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Dispersant-enhanced photodissolution of macondo crude oil: A molecular perspective

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ABSTRACT

Previous laboratory studies developed a conceptual model based on elevated non-volatile dissolved organic carbon (NVDOC) concentrations after photodegradation and subsequent dissolution of Macondo oil following the Deepwater Horizon blowout. However, those experiments did not account for the effects of ~ 1 million gallons of dispersant applied to the surface oil. Here, laboratory results show photodissolution in the presence of dispersant results in > 2x increase in NVDOC concentrations after extensive photoprocessing relative to oil without dispersant. This result corresponds with an apparent increase in the percentage of surface oil photodissolution from approximately 4% in the absence of dispersant to 7% in the presence of dispersant. The oil and dissolved products were analyzed by excitation-emission matrix spectroscopy and ultrahigh resolution mass spectrometry. The compounds that persisted in the oil phase are relatively aromatic without dispersant, while those in the

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Received 14 April 2023; Received in revised form 22 August 2023; Accepted 12 September 2023 Available online 15 September 2023 0304-3894/© 2023 Elsevier B.V. All rights reserved. presence of dispersant are highly aliphatic, paraffinic, wax-like compounds. The composition of the dissolved compounds produced from both treatment types are nearly identical after 240 h of exposure to simulated sunlight. The NVDOC and chemical composition information indicate that the photodissolution of MC252 oil in the presence of dispersant is enhanced and accelerated, suggesting that the effects of dispersants should be included in mass transfer calculations from the oil to the aqueous phase.

1. Introduction

Oil spills in aquatic environments can damage ecosystems and negatively impact human health. Once spilled, abiotic and biotic transformations of the oil into petrogenic dissolved organic matter occur, producing hydrocarbon oxidation products (HOPs). A quantitative method for HOPs is through the measurement of non-volatile dissolved organic carbon (NVDOC), non-purgeable, passes through 0.2-0.7 µm filter) concentrations. Anomalously high NVDOC and optical properties of HOPs were measured in the Gulf of Mexico following the Deepwater Horizon (DWH) blowout, including contributions from hydrocarbon seeps after hydrocarbon concentrations returned to baseline levels [1-6]. Conventional wisdom suggested biodegradation was the dominant hydrocarbon degradation pathway explaining the fate of the Macondo oil (light, sweet, aliphatic) after the spill [7]. However, studies following the DWH spill indicated that photochemical processes partially contributed to the mass transfer (i.e., dissolution, not fate) of surface oil into the aqueous phase [8].

As a countermeasure to protect shoreline habitats and biological communities, chemical dispersants are used as a remediation tool in oil response strategy plans [9,10]. There were 972,880 gallons of dispersant applied to oil spilled on the surface of the Gulf of Mexico following the DWH blowout [11]. Although eight dispersants are recognized by the U. S. Environmental Protection Agency (EPA), Corexit 9500ECA, produced by Nalco, is one of the most common dispersants [9]. Chemical dispersants mitigate the ecological effects of oil spills by breaking oil into smaller droplets and reducing the surface tension between the oil and water [12]. As such, applying dispersant to surface oil enhances the dissolution of petroleum [13–15]. In addition, tiny droplets with increased surface area are available for photochemical oxidation, enhancing dissolution.

Aeppli et al. (2012) identified oxygenated hydrocarbons ("oxyhydrocarbons") in petroleum residues due to photochemical and microbial degradation processes from the DWH spill [16]. Simultaneously, fundamental laboratory experiments revealed phototransformation pathways and mechanisms of radical formation after Macondo oil was exposed to simulated sunlight. [17-21]. The knowledge obtained from these studies, explicitly focusing on the photochemistry of Macondo oil, corroborated with earlier work published in the 1970 s and 80 s on the photo-enhanced dissolution of petroleum [22-24]. The information from this body of literature was brought back to the forefront in laboratory experiments showing the production of dissolved photodegradation products (HOPs) in the aqueous phase after Macondo oil was exposed to simulated sunlight [8]. This study by Zito et al. (2014), revealed that the chemical composition of photochemically dissolved HOPs includes thousands of compounds in the unresolved complex mixture that cannot be quantified by gas chromatography. Furthermore, they concluded that HOPs produced in the water from the photochemical oxidation of Macondo oil can be quantified as NVDOC. Follow-up studies observed increases in the photochemical production of NVDOC as a function of light exposure from oxygenated oil products to HOPs [25,26].

