PAH homologue distributions. For comparison purposes, the same concentration scale is applied to Figure 8. The relative compositions of 5 groups of alkyl PAH homologues are listed in Table 5. The decrease of the relative composition percents of C0- and C1- naphthalenes as the weathered percentage increases are the most pronounced among the 5 groups of alkyl PAH homologues (from 7.7% and 19.3%, decreased to 0% and 2.4%, respectively).

The major compositional changes of PAHs as the weathered percentage increases are summarized as follows:

(1) Among 126 identified aromatics, 33 compounds are alkyl benzenes [11]. A significant feature of the early eluted alkylated benzene (1 ring) series is their high abundance, especially the first-eluted C2-benzenes and C3-benzenes, in comparison with PAHs (Figure 7A). As the weathering percentage increases, the concentration of alkyl benzenes dramatically decreases (Figure 7B).

(2) When the weathering percentage increases from 0% to 45%, the low-boiling alkyl benzenes before retention time ~14 minutes were completely lost (Figure 7C).

(3) Pronounced decrease in naphthalene and its alkyl homologues relative to other PAHs. Among the 5 target alkylated PAH homologues, the most abundant alkyl homologues of naphthalene (2-rings) are the most easily evaporated, followed by alkyl homologues of fluorene (3 rings, 13 carbons), and benzothiophene (3-rings, 14 carbons). In general, the larger the number of rings, the more stable the compounds.

(4) Most homologous group shows the same degradation trend: C0>C1>C2>C3>C4.

(5) No degradation of alkyl chrysenes (4 rings) was observed, and they exhibit the most pronounced relative increase in abundance due to the lowest vapour pressures and the highest resistance to degradation among the 5 target PAH homologues.

(6) No noticeable sign of loss by evaporation was observed for C2-, C3-, and C4-phenanthrenes, C2- and C-3 benzothiophenes and fluorenes.

(7) For methyl-naphthalenes, the isomeric ratio of 2-methyl-naphthalene (2-M-N) to 1-methyl-naphthalene (1-M-N) was similar (2-M-N : 1-M-N = 1.3) in all but the most heavily weathered residue (44.5%) where the naphthalene was

completely lost and the 1-M-N was preferentially preserved (2-M-N : 1-M-N = 0.99);

(8) One of the most pronounced features of the extracted ion profile is that the methyl-dibenzothiophenes (M-D) show three well-resolved isomer peaks. They are identified as 4-M-D, 2-/3-M-D, and 1-M-D [11]. It is noted that the isomeric distribution within the C1-dibenzothiophenes exhibits great consistency in their relative ratio (1.00:0.76:0.28, Table 4) for 6 weathered oils.

We have found that petroleum from different geographic regions all contain these three isomers with different relative ratios [21]. Hence, this valuable ratio information can be used as marker to distinguish and identification of crudes and their products from each other. Also, this ratio can be used as an indicator for biodegradation. Microbial degradation has been shown to be isomer specific for aromatic compounds [17, 18, 22, 23], especially for isomers of methyl-dibenzothiophenes [19]. Thus, if biodegradation is involved, this ratio will greatly be altered, and the conclusion that biodegradation took place can then be drawn.

Figure 9 plots the relative abundances of 22 alkylated PAH homologues to C3-phenanthrenes (C3-P, C3-P series are chosen as reference for it is in relatively high abundance and no lost occurred by evaporation), in order to compare the PAH concentration changes on the same basis. Figures 10A through 10F plot  $C_{2m}$  and  $C_{2m}^{conv}$  of alkyl naphthalenes (10A and 10B), alkyl phenanthrenes (10C and 10D), and alkyl fluorenes (10E and 10F) versus the weathered percentages, respectively.

The gradual build-up in the relative abundances of alkyl phenanthrene and alkyl fluorene series are obvious (10C and 10E), while alkyl naphthalenes (10A) show some complicated trends as the combined results of two opposing effects on their concentration changes (decrease in concentration due to evaporation loss, and increase in concentration due to volume reduction). In contrast, Figure 10B, 10D, and 10F are clear and simple: (1) the slope of the naphthalene plot is significantly negative, indicating that its concentration decreases rapidly as the weathered percentage increases; (2) the alkyl naphthalene series and alkyl fluorene series, with the exception of C4-naphthalenes and C3-fluorenes (they are almost parallel to x-axis), exhibit downward trends in the order of C4 < C3 < C2 < C1 < C0, which means the alkyl naphthalene and fluorene series have the degradation order of C0 > C1 > C2 > C3 > C4; (3) phenanthrene only shows small degradation by evaporation weathering; (4) the plots of C2-P, C3-P, C4-P, C2-F, and C3-F are parallel to x-axis, indicating these components are virtually not lost by evaporation.

#### Composition and Concentration Changes of Biomarker Compounds

Studies on separation and identification of biomarker compounds in oil samples have greatly increased in recent years [24-32]. This is because of the importance of biomarker compounds in the recognition and distinction of oil sources, of their usefulness in oil/oil correlations, and especially of their high resistance to microbial degradation relative to aliphatic and aromatic compounds. Among the various types of biomarkers, triterpanes and steranes

are the best choice for source identification purposes due to their high molecular weight and relatively high concentration in crude oil. It has been found that hopanes have a very high resistance to photochemical and microbial degradation in comparison to the aliphatic and aromatic compounds. Hence, the analysis of biomarker hopane compounds is another valuable means to estimate percent of oil depletion, especially for highly weathered oil which has undergone not only evaporation weathering but also biodegradation, photooxidation and other kinds of degradation.

Common features of the mass spectra of triterpane and sterane compounds are a relatively large parent ion, an important parent minus a methyl ion, and a basepeak at m/z 191 and 217 respectively. It is noted that triterpane compounds in ASMB oil are distributed in a wide range from C<sub>19</sub> to C<sub>35</sub> with a series of C<sub>19</sub>-C<sub>28</sub> tricyclic and various pentacyclic hopanes being quite prominent. As examples, Figure 11 and 12 show the GC/MS chromatograms of the triterpane distribution (11A and 11B) and sterane distribution (12A and 12B) for 0% and 44.5% weathered ASMB oil samples, respectively. In addition to the ubiquitous regular hopanes, C<sub>27</sub> 17 $\alpha$ (H) 18 $\alpha$ (H) 21 $\beta$ (H)-25, 28, 30-trisnorhopane and C<sub>28</sub> 18 $\alpha$ (H) 21 $\beta$ (H)-30-norhopane were detected. They were identified based on the comparison of m/z 177 and 191 fragment chromatograms, and further confirmed by strong parent ions (370 and 398) and parent minus a methyl ions (355 and 384) at the exact same retention times [11]. The identification of isomeric steranes are mainly based on the recognition of m/z 217 fragment distribution pattern, the relative intensities of m/z 149 to 151, and of m/z 217 to 218 [11]. From Figure 12, it can be seen that the dominance of C<sub>27</sub> and C<sub>28</sub> steranes is apparent. A significant contribution from diasteranes is also noted. The most notable feature of sterane distribution is that the epimers of  $\alpha\beta$  C<sub>27</sub>, C<sub>28</sub>, and C<sub>29</sub> steranes give much higher intensities of the m/z 218 ion than of the m/z 217 ion.

As a result, 8 tricyclic (C<sub>19</sub> to C<sub>28</sub>), 4 tetracyclic (C<sub>27</sub> and C<sub>28</sub>), 19 pentacyclic triterpanes (C<sub>27</sub> to C<sub>35</sub>), and 22 sterane compounds (C<sub>20</sub> to C<sub>29</sub>) were identified in all six weathered oil samples.

Figures 11 and 12 suggest that weathering has not altered the overall pattern and profile of the hopane and sterane distribution at all. Gradual buildups in the relative abundances of hopane and steranes from 0% to 45% weathered samples are apparent. Even by eyeball comparison, it can be readily seen from Figure 11 that the intensities of hopanes relative to the internal standard C30- $\beta\beta$ -hopane for 45% weathered oil are significantly higher than 0% weathered oil.

The detailed quantitation results for triterpanes and steranes are presented in Tables 6 and 7 respectively. The values in the right side of Tables 6 and 7 are the converted concentrations obtained from Equation 1. Tables 6 and 7 demonstrate that the converted concentrations for triterpanes and steranes are virtually constant. The sum of the measured concentrations (C<sub>meas</sub>) of hopanes for six weathered oil samples are 992, 1074, 1195, 1325, 1428, and 1742  $\mu\text{g/g}$  oil, respectively, while the corresponding sum of the converted concentrations (C<sub>conv</sub>), in contrast, are 991, 968, 962, 928, 935, and 967  $\mu\text{g/g}$  oil, showing very good consistency. Plotting the concentrations of the

representative compounds C23, C24, Ts, Tm, C29  $\alpha\beta$ -, and C30  $\alpha\beta$ -hopanes against the weathered percentages, lines parallel to x-axis are obtained (Figure 13). Table 8 summarizes relative ratios of tricyclic triterpanes, pentacyclic hopanes, and C27 to C29 steranes. The most striking feature from Table 8 is that both hopanes and steranes show a great consistency in the relative ratios of paired two biomarker compounds and/or two biomarker compound classes. For example, the ratios of the paired hopanes C23/C24, Ts/Tm, and C29 $\alpha\beta$ /C30 $\alpha\beta$  for six weathered oil samples are all around 2.0, 0.79, and 0.67 respectively, and the isomeric ratios (20S/(20S+20R)) within C27, C28, and C29 sterane series are all around 0.39, 0.57, and 0.47, respectively.

A general conclusion drawn from study of the effect on the chemical composition of biomarker compounds is that tricyclic and tetracyclic triterpanes, C27 to C35 hopanes, regular steranes and rearranged diasteranes were unaltered during the evaporation weathering process. As for the resistance of biomarker compounds to microbiological degradation, several studies have shown that many biomarker compounds are relatively highly-resistant to microbiological degradation [15, 18, 33-35]. A GC/MS method using biomarker compounds especially using the relative abundance ratio of C29/C30 hopanes to characterize the 22-year-old spilled Arrow oil has been developed in our laboratory [36]. The facts found from this study demonstrate the uniqueness and usefulness of biomarker compounds for identification and characterization of highly and/or long-term weathered oil samples.

#### Determination of Weathered Percentages of Weathered Oil Samples

Equation 1 can be rewritten in the form as shown in Equation 3:

$$P = C_w/C_s - 1 \quad (3)$$

where:

- C<sub>w</sub>: the concentration of selected compounds in the weathered samples, which do not undergo weathering;
- C<sub>s</sub>: the concentrations of the corresponding compounds in the source oil;
- P: weathered percentages of the weathered samples by weight.

