Barium ion adduct mass spectrometry to identify carboxylic acid photoproducts from crude oil-water systems under solar irradiation

Journal:	*Environmental Science: Processes & Impacts*
Manuscript ID	EM-ART-09-2020-000390.R1
Article Type:	Communication

ENVIRONMENTAL SIGNIFICANCE STATEMENT

Naphthenic acids (NAs) are widely present in crude oil and are being regulated due to their toxicity and persistence in the environment. NA's are a class of carboxylic acids (COOHs) defined by their structure and number of carbon atoms. Screening for COOHs in oil contaminated waters is important when tracking the harmful effects of water-soluble petroleum products formed from sunlight. It is well-known sunlight increases bioavailability and often toxicity of oil spilled in aquatic systems, but there is still much unknown about the composition of the photoproducts, including COOHs. Barium ion adduct chemistry offers an elegant way to screen for COOHs in petroleum polluted waters.

Barium ion adduct mass spectrometry to identify carboxylic acid photoproducts from crude oil-water systems under solar irradiation

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ABSTRACT

Petroleum derived dissolved organic matter (DOM_{HC}) samples were successfully cationized with barium, revealing many $[M-H+Ba]^+$ peaks in both dark and simulated sunlight treatments. The DOM_{HC} samples generated after light exposure exhibited a greater number of $[M-H+Ba]^+$ peaks compared to the dark control. Multiple $[M-H+Ba]^+$ peaks were investigated in the irradiated DOM_{HC} using low resolution MS/MS in order to confirm the presence of diagnostic fragment ions, m/z 139, 155 and 196 in each treatment. Due to the high complexity of the bariated DOM_{HC} mixture, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS/MS) was employed to obtain molecular level information for both irradiated and dark treatments. The irradiated DOM_{HC} treatments had more bariated oxygenated species over a wide range of H/C and O/C ratios when compared to the dark controls. Doubly bariated species were also observed in DOM_{HC}, which provides evidence that photochemistry transforms DOM_{HC} to even more complex mixtures with multiple oxygenations per molecule. This study provides evidence that barium adduct mass spectrometry can be successfully applied to DOM_{HC} screening for the presence of COOHs, both in dark samples and solar irradiated samples. Furthermore, direct evidence and molecular composition of aqueous phase crude oil photoproducts is provided by this technique.

INTRODUCTION

Petroleum derived naphthenic acids (NAs) are a class of carboxylic acid (COOHs) compounds known for their toxicity to aquatic life,[1-7] vegetation[8-11] and for their persistence in the environment.[12-15] Headley and McMartin (2004) define NAs as alkyl substituted cycloaliphatic carboxylic acids (COOHs) with small amounts of acyclic aliphatic acids,[14] Shepherd et al. (2010) defined NAs as derivatives of cyclohexane and cyclopentane homologues from petroleum containing carboxylic acid groups[16] and many reports have defined them as having the formula $C_nH_{2n} + zO_2$.[17-22] Naphthenic acids, widely found in crude oil,[23] are important due to their prevalence in oil contaminated sites,[17, 24-26] chronic toxicity,[1, 2, 9, 27-31] persistence in the environment,[20] and their important role in biogeochemical cycles.[24, 32]

Naphthenic acids are present in complex mixtures such as oil sands processed water.[14, 15, 17, 33-36] and petroleum.[24, 37-41] and have be widely studied using fluorescence,[25, 42] gas chromatography coupled with mass spectrometry (GC-MS)[43, 44] and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS).[10, 45-53] Targeted and non-targeted derivatization methods have been employed in order to selectively detect NAs. Omari et al. (2019) utilized a charge tagging technique to detect NAs in petroleum fractions.[23] Gutierrez-Villagomez et al. (2017) derivatized NAs and analyzed them using GC-MS.[54] A few notable studies utilized GC x GC-TOF MS to identify derivatized NAs in petroleum and tailing waters.[16, 55, 56] Duncan et al. (2016) developed a method which used barium ion chemistry for fatty acids (FAs)[57-59] coupled with online membrane sampling to selectively ionize COOHs and FAs in wastewater samples.[60] Isolation and cationization of COOHs and FAs using barium derivatization produces barium adducts, which are selectively ionized in positive-ion electrospray ionization ((+) ESI).[57-60]

