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Coastal Bitumen Pollution of the Mediterranean City of Alexandria, Egypt

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Abstract. This work represents monitoring of beaches pollution of the Mediterranean city of Alexandria, Egypt by environmentally weathered bituminous materials. A beach bitumen residue was collected and analyzed, after chromatographic separation into aliphatic and aromatic components, by ultra high-resolution Fourier transform ion cyclotron resonance mass spectrometry to detect high-molecular weight polycyclic aromatic sulfur heterocycles. Plotting the double bond equivalents versus the Kendrick nominal mass gave the distribution pattern of high-molecular weight polycyclic aromatic sulfur heterocycles. This pattern was not observed in the studied Egyptian crude oils indicating that the Suez-Mediterranean pipeline terminal and discharge of ballast waters and tank washings from the tankers carrying foreign crudes could be suspected to be the pollution source and could have contributed significantly to the bitumen residues polluting Alexandria beaches.

Keywords: Fourier transform ion cyclotron resonance mass spectrometry; Bitumen pollution; High-molecular weight polycyclic aromatic sulfur heterocycles

1. Introduction

One of the major tourist attraction places in Egypt is the coasts of the Mediterranean city of Alexandria for their clear waters. However, the Alexandria beaches are subject to petroleum pollution in the form of bitumens from several sources such as the Suez-Mediterranean pipeline terminal (SUMED) 27 km west of Alexandria, oil transportation, natural seeps, untreated domestic sewage, industrial waste waters, oil spillage and ballast water discharge from tankers. Many case studies have used *n*-alkanes, biomarkers, low-molecular weight polyaromatic compounds as spilled oil source markers and monitoring of oil pollution [1-3]. However, almost no published data used high-molecular weight components in oil spills monitoring.

We monitored in this work the Alexandria beaches oil pollution by analyzing the high-molecular weight polycyclic aromatic sulfur heterocycles (HMSH) of coastal bitumen applying Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). We also investigated their possible source. The ultra high-resolution FT-ICR MS was introduced recently in the field of petroleum science to characterize the high-molecular weight petroleum components [4-11].

2. Experimental

2.1. Solvent Extraction of Coastal Bitumen

The coastal bitumen was weighed (2.5 g), mixed with approximately 5 g of anhydrous sodium sulfate and then extracted to obtain the extractable material according to Wang et al. [12].

2.2. Bitumen-extractable Material Fractionation

Column chromatography fractionation was used to separate the extractable material to aliphatic and aromatic fractions as indicated by Hegazi and Andersson [13].

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2.3. Derivatization of Aromatic Fraction

The HMSH of aromatics were derivatized by methyl iodide to get thiophenium salts required for the electrospray ionization FT-ICR MS analysis applied in this work [14].

2.4. Fourier Fransform Ion Cyclotron Resonance Mass Spectrometer Analysis

Mass spectra were acquired using an APEX III FT-ICR MS (Bruker Daltonics, Bremen, Germany) equipped with a 7 T actively shielded super conducting magnet and an Agilent ESI source.

3. Results and Discussion

Monitoring of oil contaminants along the coast of Alexandria is very important for pollution abatement. Here we characterized the coastal bitumen by HMSH as determined by FT-ICR MS to investigate their possible source. The mass spectra of the derivatized aromatic fraction of coastal bitumen was very complicated so that it could not give any useful information without data sorting using the Kendrick mass scale [15-17].

The distribution pattern of HMSH was illustrated by plotting the double bond equivalents (DBE), the sum of the total number of rings and double bonds present in a molecule, versus the Kendrick nominal mass (KNM) (Figures 1).

The HMSH present ranges from DBE 6 to 16 with a mass range 216-954 Da. Compounds having DBE 6 to 11 showed higher abundance than the others as indicated by the size of the circles in the Kendrick plot (the magnitude of the signals in the mass spectra is represented by the size of the circles). The most abundant benzothiophene series (DBE 6) starts at mass 218 and goes up to 890 Da, indicating the presence of C_6- to C_{54}-benzothiophenes. The lower substituted compounds (C_0-C_5) were lost by different weathering conditions. A DBE value of 7 indicates a compound with a structure similar to that of naphthenobenzothiophenes. This series contains from 1 to 54 CH_2-groups in the side chains. The next higher homologues (DBE 8) can be those of the dihydrodibenzothiophene series or benzothiophenes with two naphthenic rings containing from 5 to 53 carbon atoms as alkyl side chains. DBE 9 represents the series of dibenzothiophenes. Here, alkyl side chains are found with 3-56 carbon atoms. As the DBE increases, the probability of finding isomeric parent compounds increases to a greater extent. For instance, the next higher series (DBE 10) might consist of dibenzothiophenes with a naphtheno ring (naphthenodibenzothiophenes), acenaphthenothiophenes, or benzothiophenes with a phenyl group as a substituent. The compounds here contain up to 52 side chain alkyl carbons. This HMSH distribution was not observed in Egyptian crudes so that the presence of this beach bitumen can be explained by accidentally spillage of tankers carrying foreign oils to other countries.

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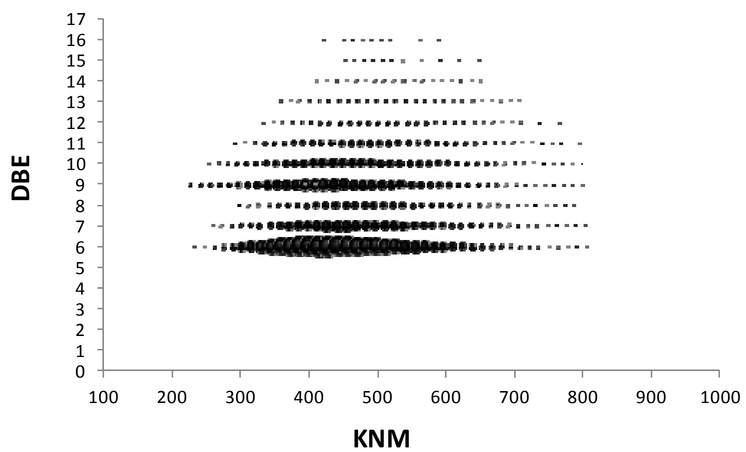

Fig. 1: Kendrick plot showing the distribution patterns of high-molecular weight polycyclic aromatic sulfur heterocycles of coastal bitumen.