Equation 3 implies that the weathered percentages of the oil can be determined by quantifying the selected compounds in the weathered samples which are not lost during the weathering process, and by comparison with the concentrations of the corresponding compounds in the source oil.

Equation 3 has been used to determine the weathered percentages of some weathered ASMB oil samples and the results were compared with those found by gravimetric method. These weathered samples were obtained using the so-called pan evaporation technique which is different from the rotovap technique described in "Experimental" section. The following briefly describes this pan evaporation weathering technique:

The pan evaporation unit has been constructed using an open pan balance (Mettler 4000) capable of measurement precision to 0.01 g. The balance is coupled to a computer for data-logging. A commercial program,

"Acquire", was purchased and modified to allow time intervals to be increased geometrically.

A glass evaporating pan is used. For most experiments, a single pan having a diameter of about 140 cm is used. This is a standard petri dish. Other diameters were used during experiments to measure the area effect. Oil of the desired weight is placed into the pan and the computer logger started. A pneumatic stirrer is put into place. This consists of a syringe with a low air-flow (175 cc/min) through it. This prevents the formation of a "skin" on top of the oil, which is a major interference in these types of experiments. The "skin" formation will slow evaporation by as much as an order or two in magnitude. The experiment is run until the weight loss is very minimal. Experiments are run for one-half day in the case of a gasoline which evaporates quickly and for several days for a heavy residual oil. At the end of the experiment, the computer is manually triggered to take a final reading and the remaining oil is saved for potential future physical property and chemical composition analysis. The weight difference between the starting oil and the finished product can be measured with an accuracy of  $\pm 0.03$  grams. This yields a typical maximum error of about one part per thousand.

Three weathered samples were randomly collected and analyzed together with the original ASMB oil. Thirteen target compounds and compound classes were quantified and their concentrations were used to determine the weathered percentages by using Equation 3. Table 9 summarizes the quantitation results. The average values of weathered percentages are determined to be 26.9 $\pm$ 2.0%, 34.3 $\pm$ 1.4%, and 40.3 $\pm$ 2.1% for weathered sample 1, 2 and 3 respectively. The corresponding values obtained by the gravimetric method are 25.9%, 33.6% and 38.6%. Clearly, these two sets of results from two totally different methods are in good agreement.

#### CONCLUSIONS

A method applying a lab-scale rotary evaporator to study the effect of weathering on the chemical composition and concentration changes of oil has been developed. The features and advantages of this study are summarized as follows:

- (1) The key to acquiring data on oil weathering is the availability of precise and reliable chemical data. These data are essential to fully understand the fate and behaviour of oil in the environment and predict oil property changes and the concentration of toxic components remaining in the oil. This study provides an effective means to obtain such information;
- (2) This study quantitatively correlates the degree of weathering by evaporation to the chemical composition changes of the oil. The chemical changes as the oil weathered were documented within homologous series (such as n-alkanes, alkylated PAHs, and biomarker compounds), between homologous series (such as n-alkanes and isoprenoids, alkyl naphthalenes and alkyl phenanthrenes), and within isomeric mixtures (such as methyl/dibenzothiophenes).

(3) The distribution of selected n-alkanes, alkylated aromatics, and triterpanes and steranes offers unique, sensitive and relatively stable fingerprints for examining the weathering behaviour of oil in the environment. The "pattern recognition" plots involving more than 100 important individual oil components and component groupings would permit deduction of a best set of values for exposure to evaporation weathering. It should be noted that there are two opposing effects during evaporation weathering: one is the loss of oil components due to evaporation, and another is build-up of oil components due to volume reduction. The complex behaviour of some components and component groups during weathering can be explained as the results of the combination of these two opposing effects.

(4) The mathematical equations derived from this work are relatively simple and very useful. They can be utilized to estimate the weathering degree and extent of oil with the weathering process being dominated by physical weathering.

(5) To increase the reliability of determination of weathered percentages, multiple fingerprints should be considered and the concentration changes of multiple target components and component classes should be calculated not only relative to themselves but also in the overall context of the oil composition change.

(6) It should be possible in principle to use the comprehensive information about chemical composition changes of oil as the oil weathering degree change, such as shown in this study, to construct a relatively simple model with oil weathering predictive capability describing the weathering fate of oil in the environment. In order to achieve this ultimate goal, more studies on weathering of various oils are being conducted in this laboratory to apply the method presented in this work and other methods to best correlate the oil chemical composition and property changes to evaporation, dissolution, and even biodegradation and photooxidation.

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TABLE 1 Comparison and Concentration Changes of Aliphatics Constituents in Weathered ASMB Oil (mg/g oil)

n-Alkane	Evaporation Percent					
	0%	9.8%	19.5%	29.8%	34.5%	44.5%
n-C8	4.088	2.771	1.085			
n-C9	4.788	4.021	2.878	0.137		
n-C10	4.345	4.120	3.528	1.355	0.083	
n-C11	4.287	4.429	4.483	3.650	1.161	
n-C12	4.150	4.185	4.337	4.438	3.109	
n-C13	4.131	4.189	4.419	4.848	4.597	0.852
n-C14	4.180	4.156	4.578	5.154	5.127	3.021
n-C15	3.918	4.078	4.515	6.124	5.225	4.983
n-C16	3.644	4.007	4.489	4.853	5.128	5.648
n-C17	3.940	4.317	5.010	5.697	5.776	6.127
pristane	1.855	2.105	2.351	2.712	2.796	3.125
n-C18	3.276	3.510	4.080	4.719	4.784	5.721
phytane	1.915	2.053	2.333	2.700	2.725	3.203
n-C19	2.592	2.736	3.099	3.494	3.824	4.544
n-C20	2.295	2.470	2.802	3.121	3.392	4.022
n-C21	2.211	2.394	2.654	2.984	3.262	3.825
n-C22	2.034	2.234	2.547	2.835	3.002	3.568
n-C23	1.784	2.007	2.303	2.530	2.714	3.144
n-C24	1.703	1.851	2.228	2.446	2.619	3.054
n-C25	1.582	1.609	1.884	2.004	2.240	2.685
n-C26	1.384	1.542	1.783	2.037	2.143	2.538
n-C27	1.267	1.425	1.647	1.853	1.993	2.337
n-C28	1.088	1.199	1.422	1.589	1.712	1.984
n-C29	0.903	0.986	1.154	1.295	1.405	1.648
n-C30	0.722	0.774	0.949	1.052	1.117	1.311
n-C31	0.616	0.674	0.782	0.910	0.960	1.163
n-C32	0.492	0.533	0.646	0.707	0.759	0.913
n-C33	0.323	0.357	0.412	0.488	0.502	0.617
n-C34	0.281	0.315	0.374	0.408	0.435	0.533
n-C35	0.192	0.217	0.254	0.281	0.303	0.373
n-C36	0.117	0.135	0.159	0.182	0.195	0.223
n-C37	0.065	0.096	0.122	0.135	0.131	0.150
n-C38	0.061	0.070	0.084	0.093	0.099	0.120
n-C39	0.048	0.057	0.065	0.073	0.095	0.095
n-C40	0.037	0.041	0.047	0.059	0.062	0.073
SUM	70.30	71.69	75.64	75.91	73.77	72.59
n-C17/pristane	2.02	2.05	2.13	2.10	2.07	2.15
n-C18/phytane	1.71	1.71	1.75	1.75	1.78	1.78
pristane/phytane	1.02	1.03	1.01	1.00	1.03	0.96
CPI	0.96	0.99	1.02	1.00	1.01	1.01
C8+C10+C12+C14/C22+C24+C26+C28	2.70	2.23	1.70	1.23	0.86	0.27

\* CPI : Carbon Preference Index = (Sum of odd n-alkanes)/(Sum of even n-alkanes)

TABLE 2 Ratios of n-alkanes Relative to n-C30 at Six Selected Degrees of ASMB Oil Weathering

n-Alkane	Evaporation Percent					
	0%	9.8%	19.5%	29.8%	34.5%	44.5%
n-C8	5.66	3.58	1.15	-	-	-
n-C9	6.63	5.20	3.05	0.13	-	-
n-C10	8.02	5.32	3.74	1.29	0.07	-
n-C11	5.94	5.72	4.73	3.47	1.04	-
n-C12	5.75	5.38	4.60	4.22	2.78	-
n-C13	5.72	5.39	4.69	4.61	4.12	0.50
n-C14	5.79	5.37	4.85	4.90	4.59	2.30
n-C15	5.43	5.27	4.79	4.87	4.68	3.79
n-C16	5.05	5.18	4.74	4.71	4.59	4.31
n-C17	5.46	5.58	5.31	5.42	5.17	5.13
pristane	2.71	2.72	2.49	2.58	2.50	2.38
n-C18	4.54	4.53	4.33	4.49	4.26	4.36
phytane	2.65	2.65	2.47	2.57	2.44	2.44
n-C19	3.55	3.53	3.29	3.31	3.42	3.47
n-C20	3.18	3.19	2.97	2.97	3.04	3.07
n-C21	3.06	3.05	2.81	2.84	2.92	2.99
n-C22	2.82	2.89	2.70	2.69	2.69	2.72
n-C23	2.47	2.59	2.44	2.40	2.43	2.40
n-C24	2.36	2.39	2.36	2.33	2.34	2.33
n-C25	2.16	2.08	2.01	1.98	2.01	2.05
n-C26	1.92	1.99	1.89	1.94	1.92	1.93
n-C27	1.75	1.84	1.75	1.76	1.78	1.78
n-C28	1.51	1.55	1.51	1.51	1.53	1.51
n-C29	1.25	1.27	1.22	1.23	1.26	1.26
n-C30	1.00	1.00	1.00	1.00	1.00	1.00
n-C31	0.85	0.87	0.81	0.87	0.86	0.89
n-C32	0.68	0.69	0.69	0.67	0.68	0.70
n-C33	0.45	0.46	0.44	0.44	0.45	0.47
n-C34	0.39	0.41	0.40	0.39	0.39	0.41
n-C35	0.27	0.28	0.27	0.27	0.27	0.28
n-C36	0.16	0.17	0.17	0.17	0.17	0.17
n-C37	0.12	0.12	0.13	0.13	0.12	0.11
n-C38	0.08	0.09	0.09	0.09	0.09	0.09
n-C39	0.07	0.07	0.07	0.07	0.07	0.07
n-C40	0.05	0.05	0.05	0.06	0.06	0.06

