Weathering of Petroleum Biomarkers: Review in Tropical Marine Environment Impacts

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Abstract

Weathering of biomarkers is a physical, geochemical and biological process that alters the oil components. Whether in petroleum geochemistry or environmental impact studies, knowledge of mechanisms, residence times and chemical intermediates is essential to describe the scientific and technical bases of oil deterioration. This report attempts to review the concepts of oil weathering and its biomarkers specifically, in order to inform studies related to the impact of spills in marine environments.

Keywords

Gammacerane, C_{30}-Hopane, Steranes, PAH, Crude Oil, Marine Environment Impacts, Oil Degradation

Subject Areas: **Environmental Sciences, Geochemistry**

1. Introduction

Petroleum is the non-renewable natural resource most used by humans. Many industrial activities use petroleum as energy source or raw material for thousands of substances and products of daily use [1]-[4]. Fossil fuel deposits are not equally distributed on the globe, but its demand is high especially in most industrialized countries, so the international transport across the world is required mainly by ship. Consequently, this excessive consumption of oil generates negative impacts on humans and environment, indirectly, either by CO_2 emissions, or directly, by possible crude oil spills and/or its derivatives [5] [6].

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Weathering, is a natural defense mechanism in ecosystems [5] [6], and it acts like the main remediation process for areas affected by the components of crude oil [7]-[10]. Knowledge of the residence time, weathering and degradation routes of a particular type of petroleum provides relevant information concerning the remediation process in case of spills [10]-[14]. The most recent studies report the mechanisms involved in degradation of oil, and it is well known that each type of oil has unique steps in its degradative process. They are not only associated with the physicochemical characteristics of the oil, but also highly influenced by the bio-physical-geochemical factors around the impacted area [1] [10] [14]-[18].

In exploration geochemistry, weathering is one of the factors that influence the quality of the stored oil in reservoirs [1]-[3] [7] [9] [19]-[21]. Weathering begins acting in depositional environment, during burial, influencing the quality of kerogen [2] and also promoting the "oxidation" of the residual kerogen (inertinite type) which is feasible and gas source. In the reservoirs, weathering processes are responsible for the loss of light components of oil, generating an increase of heavy fractions and viscosity and a decrease of fluidity, which make the oil difficult to be recovered [1]-[9] [16] [22]-[25].

This manuscript proposes a review, about the weathering of biomarker of petroleum and the parameters frequently used to monitor and evaluate this process, for different types of crude oil.

2. Weathering Process

Weathering is regulated by physical, chemical and biological processes, which act on the geological material throughout time and depend on the nature of the environment in which such material is introduce [5] [14] [19]. The interaction between these processes and the geological material generates a weathered product, *i.e.*, the geological material and mass modified [26]. The petroleum compounds, such as hydrocarbons, biomarkers and other substances [3] [20] [27], can also be weathered, degraded or altered physical and geochemically by biotic and abiotic factors [1] [18] [28] [29] still in the reservoir rock, during the processes of exploration and/or transport and possible spills [5] [12].

Petroleum weathering in marine environments [15] [19] [22] [30] [31] (or involving water as means physical contact) includes processes like adsorption, biodegradation [23], dispersion, dissolution, emulsification, spreading, evaporation, photo-oxidation (**Table 1**) [1] [5] [12] [32] acting synergistically, decomposing, deteriorating, oxidizing or weathering the crude oil (**Figure 1**) [1] [33]-[40]. There is also a special case of adsorption processes, were the oil or his derivatives aggregate on the material particles suspended in the column water, called OSA (Suspended Particulate Material Oil-Aggregates).

The time and intensity of action of each process can differ and depend mainly on the physical and geochemical characteristics of the oil spilled [1] [10]. Thus, each phenomenon depends intrinsically on the pre-existence of other to promote the degradation or attenuation of an oil patch in the environment [12] [15] [29] [41].

