Effect Of Weathering On High-Molecular Weight Sulfur-Containing Aromatics
By Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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As soon as oil is spilled into the marine environment, different weathering factors act to change its composition, which make the identification of the spill source something of a challenge. Biomarkers and low-molecular weight polyaromatic compound ratios have been used for oil source identification and monitoring of weathering and biological degradation processes. However, in some cases, the biomarkers may be absent or below the detection limit [1] or the low-molecular weight polyaromatic compound ratios are not accurate enough due to interferences between e.g. C_{x+4}-naphthalenes and C_{x}-dibenzothiophenes [2]. In this work, we investigate the effect of weathering on the high-molecular weight sulfur-containing aromatics (HMSA) by ultra high-resolution Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS). Flotta crude oil (North Sea) was subjected to six months artificial weathering experiment. After fractionation of the oil and its weathered samples into aliphatics and aromatics, the aromatics were subjected to FTICR-MS. The data were analyzed [3] and the HMSA distribution patterns were obtained by plotting the double bond equivalents (DBE) versus the nominal masses. The oil contains HMSA of a DBE range from 1 to 17 with a mass range from 188 Da to 894 Da. The weathering indicated that the compounds having DBE from 6 to 14 with a mass range from 196 Da to 640 Da remained after six months. Compounds having DBEs 6 with mass range 246-610 Da (benzothiophenes), 7 with mass range 244-608 Da (naphthenobenzothiophenes), 9 with mass range 212-618 Da (dibenzothiophenes) and 10 with mass range 210-616 Da (naphthenodibenzothiophenes) are the most abundant and resistant to the different weathering factors. Moreover, compounds having DBE 9 and 10 showed higher stability than the DBE 6 and 7 counterparts as indicated by the decrease in the ratios of benzothiophenes/dibenzothiophenes, naphthenobenzothiophenes/dibenzothiophenes, benzothiophenes/naphthenodibenzothiophenes and naphthenobenzothiophenes/naphthenodibenzothiophenes with weathering. The ratios are 1.61, 1.12, 2.05 and 1.43 in crude oil and 1.29, 0.8, 1.79 and 1.12 in the weathered sample. By examining the ratio of dibenzothiophenes/naphthenodibenzothiophenes, we found that the ratio is 1.30 and 1.36 in crude oil and six months weathered sample, respectively. Hence, the constancy of this ratio suggests that the ratio can be used as a marker of the studied oil and accordingly may be applied for spilled oil source identification, especially in cases where the light fractions have been lost due to weathering. However, further studies should be done to check how strongly the marker value varies in different oils.

References