TABLE 3 Converted Concentrations of Aliphatic Constituents in Weathered ASMB Oil (mg/g oil)

n-Alkane	Evaporation Percent					
	0%	9.8%	19.5%	29.8%	34.5%	44.5%
n-C8	4.088	2.499	0.873	-	-	-
n-C9	4.788	3.627	2.317	0.096	-	-
n-C10	4.345	3.716	2.840	0.949	0.054	-
n-C11	4.287	3.985	3.593	2.555	0.760	-
n-C12	4.150	3.757	3.491	3.107	2.036	-
n-C13	4.131	3.760	3.557	3.394	3.011	0.362
n-C14	4.180	3.749	3.685	3.608	3.358	1.677
n-C15	3.918	3.678	3.635	3.587	3.422	2.754
n-C16	3.644	3.614	3.598	3.467	3.358	3.135
n-C17	3.940	3.894	4.033	3.988	3.783	3.733
pristane	1.955	1.899	1.893	1.898	1.831	1.734
n-C18	3.276	3.166	3.284	3.303	3.120	3.175
phytane	1.915	1.852	1.878	1.890	1.785	1.778
n-C19	2.562	2.468	2.485	2.439	2.505	2.522
n-C20	2.295	2.228	2.256	2.185	2.222	2.232
n-C21	2.211	2.132	2.136	2.089	2.137	2.178
n-C22	2.034	2.015	2.050	1.985	1.966	1.980
n-C23	1.784	1.810	1.854	1.771	1.778	1.745
n-C24	1.703	1.670	1.794	1.712	1.715	1.695
n-C25	1.562	1.451	1.525	1.459	1.467	1.490
n-C26	1.384	1.391	1.435	1.426	1.404	1.407
n-C27	1.267	1.285	1.326	1.297	1.305	1.297
n-C28	1.088	1.081	1.145	1.112	1.121	1.101
n-C29	0.903	0.889	0.929	0.907	0.920	0.915
n-C30	0.722	0.698	0.759	0.736	0.732	0.728
n-C31	0.616	0.608	0.613	0.637	0.629	0.645
n-C32	0.492	0.481	0.520	0.495	0.497	0.507
n-C33	0.323	0.322	0.332	0.328	0.329	0.342
n-C34	0.281	0.284	0.301	0.286	0.285	0.296
n-C35	0.192	0.196	0.204	0.197	0.198	0.207
n-C36	0.117	0.122	0.128	0.127	0.121	0.124
n-C37	0.085	0.087	0.098	0.095	0.086	0.083
n-C38	0.061	0.063	0.068	0.065	0.065	0.067
n-C39	0.048	0.051	0.052	0.051	0.052	0.053
n-C40	0.037	0.037	0.038	0.041	0.041	0.041

TABLE 4 Measured (left side) and Converted (right side) Concentrations of Alkylated PAH Homologues in Weathered ASMB Oil ( $\mu\text{g/g}$  oil)

PAHs	Measured Concentration (C <sub>det</sub> )						PAHs	Converted Concentration (C <sub>conv</sub> )					
	0%	9.80%	19.50%	29.80%	34.50%	44.50%		0%	9.80%	19.50%	29.80%	34.50%	44.50%
C0-N	660	670	738	736	442	0	C0-N	660	604	594	515	290	0
C1-N	1660	1668	1867	2137	1929	181	C1-N	1660	1505	1503	1496	1263	100
C2-N	2704	2737	3070	3605	3830	1861	C2-N	2704	2469	2471	2524	2508	1033
C3-N	2470	2527	2810	3320	3520	3439	C3-N	2470	2279	2262	2324	2306	1909
C4-N	1095	1177	1311	1524	1666	1914	C4-N	1095	1062	1055	1067	1091	1062
SUM	8589	8779	9796	11322	11387	7395	SUM	8589	7919	7886	7925	7458	4104
C0-P	197	216	237	272	294	338	C0-P	197	195	191	190	193	188
C1-P	698	756	864	981	1054	1240	C1-P	698	682	696	687	690	688
C2-P	843	923	1036	1188	1284	1515	C2-P	843	833	834	832	841	841
C3-P	484	537	604	687	734	873	C3-P	484	484	486	481	481	485
C4-P	272	311	344	389	408	487	C4-P	272	281	277	272	267	270
SUM	2494	2743	3085	3517	3774	4453	SUM	2494	2474	2483	2462	2472	2471
C0-D	188	210	230	262	285	322	C0-D	188	189	185	183	187	179
C1-D	352	395	438	490	531	623	C1-D	352	356	353	343	348	346
C2-D	427	473	534	610	651	780	C2-D	427	427	430	427	426	433
C3-D	280	315	350	405	435	504	C3-D	280	284	282	284	285	280
SUM	1247	1393	1552	1767	1902	2229	SUM	1247	1256	1249	1237	1246	1237
C0-F	89	93	104	116	120	122	C0-F	89	84	84	81	79	68
C1-F	210	230	254	292	310	336	C1-F	210	207	204	204	203	186
C2-F	345	384	421	481	510	592	C2-F	345	346	339	337	334	329
C3-F	315	355	392	460	479	578	C3-F	315	320	316	322	314	321
SUM	959	1062	1171	1349	1419	1628	SUM	959	958	943	944	929	904
C0-C	24	29	32	36	39	46	C0-C	24	26	26	25	26	26
C1-C	37	42	47	53	56	67	C1-C	37	38	38	37	37	37
C2-C	55	62	70	77	83	101	C2-C	55	56	56	54	54	56
C3-C	54	61	66	74	77	91	C3-C	54	55	53	52	50	51
SUM	170	194	215	240	255	305	SUM	170	175	173	168	167	169
TOTAL	13459	14171	15819	18195	18737	16010	TOTAL	13459	12782	12734	12737	12272	8886
3-M-N/1-M-N	1.35	1.38	1.35	1.32	1.31	0.99							
4-M-D/2-M-D/1-M-D	1.00:0.77:0.28	1.00:0.76:0.29	1.00:0.76:0.28	1.00:0.76:0.28	1.00:0.76:0.28	1.00:0.78:0.29							

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TABLE 5 Relative Composition of Alkylated PAH Homologues at Various Weathered Percentages

PAHs	Evaporation Percent					
	0%	9.80%	19.50%	29.80%	34.50%	44.50%
C0-N	7.7%	7.6%	7.5%	6.5%	3.9%	0.0%
C1-N	19.3%	19.0%	19.1%	18.9%	16.9%	2.4%
C2-N	31.5%	31.2%	31.3%	31.8%	33.6%	25.2%
C3-N	28.8%	28.8%	28.7%	29.3%	30.9%	46.5%
C4-N	12.7%	13.4%	13.4%	13.5%	14.6%	25.9%
C0-P	7.9%	7.9%	7.7%	7.7%	7.8%	7.6%
C1-P	28.0%	27.6%	28.0%	27.9%	27.9%	27.8%
C2-P	33.8%	33.6%	33.6%	33.8%	34.0%	34.0%
C3-P	19.4%	19.6%	19.6%	19.5%	19.4%	19.6%
C4-P	10.9%	11.3%	11.2%	11.1%	10.8%	10.9%
C0-D	15.1%	15.1%	14.8%	14.8%	15.0%	14.4%
C1-D	28.2%	28.4%	28.2%	27.7%	27.9%	27.9%
C2-D	34.2%	34.0%	34.4%	34.5%	34.2%	35.0%
C3-D	22.5%	22.6%	22.6%	22.9%	22.9%	22.6%
C0-F	9.3%	8.8%	8.9%	8.6%	8.5%	7.5%
C1-F	21.9%	21.7%	21.7%	21.6%	21.8%	20.6%
C2-F	36.0%	36.2%	36.0%	35.7%	35.9%	36.4%
C3-F	32.8%	33.4%	33.5%	34.1%	33.8%	35.5%
C0-C	14.1%	14.9%	14.9%	15.0%	15.3%	15.1%
C1-C	21.8%	21.6%	21.9%	22.1%	22.0%	22.0%
C2-C	32.4%	32.0%	32.6%	32.1%	32.5%	33.1%
C3-C	31.8%	31.4%	30.7%	30.8%	30.2%	29.8%

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TABLE 6 Measured (left side) and Converted (right side) Concentrations of Triterpanes in Weathered ASMB Oil (µg/g oil)