The physico-chemical characteristics of oil can change depending on its stage of maturation or degradation. The American Petroleum Institute (API) has established a standard hydrometric scale (API gravity) to classify the oils and its derivatives [41]. The API gravity is a physical property that relates the density and the fluidity of a crude oil. This property is directly related to their geochemical composition, which will directly influence the weathering processes and the residence time of a given oil into the ecosystem. The **Figure 2** presents the behavior for different kind of petroleum. For example, for light crude oils, with higher API gravity (Group 1), present a short weathering time, which reach no more than some weeks. However, in oils with low API gravity, less than 25 (Group 4), the weathering time can take decades because the predominance of fractions of higher chemical complexity and molecular weights, such as resins and asphaltenes, which are practically unalterable by weathering processes, and cause, therefore, a significant environmental impact [1] [5] [19] [26] [31] [42] [43].

The **Table 2** present a classification for different oils, according to their density (API gravity) and composition for some international agencies related to the oil industry.

3. Biomarkers

Geochemical biomarkers, also known as molecular markers or geochemical fossils, are complex and stable organic molecules, which is present in oils and can be analyzed, identified and quantified [1] [44]. These molecules are derived from the cell membrane of alive organisms (prokaryotic or eukaryotic), so they are called precursor and have a high degree of specificity [45]. The similarity between biomarkers and their precursor molecules (synthesized by alive organisms) and the relation between different biomarkers provide information about

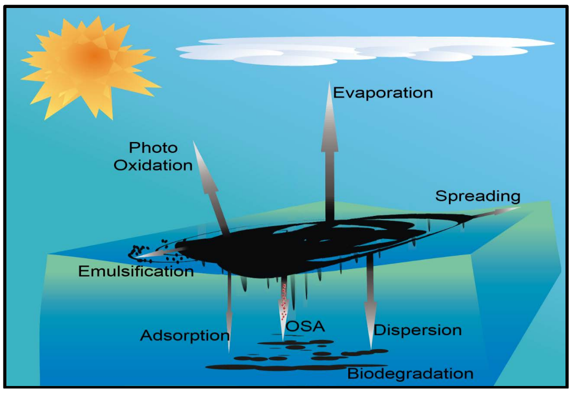
Table 1. Weathering process associated with the oil spill in marine environments.

Process	Type	Mechanism and/or Reaction	Effect
Adsorption	Physical-chemical	Electrostatic interactions	Adhesion of oil components to suspended particulate matter and OSA [5] [36].
Biodegradation	Biochemical	Oxidation/decomposition by microorganisms	Modification of physical-chemical properties of molecules [1] [5] [11] [17] [31] [36].
Dispersion	Physical	Water turbulence	Break-up the oil patch into droplets [5] [36].
Dissolution	Physical-chemical	Water temperature and turbulence	Solubilization of petroleum compounds, especially those with low molecular weight and size [5] [36].
Emulsification	Physical-chemical	Water temperature and turbulence	Formation of double or triple emulsions, *i.e.*, tiny oil droplets (disperse phase) in water (continuous phase), forming a metastable mixture [5] [36].
Spreading	Physical	Action of winds, tides, waves and currents	Oil patch expansion. If the petroleum has light composition, the spread of the patch is easier [5] [36].
Evaporation	Physical-chemical	Water temperature and turbulence	Volatilization of oil compounds [1] [5] [36].
Photo-oxidation	Physical-chemical	Action of light, especially ultraviolet radiation, and oxygen	Break oil constituents in simple molecules [1] [5] [32] [36].

Table 2. API gravity classification by different world agencies.