It is well known that photochemistry plays a major role in the fate of petroleum spilled in areas with sunlight exposure.[61-68] Recent work has shown that a wide array of photoproducts are generated by natural photochemistry of crude oil under solar irradiation.[69-73] In studying the photochemical mechanisms of oil transformations, previous studies observed increased concentrations of aldehyde and ketone photoproducts in the aqueous phase with solar irradiation time.[73] Given that oil sand processed waters (OSPW) from bitumen has been thoroughly characterized[35, 43, 47, 74-77] and shown to contain up to 2 % weight of NAs per total bitumen,[14] we hypothesize that a portion of photooxygenated petroleum which has been previously shown to produce NAs,[78] contains NAs which eventually diffuse into the water once petroleum is exposed to sunlight. Zito et al. (2019) have shown that after the first 24 hours of light exposure, the DOM_{HC} exhibited bioluminescence inhibition to *Vibrio fischeri*.[69] This response may be partially due to the presence of NAs produced from the petroleum after sunlight exposure as shown in previous reports on toxicity of oil sands processed water containing naphthenic acids.[26, 27, 30, 34, 79-84] However, more sophisticated toxicity studies are needed in order have a deeper understanding of the toxic effects of DOM_{HC} on human and aquatic life. In order to characterize NAs and other COOHs in DOM_{HC}, which is a complex mixture, we employed the use of barium ion chemistry known to work for NAs[60] and fatty acids (FAs)[57-59] to selectively identify COOHs present in the DOM_{HC} mixture.

This study presents a preliminary investigation on the barium cationization of DOM_{HC} generated in pure water from thin petroleum films exposed to simulated sunlight. We know that the composition of DOM_{HC} is highly oxygenated,[69] however, it is unknown what portion of the oxygen containing compounds is comprised of NAs or other COOHs. This study utilizes the methods employed by Duncan et al. (2016) and FT-ICR MS to gain a deeper understanding of the presence of COOHs, which make up a portion of DOM_{HC}. The use of barium ion chemistry provides an elegantly simple approach that is selective to COOHs and eliminates contamination. Controlled laboratory studies of acid photoproducts generated in DOM_{HC} from pure water are useful because they eliminate potential contamination from background DOM sources and biota, which are known interferences and make NAs and COOHs hard to characterize.[85-87] The results obtained by using this approach provide insight into the composition of acids present in DOM_{HC} and have important implications for understanding the fate and persistence of hydrocarbons released by oil spills.

EXPERIMENTAL

Materials

The oil used in this study was a surrogate Macondo oil (MC), (provided by BP August 2011, chain of custody number 20110803-Tarr-072). All glassware was acid cleaned and combusted at 550 °C prior to use. Nanopure water was collected from an Aeries nanopure system. Barium acetate was purchased from Sigma Aldrich. Methanol was HPLC grade and purchased from Fischer Scientific.