	Measured Concentration (Cdet)						Converted Concentration (Cconv)					
	0%	9.80%	19.50%	29.80%	34.50%	44.50%	0%	9.80%	19.50%	29.80%	34.50%	44.50%
<b>Triterpanes</b>												
1 C19 tricyclic terpane	14.6	15.6	17.5	19.8	21.6	26.4	14.6	14.1	14.1	13.9	14.1	14.6
2 C20 tricyclic terpane	26.2	26.4	28.8	33.6	37.6	44.6	26.2	23.8	23.1	23.5	24.6	24.8
3 C21 tricyclic terpane	31.2	32.2	35.0	41.6	42.6	51.3	31.2	29.0	28.2	29.1	27.9	28.5
4 C22 tricyclic terpane	17.6	18.7	23.3	24.5	25.3	32.6	17.6	16.9	18.8	17.1	16.6	18.1
5 C23 tricyclic terpane	80.1	82.6	94.5	102.8	117.3	143.6	80.1	74.5	76.0	72.0	76.8	79.7
6 C24 tricyclic terpane	41.6	41.8	48.8	52.4	58.5	71.0	41.6	37.7	39.3	36.7	38.3	39.4
7 C25 tricyclic terpane	38.1	42.6	45.6	50.8	55.6	66.2	38.1	38.4	36.7	35.6	36.4	36.7
8 C26 tricyclic terpane	53.2	54.1	58.4	65.9	74.3	86.2	53.2	48.8	47.0	46.1	48.6	47.8
<b>Tetracyclic terpanes</b>												
9 C27 tetracyclic terpane	37.5	41.7	47.7	51.6	53.7	69.7	37.5	37.6	38.4	36.1	35.1	38.7
10 C27 tetracyclic terpane	(peak 9+10)	(peak 9+10)	(peak 9+10)	(peak 9+10)	(peak 9+10)	(peak 9+10)	(peak 9+10)	(peak 9+10)	(peak 9+10)	(peak 9+10)	(peak 9+10)	(peak 9+10)
11 C28 tetracyclic terpane	38.7	41.9	45.5	52.3	53.5	68.4	38.7	37.7	36.6	36.6	35.0	37.9
12 C28 tetracyclic terpane	(peak 11+12)	(peak 11+12)	(peak 11+12)	(peak 11+12)	(peak 11+12)	(peak 11+12)	(peak 11+12)	(peak 11+12)	(peak 11+12)	(peak 11+12)	(peak 11+12)	(peak 11+12)
<b>Pentacyclic triterpanes</b>												
13 Ta: 18a(H),21b(H)-22,29,30-trisnorhopane (C27H46)	40.0	41.1	45.3	51.4	56.6	69.1	40.0	37.0	36.4	35.9	37.1	38.3
14 17a(H),18a(H),21b(H)-25,28,30-trisnorhopane (C27H46)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)
15 Ta: 17a(H),21b(H)-22,29,30-trisnorhopane (C27H46)	50.1	52.7	57.8	64.3	72.3	86.1	50.1	47.5	46.5	45.0	47.3	47.8
16 17a(H),18a(H),21b(H)-28,30-bisnorhopane (C28H48)	13.1	15.1	17.5	17.0	19.5	22.7	13.1	13.6	14.0	11.9	12.8	12.6
17 (C29) 17a(H),21b(H)-30-norhopane	87.8	95.0	102.5	117.9	129.3	154.8	87.8	85.6	82.5	82.5	84.7	85.9
18 (C29) 18a(H),21b(H)-30-norhopane	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)
19 (C30) 17a(H),21b(H)-hopane	127.9	145.5	160.8	181.0	190.0	229.0	127.9	131.2	129.4	126.7	124.5	127.1
20 (C30) 17b(H),21a(H)-hopane	17.1	17.8	20.0	23.3	23.3	27.3	17.1	16.1	16.1	16.3	15.2	15.1
21 (C31) 22S-17a(H),21b(H)-30-homohopane	52.9	59.0	64.8	71.0	76.4	93.5	52.9	53.2	52.2	49.7	50.0	51.9
22 (C31) 22R-17a(H),21b(H)-30-homohopane	42.6	46.2	53.0	54.7	58.8	75.8	42.6	41.6	42.7	38.3	38.5	42.0
23 (C31) 17b(H),21a(H)-hopane	Internal Std.	Internal Std.	Internal Std.	Internal Std.	Internal Std.	Internal Std.	Internal Std.	Internal Std.	Internal Std.	Internal Std.	Internal Std.	Internal Std.
24 22S-17a(H),21b(H)-30,31-bisnorhopane	42.0	45.1	50.5	56.5	59.1	73.6	42.0	40.7	40.6	39.5	38.7	40.8
25 22R-17a(H),21b(H)-30,31-bisnorhopane	29.4	31.6	34.7	38.2	40.9	50.3	29.4	28.5	27.9	26.7	26.8	27.9
26 22S-17a(H),21b(H)-30,31,32-trisnorhopane	27.5	32.0	34.7	39.6	38.8	50.5	27.5	28.8	27.9	27.7	25.4	28.0
27 22R-17a(H),21b(H)-30,31,32-trisnorhopane	19.2	22.2	23.9	26.3	26.9	33.6	19.2	20.0	19.2	18.4	17.6	18.6
28 22S-17a(H),21b(H)-30,31,32,33-tetrakisnorhopane	21.9	25.1	29.1	29.9	32.1	38.2	21.9	22.6	23.4	20.9	21.0	21.2
29 22R-17a(H),21b(H)-30,31,32,33-tetrakisnorhopane	12.1	13.7	15.5	17.0	18.0	21.4	12.1	12.3	12.5	11.9	11.8	11.8
30 22S-17a(H),21b(H)-30,31,32,33,34-pentakisnorhopane	18.3	21.2	24.8	26.5	29.0	33.9	18.3	19.1	19.9	18.5	19.0	18.8
31 22R-17a(H),21b(H)-30,31,32,33,34-pentakisnorhopane	11.5	13.5	15.9	16.1	17.1	22.8	11.5	12.1	12.8	11.3	11.2	12.7
<b>Total</b>	<b>991.5</b>	<b>1073.7</b>	<b>1195.4</b>	<b>1325.4</b>	<b>1427.7</b>	<b>1741.9</b>	<b>991.5</b>	<b>968.4</b>	<b>962.3</b>	<b>927.7</b>	<b>935.1</b>	<b>966.7</b>

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TABLE 7 Measured (left side) and Converted (right side) Concentrations of Steranes in Weathered ASMB Oil (µg/g oil)

	Measured Concentration (Cdet)						Converted Concentration (Cconv)					
	0%	9.80%	19.50%	29.80%	34.50%	44.50%	0%	9.80%	19.50%	29.80%	34.50%	44.50%
<b>Steranes</b>												
32 C20 5a(H),14a(H),17a(H)-sterane	14.3	14.9	16.1	17.9	19.6	23.8	14.3	13.4	12.9	12.5	12.8	13.2
33 C21 5a(H),14b(H),17b(H)-sterane	31.8	32.8	35.2	41.5	44.7	53.5	31.8	29.5	28.3	29.1	29.2	29.7
34 C22 5a(H),14b(H),17b(H)-sterane	14.2	15.0	16.1	19.1	20.5	24.1	14.2	13.5	13.0	13.3	13.4	13.3
35 C27 20S-13b(H),17a(H)-diasterane	31.8	33.7	37.5	42.8	47.3	55.0	31.8	30.4	30.1	30.0	30.9	30.5
36 C27 20R-13b(H),17a(H)-diasterane	18.0	19.5	22.4	25.2	28.4	32.4	18.0	17.6	18.0	17.6	18.6	18.0
37 C27 20S-13a(H),17b(H)-diasterane	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)
38 C27 20R-13a(H),17b(H)-diasterane	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)
39 C28 20S-13b(H),17a(H)-diasterane	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)
40 C29 20S-13b(H),17a(H)-diasterane	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)
41 C29 20R-13a(H),17b(H)-diasterane	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)	(not quantified)
42 C27 20S 5a(H),14a(H),17a(H)-cholestane	20.5	23.5	26.2	26.3	25.1	34.7	20.5	21.2	21.1	18.4	16.4	19.3
43 C27 20R 5a(H),14b(H),17b(H)-cholestane	55.2	59.7	67.4	72.3	77.4	96.5	55.2	53.8	54.3	50.6	50.7	53.6
44 C27 20S 5a(H),14b(H),17b(H)-cholestane	29.3	31.7	37.6	39.4	42.2	50.8	29.3	28.6	30.3	27.6	27.6	28.2
45 C27 20R 5a(H),14a(H),17a(H)-cholestane	21.6	23.4	26.4	29.2	30.2	35.3	21.6	21.1	21.2	20.4	19.8	19.6
46 C28 20S 5a(H),14a(H),17a(H)-ergostane	20.0	20.3	22.2	24.4	27.6	30.6	20.0	18.3	17.9	17.1	18.0	17.0
47 C28 20R 5a(H),14b(H),17b(H)-ergostane	15.8	17.1	20.6	21.4	22.6	27.4	15.8	15.4	16.5	14.9	14.8	15.2
48 C28 20S 5a(H),14b(H),17b(H)-ergostane	19.4	20.8	23.7	26.5	28.3	33.5	19.4	18.7	19.0	18.6	18.5	18.6
49 C28 20R 5a(H),14a(H),17a(H)-ergostane	13.3	13.6	16.6	17.4	18.7	22.6	13.3	12.3	13.3	12.2	12.2	12.5
50 C29 20S 5a(H),14a(H),17a(H)-stigmastane	21.0	22.9	26.9	28.1	30.0	37.2	21.0	20.6	21.6	19.6	19.7	20.6
51 C29 20R 5a(H),14b(H),17b(H)-stigmastane	28.2	30.5	35.0	36.7	40.5	52.2	28.2	27.5	28.1	25.7	26.5	28.9
52 C29 20S 5a(H),14b(H),17b(H)-stigmastane	22.6	24.8	30.1	31.0	33.3	42.3	22.6	22.4	24.2	21.7	21.8	23.5
53 C29 20R 5a(H),14a(H),17a(H)-stigmastane	20.0	22.6	25.9	27.4	29.1	34.9	20.0	20.4	20.8	19.1	19.1	19.4
<b>Total</b>	<b>396.6</b>	<b>426.4</b>	<b>485.4</b>	<b>526.4</b>	<b>565.1</b>	<b>686.3</b>	<b>396.6</b>	<b>384.6</b>	<b>390.7</b>	<b>368.4</b>	<b>370.1</b>	<b>380.9</b>

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TABLE 8 Relative Ratios of Triterpanes and Steranes at Six Degrees of ASMB Oil Weathering

Weathered (%)	Hopanes								
	C23/C24	Ta/Tm	C29aB/C30aB	C31 S/(S+R)	C32 S/(S+R)	C33 S/(S+R)	C34 S/(S+R)	C35 S/(S+R)	C31-C35 S/(S+R)
0.0	1.92	0.80	0.69	0.55	0.59	0.59	0.64	0.61	0.60
9.8	1.98	0.78	0.65	0.56	0.59	0.59	0.65	0.61	0.60
19.5	1.94	0.78	0.65	0.55	0.59	0.59	0.65	0.61	0.60
29.8	1.96	0.80	0.65	0.56	0.60	0.60	0.64	0.62	0.60
34.5	2.00	0.78	0.68	0.57	0.59	0.59	0.64	0.63	0.60
44.5	2.02	0.80	0.69	0.55	0.60	0.60	0.64	0.61	0.60

Weathered (%)	Steranes					
	20S/(20a+20R)			aB/(aB+aA)		
	C27	C28	C29	C27	C28	C29
0.0	0.37	0.58	0.45	0.67	0.51	0.55
9.8	0.40	0.57	0.47	0.66	0.53	0.55
19.5	0.40	0.55	0.48	0.67	0.53	0.55
29.8	0.39	0.57	0.48	0.67	0.53	0.55
34.5	0.39	0.57	0.48	0.67	0.52	0.55
44.5	0.39	0.56	0.48	0.68	0.53	0.57

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TABLE 9 Determination of Weathered Percentages of Weathered Oil Samples

Target Compounds	% Weathered Determined by Equation 3		
	Sample 1	Sample 2	Sample 3
n-C26	27.6	35.5	40.4
n-C27	27.5	35.6	40.3
n-C28	26.2	33.7	38.4
n-C29	25.1	33.0	38.5
n-C30	25.5	34.2	39.6
C2-P	28.7	33.8	39.2
C3-P	26.5	35.8	40.0
C2-D	28.6	35.9	42.0
C3-D	31.6	35.1	43.0
C23 - triertpane	23.4	33.1	40.0
Ta	25.6	31.1	42.0
Tm	26.9	35.4	44.0
C30 al-hopane	26.7	34.2	36.1
Average (%)	26.9 ± 1.0	34.3 ± 1.4	40.3 ± 2.1
Gravimetrically Determined Weathered Percentage (%)	25.9	33.6	38.6