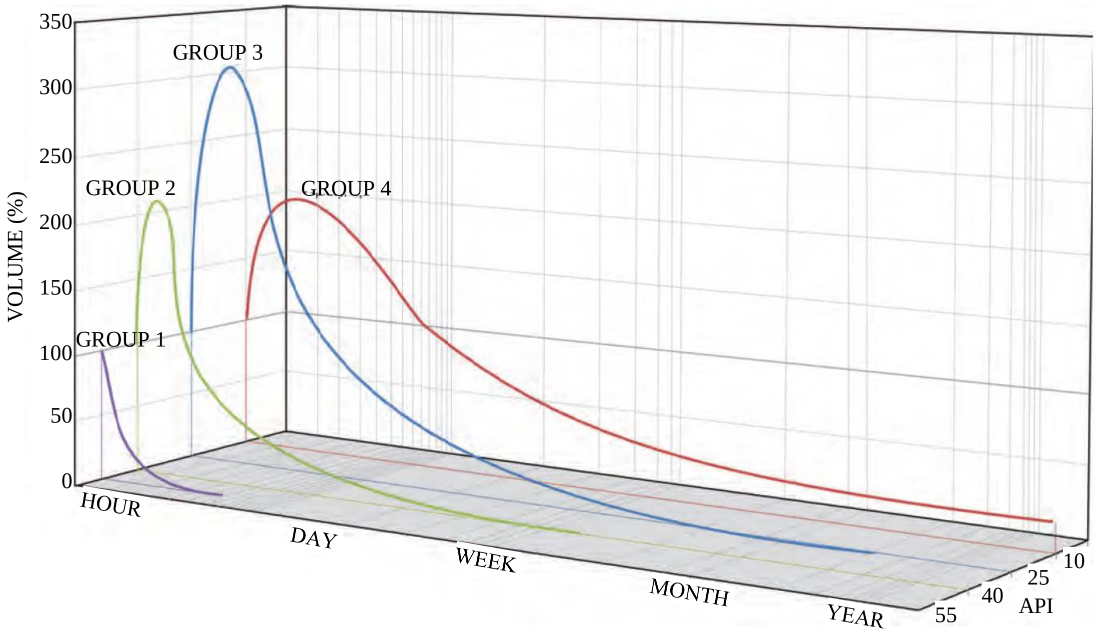
Agency	Grau API			
	Light	Medium	Heavy	Ultra Heavy
Alberta Government/Canada[1]	≥34.0	25.0 - 34.0	10.0 - 25.0	≤10.0
US Deparment of Energy[2]	≥35.1	25.0 - 35.1	10.0 - 25.0	≤10.0
Organization of the Petroleum Exporting Countries (OPEC)[3]	≥32.0	26.0 - 32.0	10.5 - 26.0	≤10.5
Petrobras Offshore[4]	≥32.0	19.0 - 32.0	14.0 - 19.0	≤14.0
Petrobras Onshore[4]	≥32.0	18.0 - 32.0	13.0 - 18.0	≤13.0
ANP/Brasil[5]	≥31.1	22.3 - 31.1	12.0 - 22.3	≤12.0
Americam Petroleum Institute (API)[6]	≥30.0 Basically 15% alkanes and 25% alkanes cycle	22.0 - 30.0 Alkanes and 25% to 30% hydrocarbons	10.0 - 22.0 Aromatic hydrocarbons	≤10.0 Long chain hydrocarbons (higher than pentane)

Source: 1: Governo do Estado de Alberta, Canada, http://www.gov.ab.ca; 2: Departamento de Energia dos Estados Unidos, http://www.energy.gov; 3: OPEC (Organization of the Petroleum Exporting Countries), http://www.opec.org; 4: Petróleos Brasileiros S. A., http://www.petrobras.com.br; 5: Agência Nacional de Petróleo, http://www.anp.gov.br; 6: American Petroleum Institute, http://www.api.org.



Source: Modified from No. 6 Fuel Oil (Bunker C) Spills, NOAA's National Ocean Service, 2006.

Figure 1. Weathering process associated to petroleum spill in marine environment.



Source: http://www.itopf.com/marine-spills/fate/models/index.html, 2014.

Figure 2. Residence time of petroleum in marine environment according to its API grade.

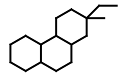
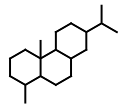
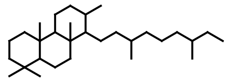
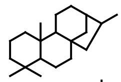
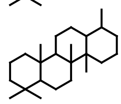
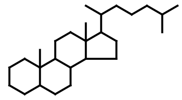
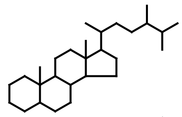
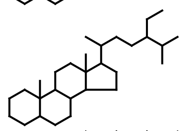
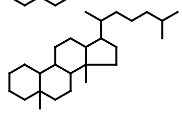
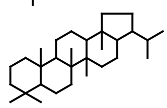
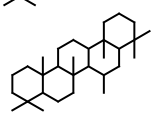
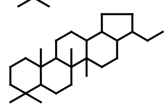
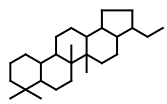
the organic matter source, paleo environmental characteristics, thermal evolution degree, oil identification (fingerprint) and rock-oil, oil-oil and rock-rock ratio [46]-[48]. However, the separated information is not absolutely reliable; it requires the largest number of possible relations to obtain a good interpretation [1] [9] [28] [31] [44] [45] [49]-[51].