Irradiation experiments

Photoirradiations were performed in batches of three at a single time point for dark and light samples using an Atlas CPS + solar simulator in nanopore water (refer to Zito et al. (2019) for experiment details).[69] Briefly, thin films of MC oil were prepared by pipetting 385 μL over 50 mLs of nanopore water. The beakers were subsequently covered with quartz lids to prevent evaporation and thermostatically controlled at 27°C. Dissolved organic carbon concentration (DOC) was measured on all samples, which were preconcentrated by the solid–phase extraction technique described in detail elsewhere.[88] Briefly, after DOC analysis, each sample was acidified to pH 2 prior to loading onto a Bond Elut PPL (Agilent Technologies) stationary phase cartridge. Each sample was eluted with methanol at a final concentration of 50 μgC mL^{-1}. The extracts were stored in the dark at 4°C in pre-combusted glass vials until analysis. Methanol extracts were subsequently mixed with 20 μL of 0.1 mM barium acetate prior to analysis in order to target carboxylate moieties per previously published methods for wastewater.[60] Elemental formulas of the barium adducts were obtained using (+) electrospray ionization (ESI) on a 9.4 T FT-ICR-MS using PetroOrg © software developed at the National High Magnetic Field Laboratory (NHMFL).[89-91] Molecular formulas were assigned within a tolerance of 1 ppm. Elemental constraints for each assignment iteration are listed Supporting Information (Table S1). Identification of molecular formulas using high resolution MS allows verification of barium adduct formation and determination of the number of oxygen molecules present in each photoproduced acid. Tandem mass spectrometry by infrared multiple photon dissociation (IRMPD; Synrad 48-2, $\lambda = 10.6$ μm, Mukilteo, WA) was used to confirm barium acetate derivatives. A single m/z at 302.9810, corresponding to a molecular formula of $C_6H_{13}O_5{}^{138}Ba_1$ (DBE = 1), was quadrupole isolated prior to high-resolution stored waveform inverse Fourier transform (SWIFT) isolation[92] and

IRMPD. In addition, quadrupole isolation of ~2 m/z segments were followed by IRMPD to track diagnostic bariated product ions (m/z 196.9186). The photon energy of the laser was fixed at 116.9 meV, using a total energy of ~20 J (25 W with an irradiation time of 800 ms). Lower energy would yield only the most labile losses, typically neutral loss. Experimental conditions were chosen to limit dimer formation. In addition, IRMPD experiments did not yield spectra indicative of multimer formation.

RESULTS AND DISCUSSION

Product ion scans using low resolution mass spectrometry (Figure S1) were performed, confirming the presence of bariated compounds with product ions of m/z 155 $[BaOH]^+$. The low-resolution MS-MS technique allowed determination of nominal masses for the presence of COOHs in the DOM_{HC}. These results also demonstrated an increased abundance of COOHs after exposure to simulated sunlight, including the presence of higher molecular weight species in the aqueous phase. However, due to the large number of peaks observed in both the dark and irradiated treatments, the use of FT-ICR MS was necessary to provide detailed characterization of the DOM_{HC} photoproducts.

Samples analyzed by FT-ICR MS confirmed the presence of known bariated diagnostic product ions, m/z 196 and m/z 139,[60] in the dark and irradiated DOM_{HC}. Figure 1 shows a heteroatom class graph of the percent relative abundance of molecular formulas derived from FT-ICR MS data versus number of oxygens per molecule (heteroatom class). Data for both dark (black) and irradiated (red and blue) DOM_{HC} samples are presented. The dark (black) and irradiated (red) DOM_{HC} samples both contained O_x species cationized with one barium atom, but only the irradiated sample contained O_x species cationized with two barium atoms (blue). Notably, there is a shift to higher oxygenated species after irradiation from O_2 to O_{10} as observed in previous studies.[69, 72] Figure 1 also shows that the bariated acid species have a wide range of oxygen content. These data not only confirm that the barium derivatization was successful, but they also show the presence of two barium atoms complexed with the