\* P and D represent phenanthrene and dibenzothiophene, respectively

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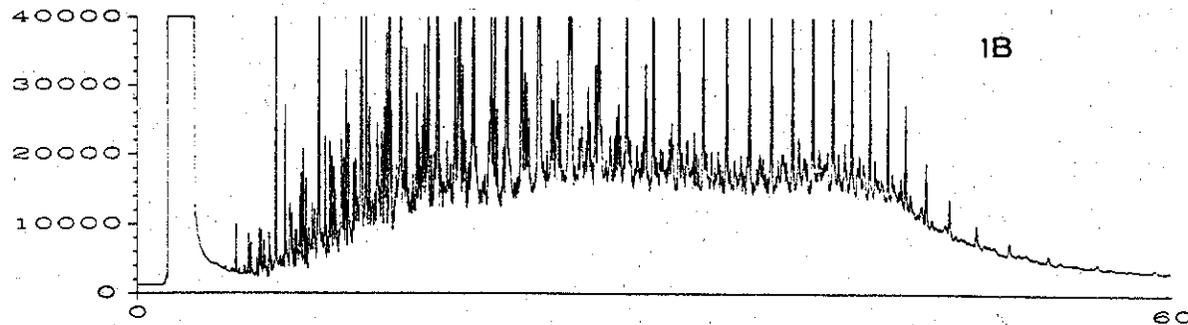
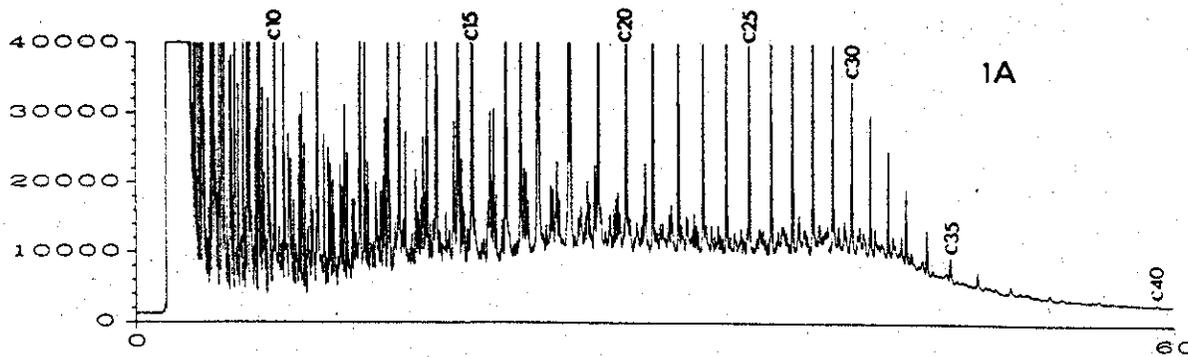
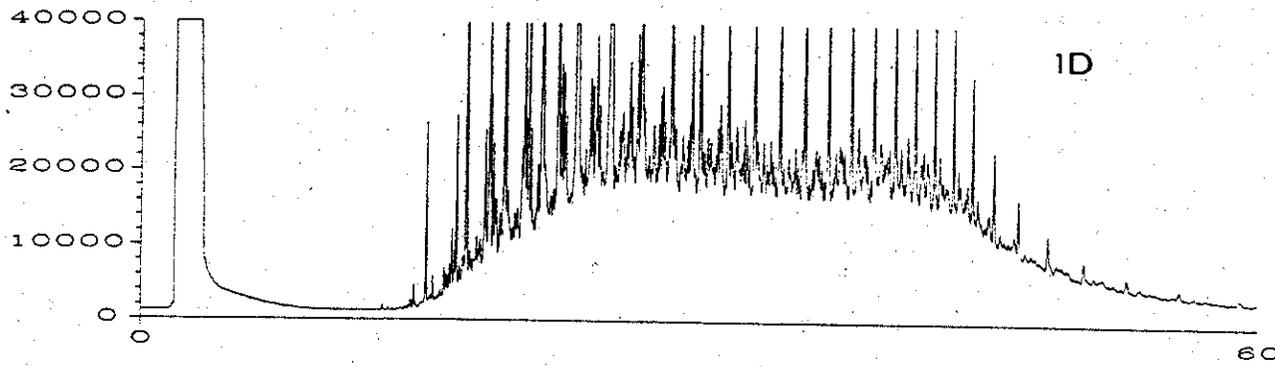
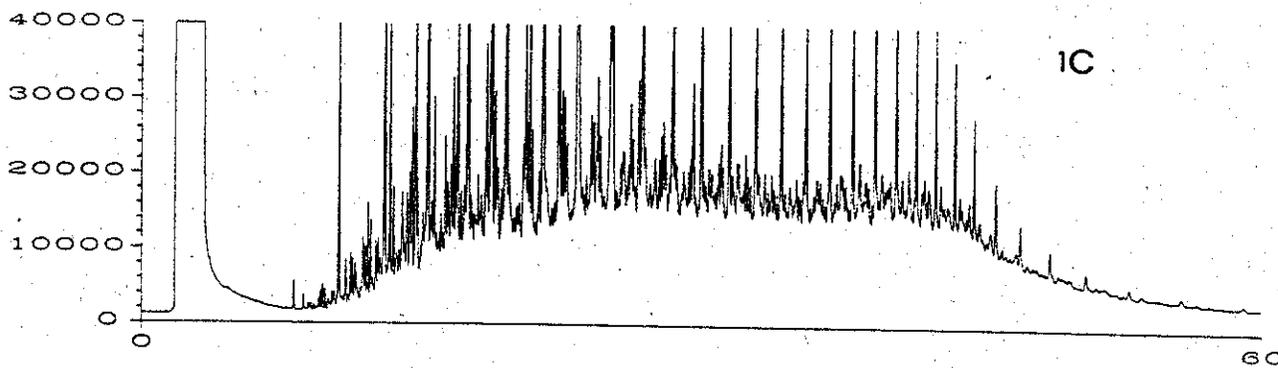


Figure 1 GC/FID chromatographic profiles of aliphatic hydrocarbons (F1) of ASMB oil at 4 different weathering percentages: 0% (1A); 29.8% (1B); 34.5% (1C); and 44.5% (1D)



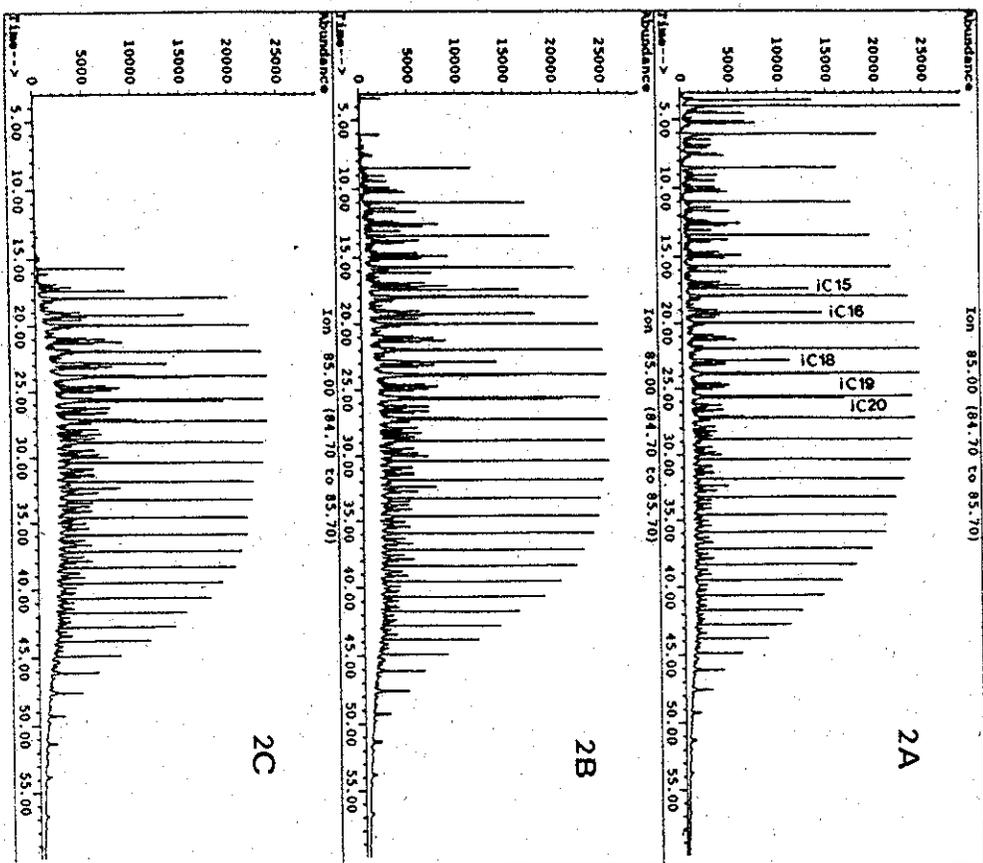


Figure 2 GC/MS chromatograms of saturated hydrocarbons (m/z : 85) in weathered ASMB oil samples : 0% (2A); 29.8% (2B); and 44.5% (2C)

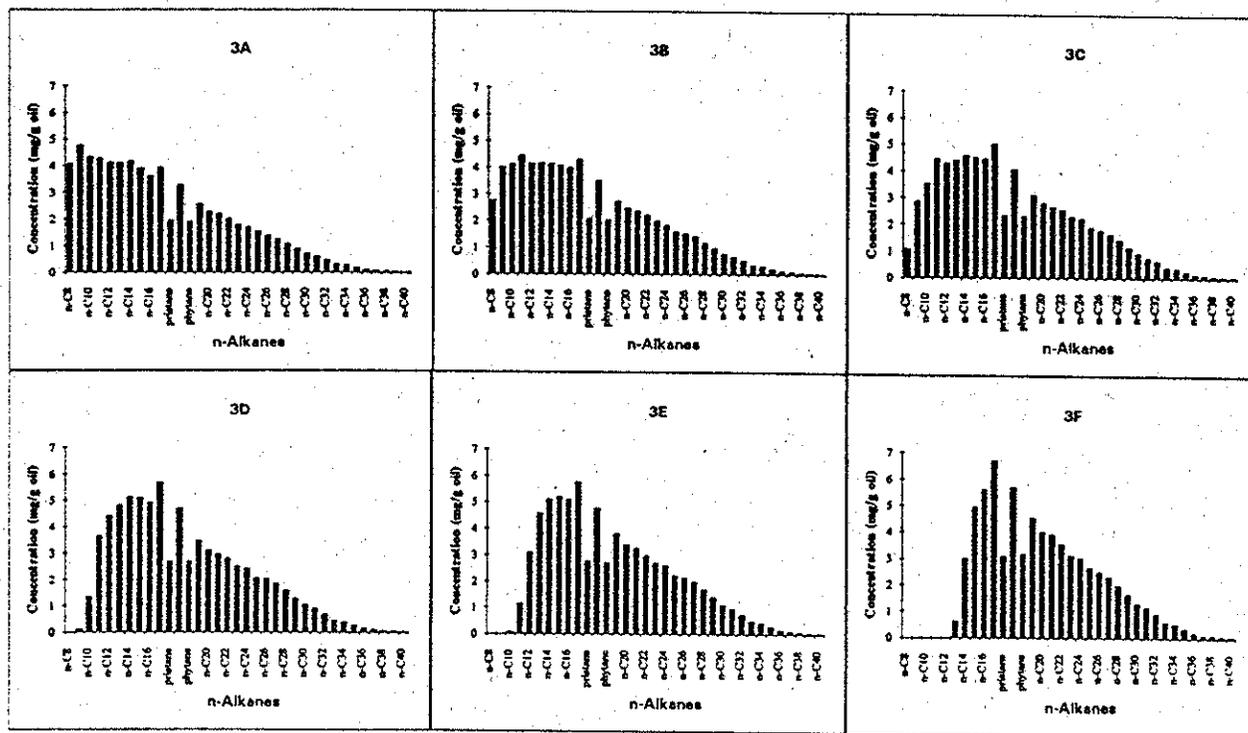


Figure 3 n-Alkane Distribution in Weathered ASMB Oil Samples: 0% (3A), 9.8% (3B), 19.5% (3C), 29.8% (3D) 34.5% (3E), and 44.5% (3F)