Therefore, petroleum biomarkers are the components of most geochemical interest because they allow to define the factors genetics of each oil [1] [22] [23] [47] [52]. The petroleum biomarkers more commonly used in geochemistry are branched, cyclic and alkylated cyclicalkanes, like pristane (C_{19}; 2,6,10,14-tetramethylpen-tadecane) and phytane (C_{20}; 2,6,10,14-tetramethyl hexane), for acyclic alkanes [1]. Cyclic saturated biomarkers include tricyclic, tetracyclic as the C_{27}, C_{28} and steranes C_{29} (cholestane, ergostane and stigmastane respectively, so-called diamondoid). Pentacyclics [53], such as C_{30}-hopane, are the most abundant biomarkers in oil, and they are followed by gammacerane, the homologous series of homohopanes and norhopanes (T_s, T_m) [18] [54] [55], and others [1] (**Table 3**).

Molecules of biological origin such as biomarkers exhibit stereoisomerism [1] [7] [9] [54] [55], *i.e.*, isomers exhibit same formula and molecular weight, but differ in spatial arrangements of their atoms [55]. The same occurs for homologous series of petroleum biomarkers, which present isomers S, R, $\alpha\alpha\alpha$, $\alpha\beta\beta$, $\beta\beta\beta$, for hydrogen bound to a particular(s) carbon(s) in the biomarker. These variations are according to their origin, geochemical maturity degree or degradation level [1] [54] [56] [57]. The C_{29} sterane epimers are examples; they are used as paleotemperature or geochemical maturity parameters (**Figure 3**) [57]. In environmental geochemistry, stereoisomerism can be used to estimate degradation level (weathering) of crude oil or assessing remediation processes in areas impacted by petroleum activities [1] [9] [10] [44].

Another important petroleum biomarker is chemically classified as aromatic hydrocarbon [1] [8], can be use as indicators of input of organic matter, to assess the maturity level or environmental applications, or also to assess the source and composition of these compounds in a contaminated ecosystem [1] [56] [58]. Geochemically the poliaromatic hydrocarbon (PAH) may have different sources [59]. When originate from incomplete combustion processes and include molecules with up to six aromatic rings, the source is called pyrolytic. Petrogenic source correspond to aromatic compounds of higher molecular weight and it includes the pyrolytic. Due to the PAHs physicochemical characteristics, they are considered priority pollutant substances by global control agencies [56] [59] (**Table 4**). According to the classification and the legislative rules, hydrocarbons with 16 or 32 aromatic hydrocarbons should be monitored, because some of them can be carcinogenic and very dangerous for human healthy and the environmental.

Table 3. Examples of tricyclic, tetracyclic, and pentacyclic saturated biomarkers [1].

Biomarker Type	Biomarker Name	Molecular Formula Minimum	Molecular Structure
Tricyclic	Pimarane	$C_{17}H_{30}$	
	Phychtelite	$C_{19}H_{34}$	
	C_{30}-Tricyclohexaprenane	$C_{30}H_{56}$	
Tetracyclic	Kaurane	$C_{20}H_{34}$	
	C_{24} Secohopane	$C_{24}H_{42}$	
	Colestane	$C_{27}H_{48}$	
	Ergostane	$C_{28}H_{50}$	
	Estigmastane	$C_{29}H_{52}$	
	Diacolestane	$C_{27}H_{48}$	
Pentacyclic	C_{30} Hopane	$C_{30}H_{52}$	
	Gammacerane	$C_{30}H_{52}$	
	28,30-Bisnohopane	$C_{28}H_{48}$	
	25,28,30-Trisnohopane	$C_{27}H_{46}$	