The collective results from these studies indicate that dissolved HOPs produced from the photodegradation of Macondo oil are a plausible explanation for anomalously high NVDOC concentrations measured in the Gulf of Mexico [5]. Indeed, laboratory and controlled field experiments reported by Roman-Hubers et al. (2022) indicate photodissolution accounts for approximately 0.5–4% of the carbon mass

transfer from Macondo crude oil into the aqueous phase [27]. However, these calculations did not consider the influence of chemical dispersants on carbon mass transfer processes. Moreover, fundamental laboratory studies are necessary to examine the role of dispersants and how they impact the photodissolution of Macondo oil into HOPs.

In this study, laboratory experiments were conducted to measure the effect of chemical dispersants on the long-term photo-processing of oil and the subsequent formation of dissolved HOPs. Like previous laboratory studies, this research aims to provide fundamental information and add to the conceptual model of photodissolution of crude oil that can be considered by those that create environmental models and oil spill responders. We hypothesize that dispersant enhances the photochemical dissolution of Macondo oil into HOPs. NVDOC concentrations of photoproduced HOPs from Macondo oil in the presence and absence of dispersant are measured. Optical spectroscopy and ultrahigh resolution mass spectrometry are utilized to characterize the molecular-level composition of Macondo oil and subsequent dissolved HOPs produced in the presence and absence of dispersant to determine if the molecularlevel processes observed for oil and dissolved HOPs are consistent with dispersant-enhanced photoproduction of NVDOC. To the best of our knowledge, there are no previous reports of the effect of dispersant on photodissolution of light, sweet, aliphatic surface oil.

2. Methods and materials

2.1. Samples and reagents

Crude oil from the Deepwater Horizon platform (referred to as Macondo oil throughout) was provided by BP in August 2011, chain of custody number 20110803-Tarr-072. Nalco donated Corexit EC9500A and will be referred to as "Corexit." The Louisiana Universities Marine Consortium (LUMCON) provided seawater obtained from the Gulf of Mexico which was preirradiated for 12 h before analysis to minimize background DOM signatures (35 ppt salinity, pH 8.3, final NVDOC 1.5 mgC L⁻¹). Seawater and HOPs water samples were filtered through precombusted (450 °C, > 5 h) 0.27 µm glass microfiber filters (Advantec) before analysis. All glassware was acid cleaned and combusted at 450 °C before use. Nanopure water was collected from an Aeries nanopure system. All reagents used in this study were HPLC grade purchased from Sigma Aldrich.

2.2. Irradiation studies

325 mg of MC252 crude oil (36° API) was used to create 120 µm films over 50 mL of water (6.5 g L⁻¹ oil loading) [27]. The relatively thick films were utilized to "shield" the HOPs from photodegradation during the experiments. Moreover, 120 µm is within the oil films reported by Fay et al. (1971) [28]. The authors acknowledge that the film thickness chosen for this study may not comprehensively represent those observed in the Gulf of Mexico after the oil spill. Although triplicate experiments and sample analyses were not feasible within the scope of this study for the irradiation experiments, sampling across a concentration and compositional gradient provided the ability to identify outliers [25,29]. No outliers (Grubb's Test, $\rho > 0.05$) were identified, and the results followed expected trends. Moreover, a standard deviation of \pm 7.3% was previously reported for NVDOC values on triplicate irradiation analyses for a single timepoint [26].

Corexit was added to the oil at a 1:50 ratio (v/v), slightly less than

the range used by other researchers [30–32]. This ratio was selected to ensure that the FT-ICR MS signal would be distinguishable from DOSS and was validated by LC-MS (Fig. S1). Herein, samples labeled "WD" were prepared with dispersant, "WOD" was prepared without dispersant, and all samples not exposed to sunlight are labeled as "D₂₄₀" (the samples labeled "D₂₄₀" were kept in the dark for 240 h). There are four treatment groups, Oil + Dispersant + Sunlight, Oil + Sunlight, Oil + Dispersant, Oil. Refer to Table 1 for a summary of the acronyms used in this study.