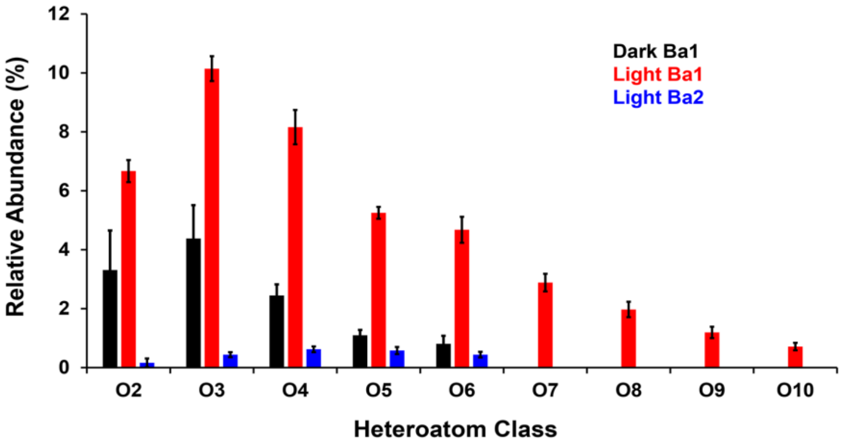

Figure 1: Heteroatom class graphs of bariated oxygen containing species for dark (black), Light (red) and double bariated light (blue) DOM_{HC} formula derived from FT-ICR MS. Error bars represent standard deviation (n=3).

O_x species. Because barium only forming adducts with COOHs,[60] the presence of two bound barium ions suggests that three acids are present in these species (two bariated and one free acid) to yield a singly charged species. Moreover, Duncan et al. (2016) confirmed that this technique was only selective to carboxylic groups containing hydrogen atoms located in the β and Ɣ positions,[60] Therefore, we can conclude with confidence that the compounds in the DOM_{HC} containing bariated adducts are indeed COOHs.

Figure 2 shows van Krevelen plots for all molecular formulas observed by FT-ICR MS (each dot on the plot) for the dark (a) and irradiated (b) DOM_{HC} bariated samples.

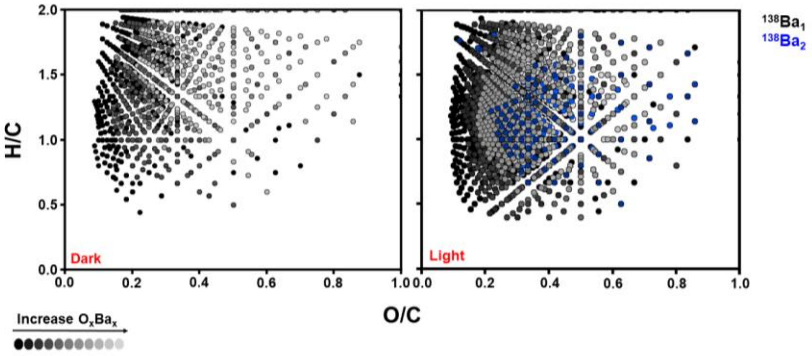

Figure 2: van Krevelen plots derived from FT-ICR MS data for the dark (left) and irradiated (right) DOM_{HC} bariated samples.

These data show that the bariated compounds span a large range of H/C and O/C. These data also show that there are more bariated compounds present in the irradiated versus the dark DOM_{HC} sample, confirming that more COOHs were present after sunlight exposure. Therefore, we can conclude that sunlight exposure results in the production of COOHs that partition to the aqueous phase. This process can be problematic when the DOM_{HC} enters aquatic systems due to the persistence and toxicity of NAs[26, 27, 34, 81] that are likely present among the carboxylated photoproducts. We also observed bariated compounds containing nitrogen and sulfur (Supporting S2), which have been previously reported for petroleum after light exposure.[78]

Figure 3 compares dark and irradiated treatments as a function of DBE versus percent relative abundance from the data derived from FT-ICR MS. There is a strong predominance of six to nine DBE heavily represented in the irradiated treatment.