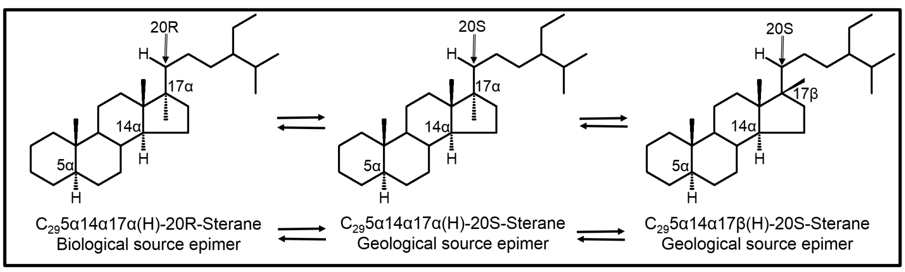
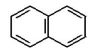
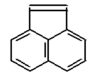
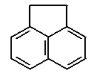
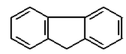
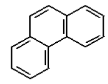
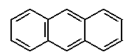
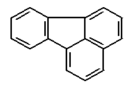
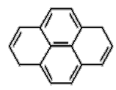
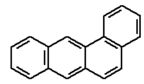
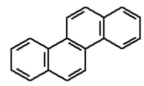
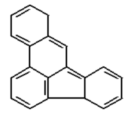
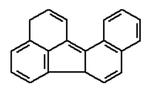
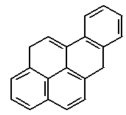
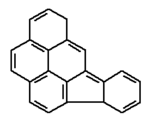
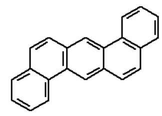
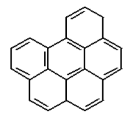


Figure 3. Stereoisomery of C_{29} steranes [1].

Table 4. Priority PAHs indicating the number of aromatic rings, the molecular formula minimum, molecular mass, and the associated health risks.

Source		PAH	Rings*	Molecular Formula Minimum	Molecular Mass [g/Mol]	Health Risk (NOAA)	Molecular Structure
Petrogenic	1	Naphthalene	2	$C_{10}H_8$	128.19	Not carcinogenic	
	2	Acenaphthylene	3	$C_{12}H_8$	150.20	-	
	3	Acenaphthene	3	$C_{12}H_{10}$	154.21	-	
	4	Fluorene	3	$C_{13}H_{10}$	166.20	Not carcinogenic	
	5	Phenanthrene	3	$C_{14}H_{10}$	178.20	Not carcinogenic	
	6	Anthracene	3	$C_{14}H_{10}$	178.20	Not carcinogenic	
Pyrolytic	7	Fluoranthene	4	$C_{16}H_{10}$	202.30	-	
	8	Pirenne	4	$C_{16}H_{10}$	202.30	Not carcinogenic	
	9	Benzo (a) anthracene	4	$C_{18}H_{12}$	228.30	Carcinogenic	
	10	Crisene	4	$C_{18}H_{12}$	228.30	Weakly carcinogenic	
	11	Benzo (b) fluoranthene	5	$C_{20}H_{12}$	252.32	Weakly carcinogenic	
	12	Benzo (k) fluoranthene	5	$C_{20}H_{12}$	252.32	-	
	13	Benzo (a) pirenne	5	$C_{20}H_{12}$	252.32	Strongly carcinogenic	
	14	Indeno (1,2,3-cd) pirenne	6	$C_{22}H_{12}$	276.34	Carcinogenic	
	15	Dibenzo (a,h) anthracene	5	$C_{22}H_{14}$	278.35	Strongly carcinogenic	
	16	Benzo (g,h,i) perylene	6	$C_{21}H_{16}$	268.36	Not carcinogenic	

Source: Modified from Veiga, 2003.

3.1. Weathering Biomarker

Oil weathering can be assessed in three different ways: 1) by the presence or absence of oil compounds and biomarkers [60]; 2) by the oil relative molecular abundance e; 3) parametrically, using relations between heights, areas or concentrations of biomarkers and/or compounds of geochemical interest [31] [61] [62]. Weathering processes affect the status of different biomarkers and crude oil compounds [1] [60] and its molecular abundance over indicates deterioration, degradation or weathering level and residence time of certain petroleum. The **Figure 4**, show some biochemical reactions them occur in the weathering process for biomarker of petroleum. This reaction includes hydrolysis (chemical oxidation and reduction), cracking, metabolization, free radicals formation and others.