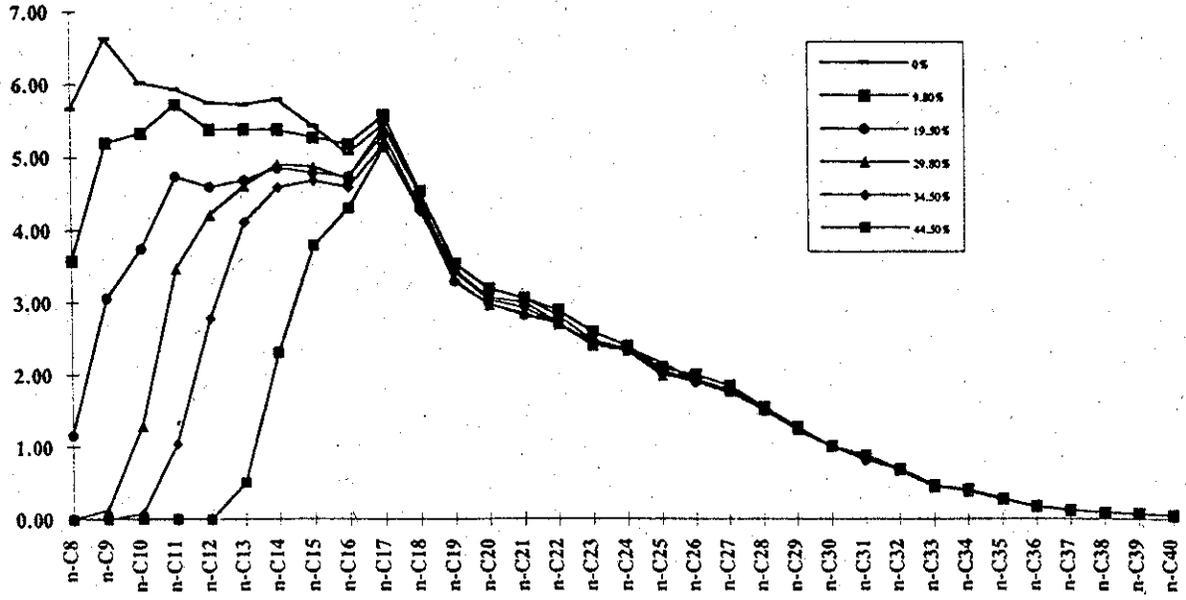


Figure 4 Plots of Abundances of n-Alkane in Weathered ASMB Oil Samples Relative to n-C30.

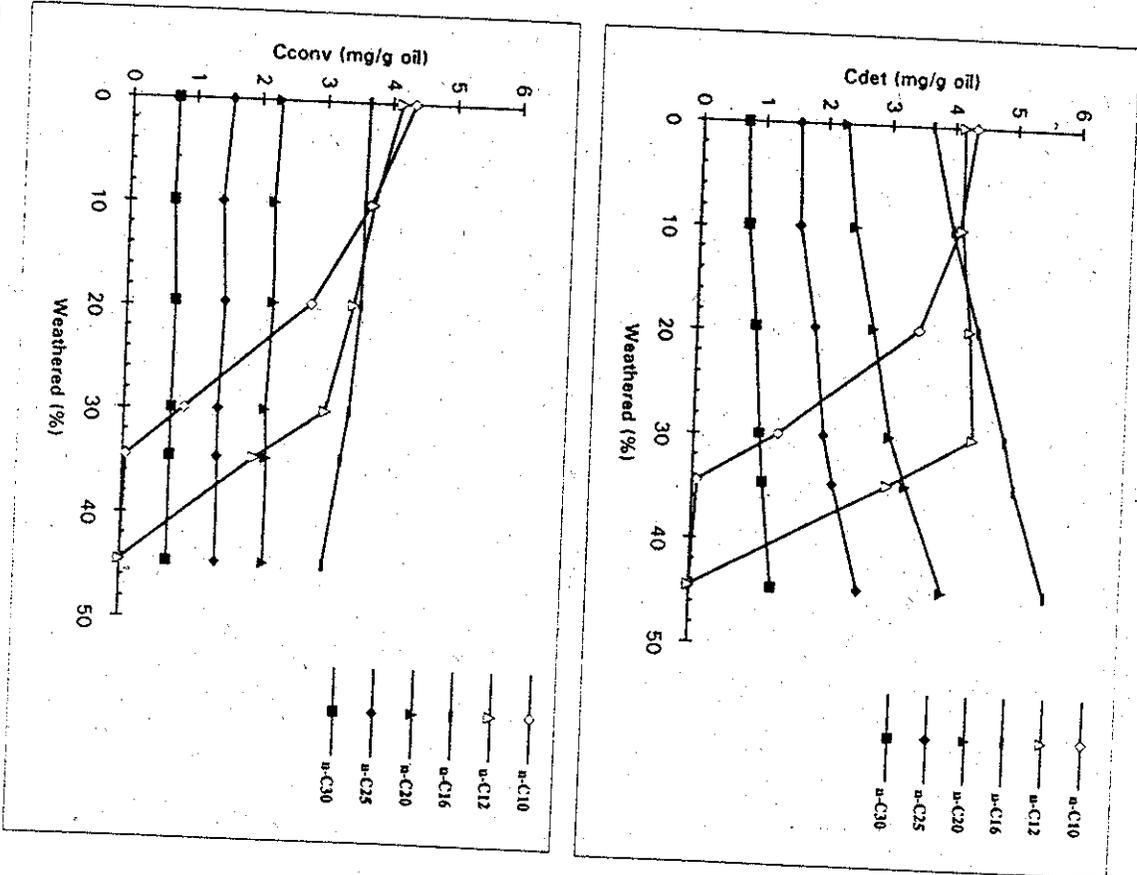


Figure 5 Comparison of Plots of Cdet (top) and Cconv (bottom) Versus Weathered Percentages for Selected n-Alkanes in ASMB Oils