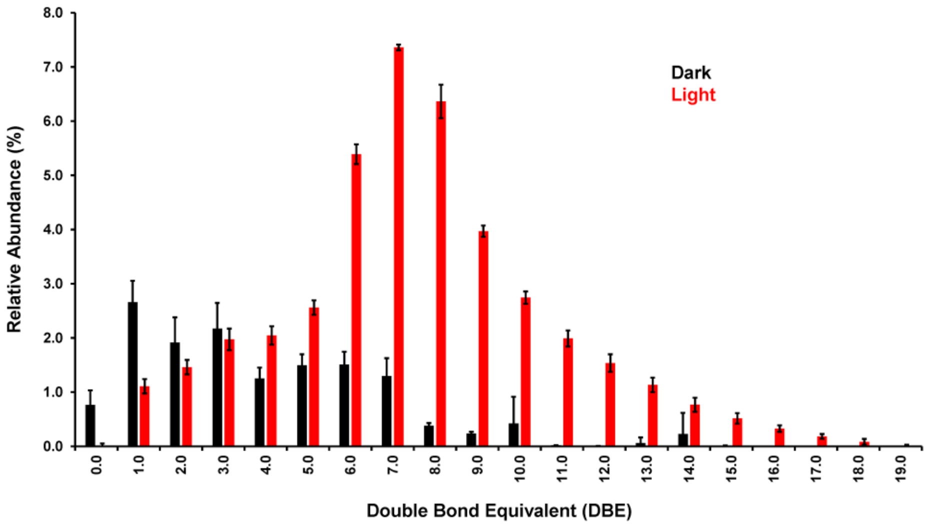

Figure 3: Compares dark (black) and light (red) DBE equivalents vs. percent relative abundance for bariated species data derived from FT-ICR MS in DOM_{HC}. Error bars represent standard deviation (n=3).

This result suggests that there are ring or aromatic species present in DOM_{HC} that are COOHs. Also, an increase in DBE was observed for the detected bariated species after irradiation. The increase in DBE after irradiation is for aqueous species and occurs specifically because of oxygenation. The photoproducts become more water soluble due to the presence of carboxylic acids created by photochemistry. The higher DBE species in the oil are not very water soluble because of their large size and non-polar nature. These large molecules are susceptible to oxygenation, which results in solubilization in the aqueous layer. While photobleaching does occur, its time dependence is slower than that for the formation of the oxygenated species. The DBE data can help identify the different types of COOHs present in the samples before and after irradiated exposure. Figure 3 also shows the presence of DBE zero compounds, which may represent alcohols. Previous reports using this method with alcohols did not observe a signal for hydroxylated species;[60] however, the use of FT-ICR MS allows for ultra-high resolution enabling for these compounds to be resolved and detected. Since NAs are commonly identified by structure and Ba cationization is selective to COOHs[60] high resolution MS and MS-MS data can be used to postulate what possible NAs are produced in water from irradiated petroleum. Petroleum initially contains NAs that are predominantly alkyl substituted cycloaliphatic carboxylic acid with a mixture of acyclic aliphatic acids, olefinic, hydroxyl or dibasic acids.[14] In addition to providing important new tools for assessing the behavior of oil in natural environments, this project also advances the understanding of barium adducts for analysis of COOHs in environmental, biological, and other samples.

Figure 4 shows the IRMPD data for the bariated DOM_{HC} after light treatment. IRMPD was used to verify the presence of m/z 196 which was the qualifier ion proposed by Duncan et al. (2016) for confirmation of the presence of COOHs in a sample.[60] Although m/z 196 was observed in low resolution MS so was m/z 197. FT-ICR MS was used to verify if the peaks observed at low resolution were correct. Figure 4 shows that when m/z 302.98108 with the formula $C_6H_{13}O_5Ba_1$, DBE = 1 was isolated, the fragment m/z 196.9186 was observed. This mass corresponds to the formula $C_2H_3O_2{}^{138}Ba$ rather than $C_2H_2O_2{}^{137}Ba$ as reported by Duncan et al. (2016) for m/z 196, and represents a characteristic fragment of bariated COOHs. Figure S3 presents the m/z quad isolation vs. signal magnitude for m/z 196.918 for $C_2H_3O_2{}^{138}Ba$ and shows all the precursor ions that yielded the fragment. These precursors are present over the whole mass range observed and represent carboxylic acid containing molecules formed by exposure of the oil to light.