3.2. Biomarker Analyses

Analytically, biomarkers are detected by gas chromatography coupled to mass spectrometry (GC-MS), using single ion monitoring (SIM) [1] [27] [31] [42] [56] [62] [63]. Is monitoring ion mass-charge *m/z* 169 and *m/z* 197 to pristane and phytane, *m/z* 177 and *m/z* 191 for homologous series of tricyclic, for C_{30}-hopane (**Figure 5(a)**), T_s and T_m hopanes, oleanane, gammacerane, and homohopane homologous series (C_{31}-C_{35}) [1] [54] [57] [62] [63]. Steranes are monitored by ions at *m/z* 217 and *m/z* 218 (**Figure 5(b)**) [1].

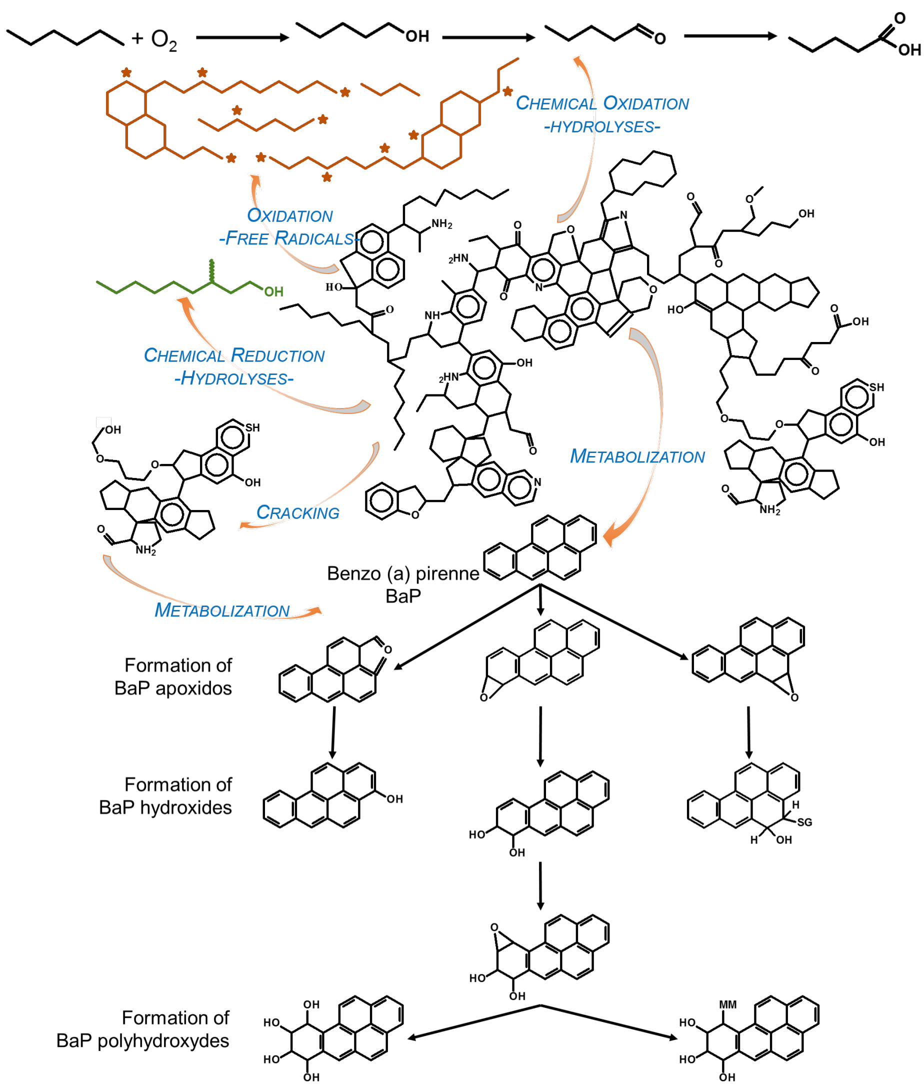


Figure 4. Biomarker weathering and compounds for a sample of petroleum.