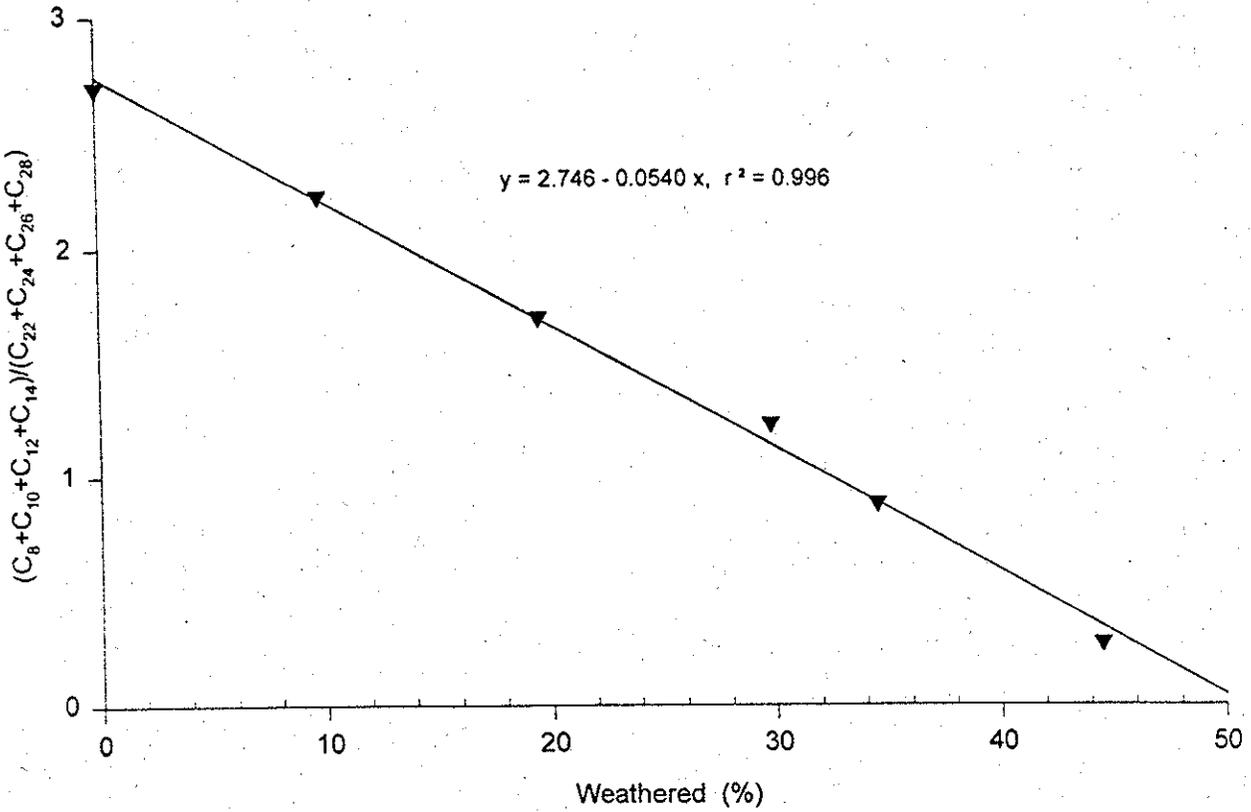
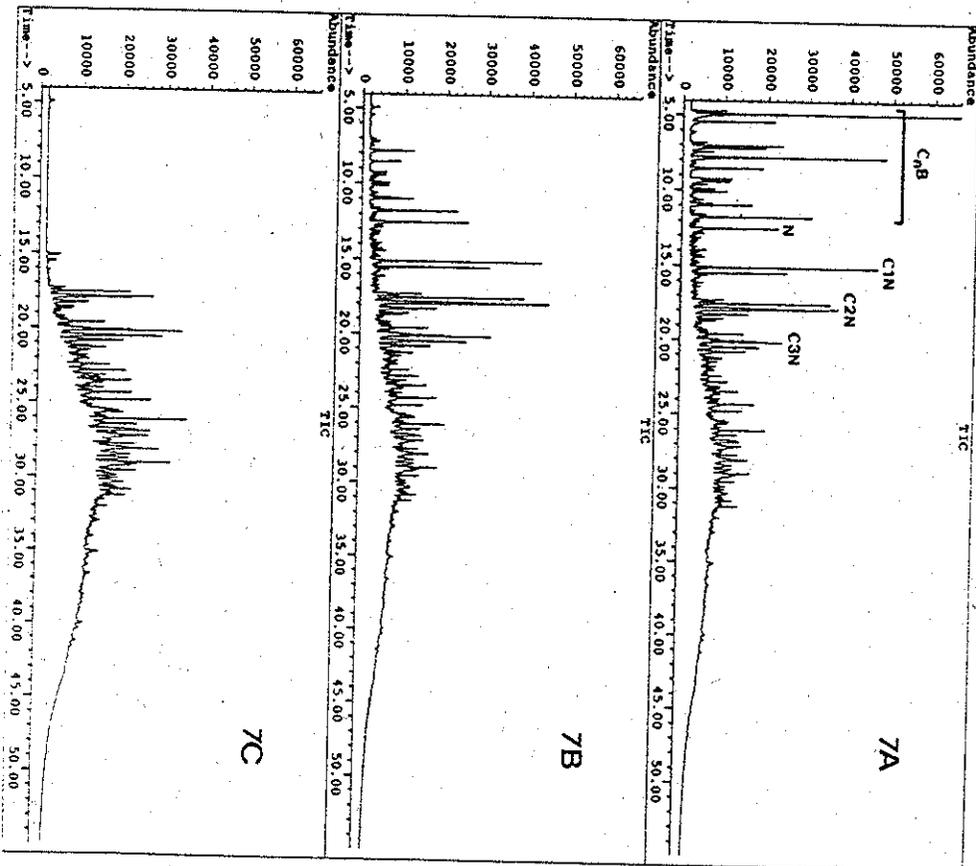
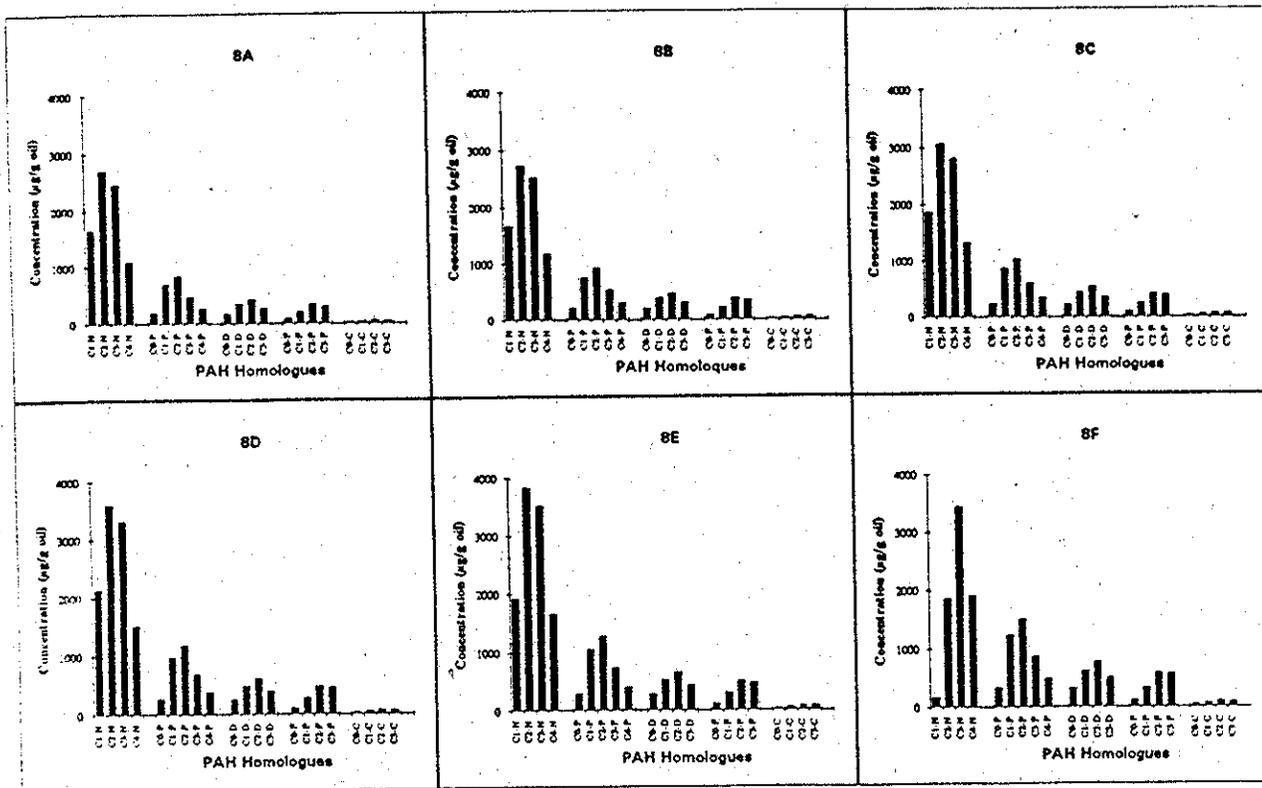


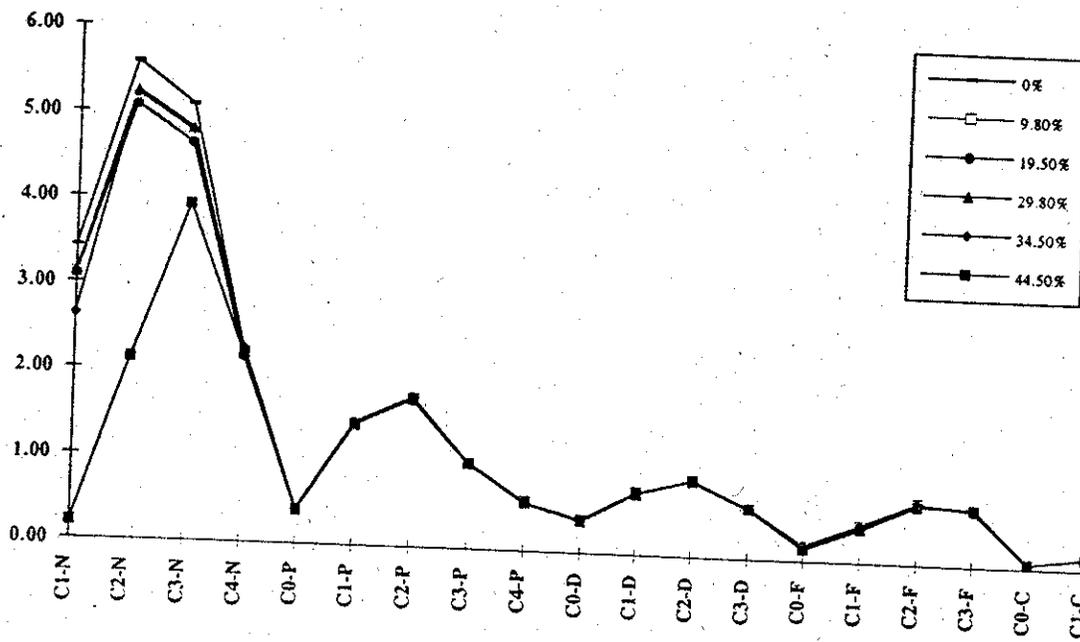
Figure 6 Plot of Weathering Index  $(C_8+C_{10}+C_{12}+C_{14})/(C_{22}+C_{24}+C_{26}+C_{28})$  Versus Weathered Percentages





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Figure 8 Distribution of Alkylated PAH Homologues at Six Weathering Percentages: 0% (8A), 9.8% (8B), 19.5% (8C), 29.8% (8D), 34.5% (8E), and 44.5% (8F)



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Figure 9 Plots of Abundances of Alkyl PAH Homologues in Weathered ASMB Oil Relative to C3-P

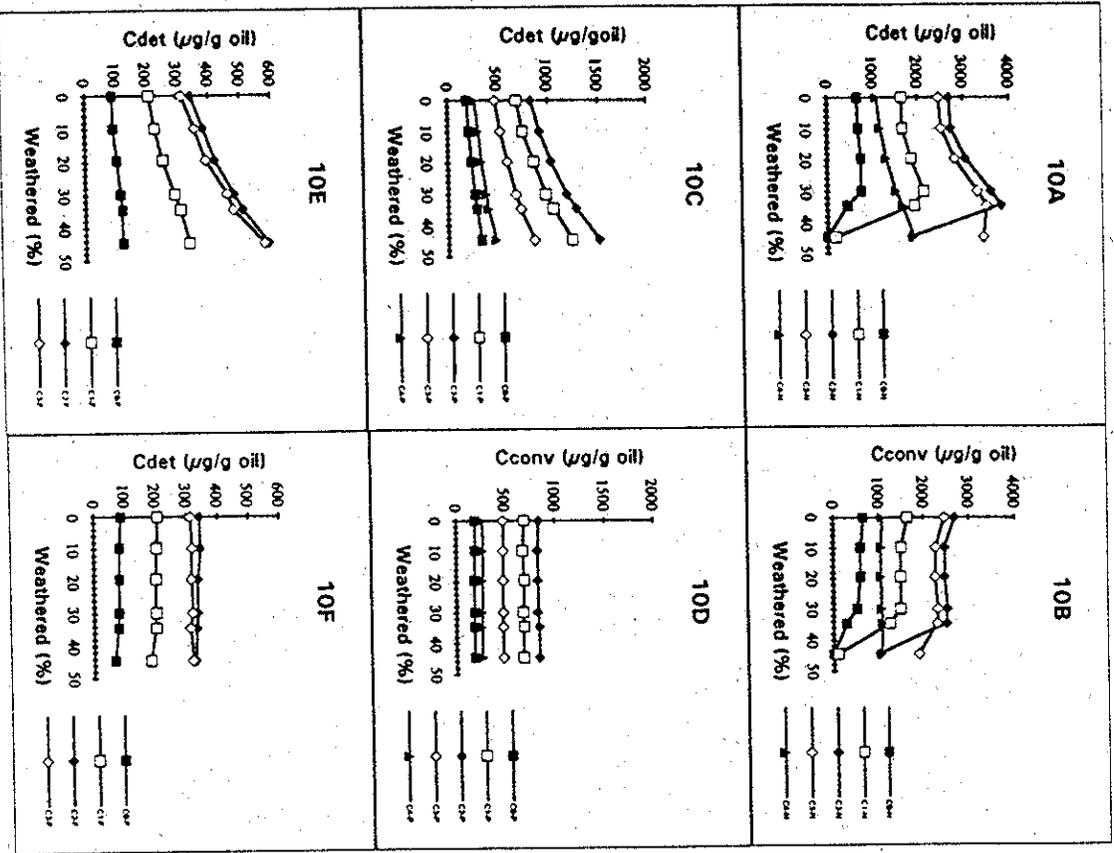


Figure 10 Plots of Cdet and Cconv Versus Weathered Percentages of Naphthalenes (10A and 10B), Phenanthrenes (10C and 10D), and Fluorenes (10E and 10F)