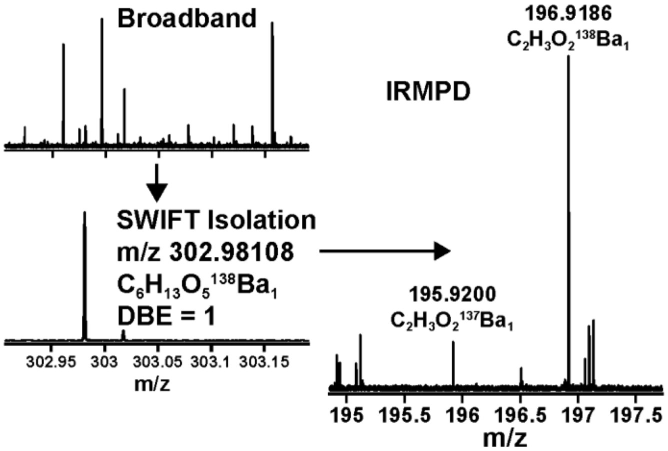

Figure 4: IRMPD data from SWIFT isolation at m/z 302.98108 in bariated DOM_{HC} after light treatment showing the presence of m/z 196.9186.

CONCLUSION

NAs are regulated due to their toxicity and persistence in the environment. They are recalcitrant to biodegradation and photodegradation alone, making them persistent. This study provides a preliminary investigation into the presence of carboxylic acid photoproducts in DOM_{HC} generated from thin petroleum films first utilizing low resolution then verification using FT-ICR MS/IRMPD. Based on prior work, these photoproduced carboxylic acids likely contain naphthenic acids, which are known to be toxic. Other carboxylic acid photoproducts are also potentially toxic as their bioavailability is increased compared to their petroleum precursors. Data presented here show the existence of more bariated acid species in DOM_{HC} after solar treatment, demonstrating that photochemistry plays a role in the dissolution of petroleum derived COOHs. This transformation is an important factor to consider when petroleum comes in contact with sunlight and water, thereby making it bioavailable to surrounding ecosystems. The use of low-resolution MS to prescreen for COOHs provides a quick screening tool for water bodies contaminated by petroleum, and high-resolution MS can provide more compositional detail.

Acknowledgements

This work is supported by the National Science Foundation (CHE-1507295). PZ partially supported by Shell Global Solutions, Inc. A portion of this work was performed at the National High Magnetic Field Laboratory ICR User Facility, which is supported by the National Science Foundation Division of Chemistry through DMR-1644779 and the State of Florida. R. Ghannam was supported by the

Undergraduate Oscar J. Tolmas Scholar grant. Special thanks to the Chemical Analysis Mass Spectrometry (CAMS) Facility at the University of New Orleans.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflict of interest

There are no conflicts to declare.

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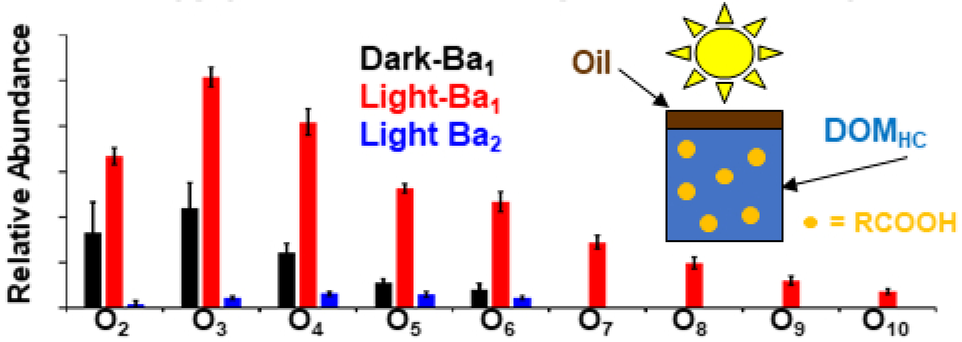
Photochemistry plays a role in the dissolution of petroleum derived carboxylic acids.



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