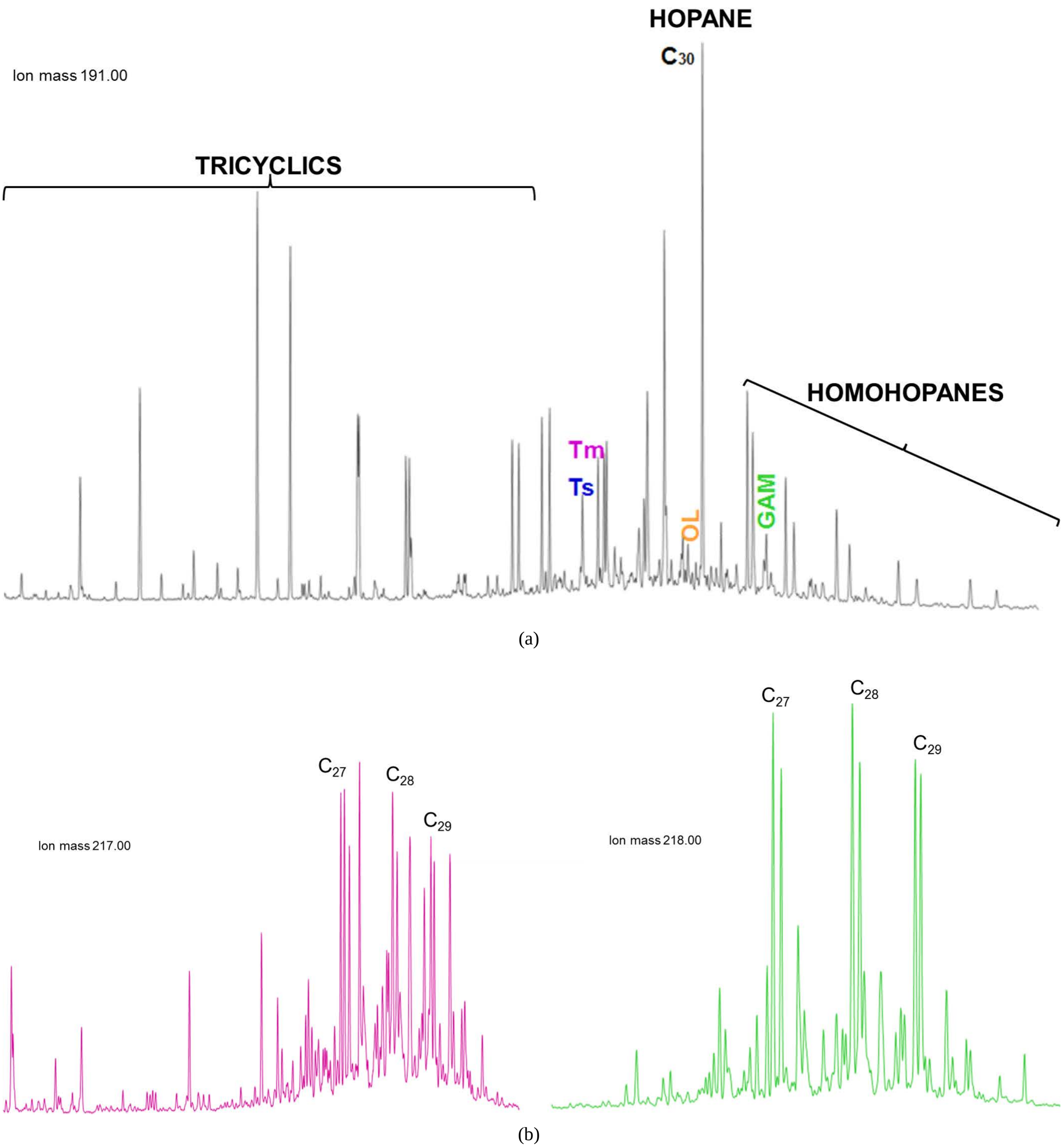


Figure 5. Fragments for biomarker of petroleum monitoring for GC-MS in SIM mode. (a) Ion fragment *m/z* 191 for petroleum biomarkers: tricyclic homologous series, T_s, T_m, C_{30}-hopane, gammacerane and homologous series of C_{31} to C_{35} homohopanes. T_s: $C_{27}18\alpha$(H)-22,29,30-trisnorneohopane. T_m: $C_{27}17\alpha$(H)-22,29,30-trisnorhopane; (b) Fragment ions *m/z* 217 and *m/z* 218 for C_{27}, C_{28}, and C_{29} steranes.