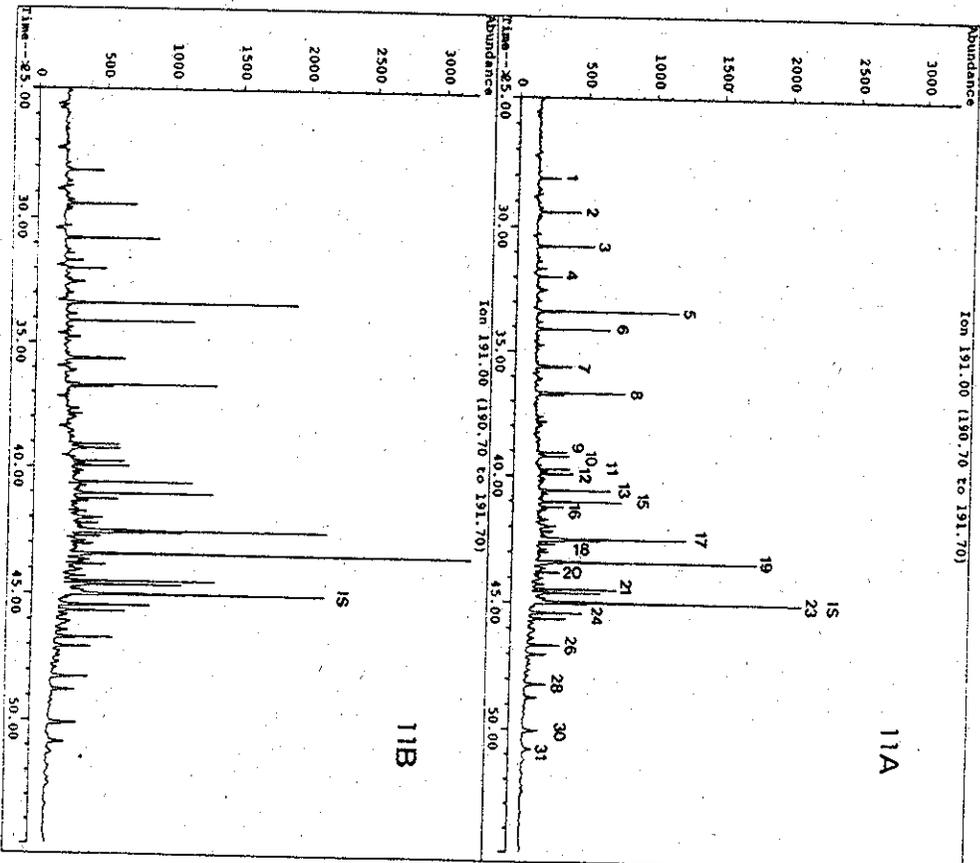


Figure 11 Distribution of Interpanes (m/z 191 mass fragmentogram) of 0% (top) and 44.5% (bottom) weathered ASMB oil

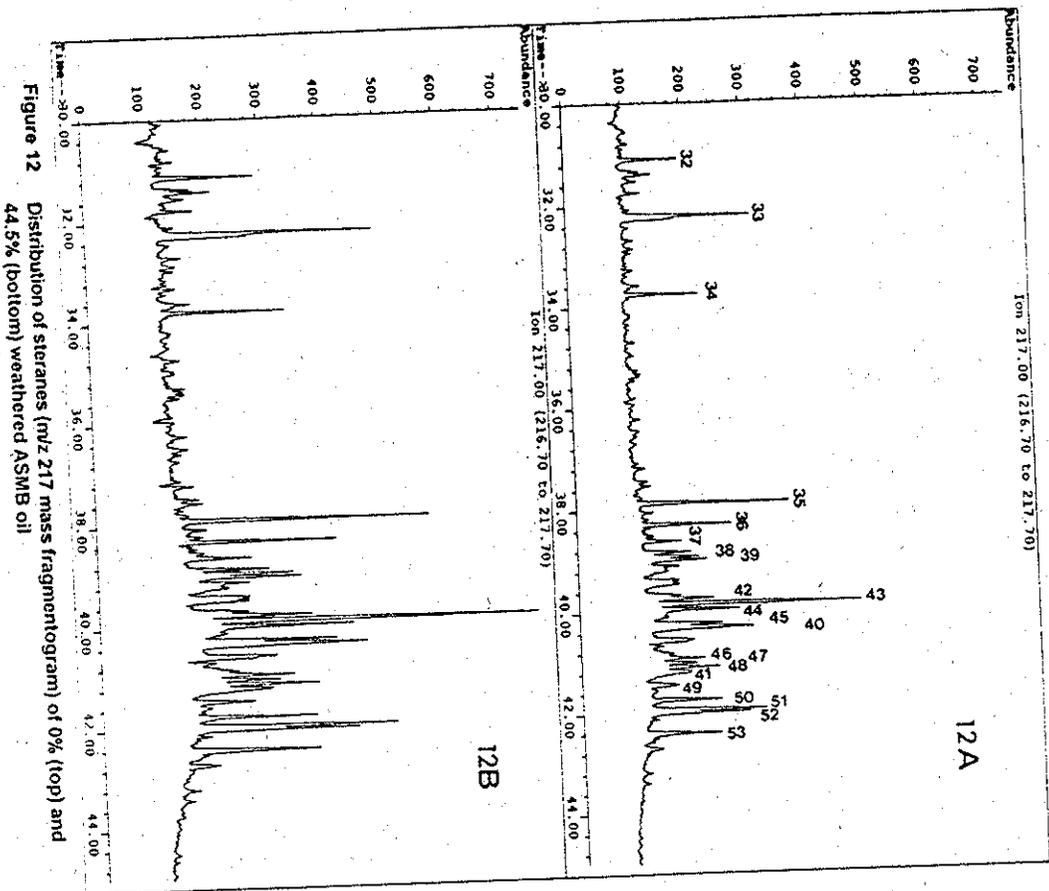


Figure 12 Distribution of steranes (m/z 217 mass fragmentogram) of 0% (top) and 44.5% (bottom) weathered ASMB oil

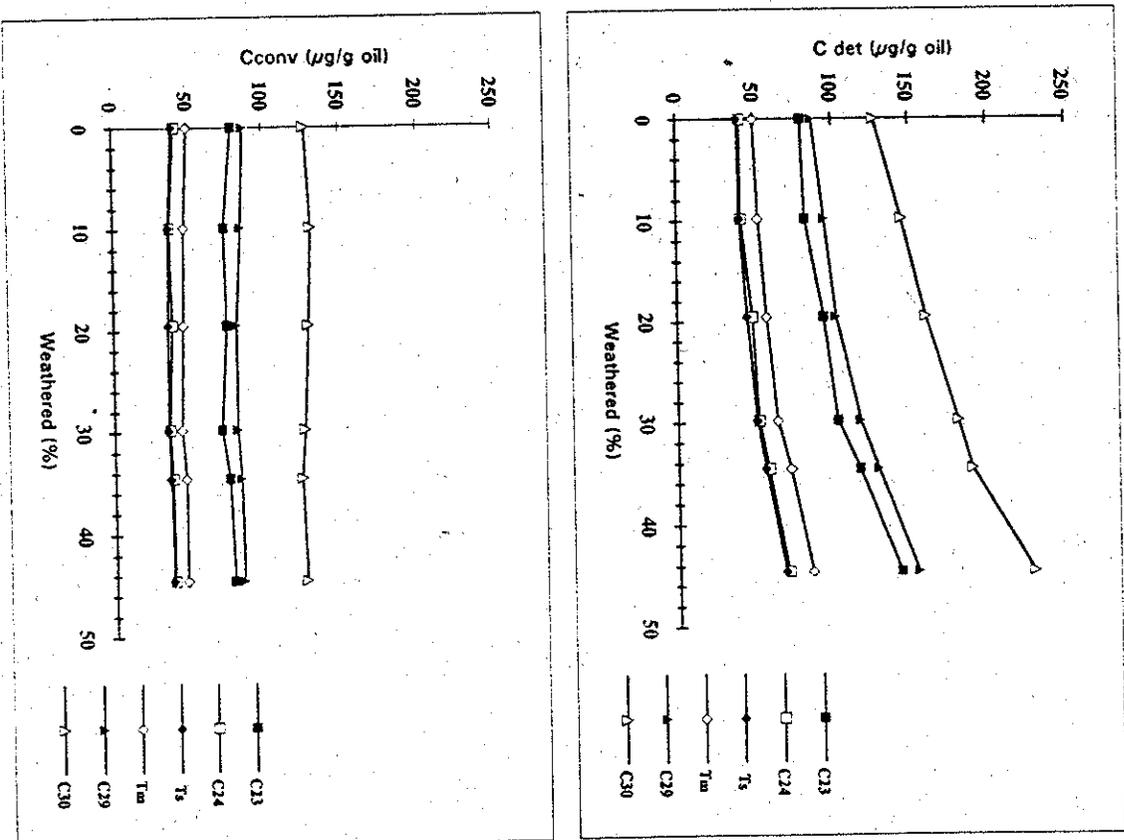


Figure 13 Plots of Converted Concentration (Cconv) of Ts, Tm, C23, C24, C29aβ-, and C30 αβ-Hopane Versus Weathered Percentages