3.3. Weathering Biomarker Parameters

Parametrically, the values evaluated in petroleum weathering are the ratios between pristane/C_{17}, phytane/C_{18}, pristane/fitane [1] [64], depletion percentage, %C_{27}, C_{28}, C_{29}-steranes, C_{30}-hopane/gammacerane index, T_s/T_m, stereoisomery index C_{29}-steranes and 22R/22S-homohopane [1] [37] [54] [57]. Some equations are used to assess these relations, and thus estimate the degradation level or weathering of crude oil (Equations (1), (2), (3) and (4)). There are several import parameters that must be calculated in order to check and interpreting the overall weathering process [37] [54] [56] [60] [65]-[67].

The depletion percentage evaluates the time the decrease in molecular abundance of specific biomarker, based on the relative abundance of C_{30}-hopano. Where the initial biomarker concentration of interest (A_0); are measure by the ratio of the initial concentration of C_{30}-hopane (H_o) at time initial (0). After the spill of the weathered is calculate by the ratio biomarker of interest concentration at time (A_t) and the concentration the C_{30}-hopane (H_t,) (Equation (1)) [30].

$$\%\mathbf{Depletion} = \left(\frac{\mathbf{A}_0}{\mathbf{H}_0} - \frac{\mathbf{A}_t/\mathbf{H}_t}{\mathbf{A}_0/\mathbf{H}_0}\right) * 100 \tag{1}$$

The steranes percentage of C_{27}, C_{28} and C_{29}-steranes, estimate the weathering process or maturate index for determinate steranes and can be determined by the ratio of esterano study and sum of C_{27}, C_{28} and C_{29} steranes. It is calculated by substituting the $\%C_{28}$-sterane and $\%C_{29}$-sterane (Equation (2)) [1] [33] [54].

$$\%\mathbf{C}_{27}\left(\mathbf{sterane}\right) = \frac{\mathbf{C}_{27}}{\mathbf{C}_{27} + \mathbf{C}_{28} + \mathbf{C}_{29}} * 100 \tag{2}$$

The T_s/T_m index possibility the assess input matter, maturity and degradation or weathering. Peters and collages (2005), describe that for particulars cases, T_m is more easy degradable then T_s, so the T_s/T_m Index increase with the weathering process (Equation (3)) [1] [33] [54].

$$\mathbf{T_s/T_m\,Index} = \frac{\mathbf{T_s}}{\mathbf{T_s} + \mathbf{T_m}} \tag{3}$$

Stereoisomerism steranes index determining levels of maturate, degradation, or weathering for mixture racemic the steranes (**Figure 3**) [1] [33].

$$\mathbf{C}_{29}\textbf{-sterane Index} = \frac{\mathbf{C}_{29}\alpha\alpha\alpha(\mathbf{H})\textbf{-20S}}{\mathbf{C}_{29}\alpha\alpha\alpha(\mathbf{H})\textbf{-20S} + \mathbf{C}_{29}\alpha\alpha\alpha(\mathbf{H})\textbf{-20R}} \tag{4}$$

Aromatic biomarkers can be parametrically assessed through different equations in accordance with the aromatic compounds monitored and geochemical interests [1] [8] [24] [33] [48] [68] [69]. Peters *et al*. (2005) and Veiga (2003) broadly describe the geochemical and parametric use of these compounds.

The data generated will be analyzed in comparison with literature data, and also analyzed statistically, based on the Multivariate Statistics applied to environmental studies and research [39] [65] [66]. Besides the use of descriptive statistical analyzes to achieve the proposed goal will be used the *Statistica* program for *Windows*, version 7.0 of the *Statsoft* Inc. for statistical analysis. Thus, the steps carried out in the statistical treatment of the data will be as following [1] [56] [57] [60]-[63] [65] [66] [70]-[72].

4. Limitation of the Study

For aromatic compounds, this review focused on the environmental purpose of the PAHs, more than in the aspect related to the derivative geochemistry description of their molecular abundance in particular oil.

5. Conclusion

Assessment, monitoring, and modeling of weathering processes associated with petroleum biomarkers are important tools for geochemistry of petroleum and environment. This allows predicting, with relative certainty, the residence time and what kind of compounds was generated during a probable oil spill, and indicates which kind of technology would be more appropriated to rapidly recover an impacted area or ecosystem. In a scientific view, this study provides technical-scientific knowledge, innovation base needed in processes associated with the petroleum industry and environmental impact studies.

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