Oil-WD samples were vortexed for 30 s to ensure mixing, and the oil-WD mixture was pipetted over 50 mL of water in a 250 mL jacketed beaker. A magnetic stirrer was used to simulate motion and prevent Corexit from sticking to the beaker wall during irradiation. [33,34] fifteen samples and irradiations were performed in batches of two beakers at a time using an Atlas CPS + solar simulator set at 765 W/m^2 calibrated annually by Atlas. During irradiation, the jacketed beakers' tops were covered with quartz glass to limit evaporation, and the sample temperature was maintained at 27 °C using a water circulator. Refer to King et al. (2014) for internal light intensity calibration procedure [35]. Irradiations were performed in 24 h increments (24, 48, 72, 96, 120, 144, 168, 192, 216, and 240 h). Dark controls (D₂₄₀) were prepared similarly but without light treatment. The 240 h time period is the most extended irradiation period representing the maximum possible NVDOC generated. After each irradiation period, the water was separated from the oil by making a hole in the film and quantitatively pipetting the water to check for evaporation. If water loss occurred, nanopure water was added to the water correcting for evaporation ensuring the final water volume for each sample was 50 mL. HOPs samples were filtered through a 0.27 µm glass fiber filter (Advantec) combusted at 450 °C, and subsequently prepared for NVDOC analysis. After removing the HOPs layer, the oil-WD was extracted from the beaker using toluene and dichloromethane, dried over nitrogen, blanketed with argon, and stored at -20 °C until analysis.

2.3. Non-volatile dissolved organic carbon measurements

Non-volatile dissolved organic carbon measurements are described in detail elsewhere [36]. Briefly, after irradiation experiments, dissolved HOPs (and control) were filtered as described above, diluted to 80% nanopure water, and acidified to pH < 3 using 12 M HCl. Non-volatile dissolved organic carbon (NVDOC) measurements were analyzed with a Shimadzu total organic carbon analyzer with the best 3 out of 7 injections and a CV < 2%. Bracketing potassium hydrogen phthalate reference standard (Sigma Aldrich 99.9% purity) curves ranging from 1 to 50 ppm were analyzed every 10 sample injections. Blanks (pH 2 water) were analyzed after every injection to prevent carryover, and a check standard was run every five samples to ensure system suitability was consistent throughout the analyses. Complete instrument details and parameters are described elsewhere [36]. NVDOC concentrations of photoproduced minus NVDOC concentration of darks (ANVDOC) and the % oil photodissolution from thin films of oil-WD and oil-WOD after 0-240 h of simulated sunlight were determined.

Table 1

Definition of acronyms used in this study. The symbol "w" stands for with, and "w/o" is without. Darks were collected after 240 h in the presence and absence of dispersant (D_{240}).

Sample	Description	Acronyms
Oil	Oil w/o dispersant	Oil-WOD
Oil + Dispersant	Oil w/dispersant	Oil-WD
HOPs	Dissolved HOPs produced w/o dispersant	HOPs-WOD
HOPs + dispersant	Dissolved HOPs produced w/dispersant	HOPs-WD
240 h Dark	Samples without light treatment for 240 h	D ₂₄₀

2.4. Excitation-emission matrix spectroscopy

Dissolved HOPs were qualitatively analyzed with a Horiba Aqualog collecting an excitation range from 240 to 800 nm every 5 nm and emission range from 230 nm to 800 nm every 2 nm as described elsewhere [36]. Briefly, the pH of the samples was measured and adjusted to pH 8 (if necessary) using 0.1 M NaOH [37]. Dried oil-WD samples were prepared at 2.5 μ g/mL (or absorbance value at 254 nm < 0.1) in dichloromethane and normalized to quinine sulfate units. A subset of samples was screened to ensure samples followed Beer's law [38]. Note that fluorescence spectroscopy is selective for aromatic compounds (not all compounds in crude oil).

2.5. Mass spectrometry

A 9.4 tesla Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS) was used to analyze all samples qualitatively. HOPs were solid phase extracted and normalized to 100 µgC/mL in MeOH with Agilent Bond Elut PPL as described elsewhere [39]. The extraction also helped remove DOSS from the water [34]. Toluene/-MeOH (50%) was used to dilute oil residues to a concentration of 250 ug/mL (w/v) for FT-ICR MS analysis. Negative electrospray (-ESI) was used to analyze all samples, and parameters and details are described elsewhere [36]. Negative ESI was chosen for selective and efficient ionization of oxygen-containing compounds (not all compounds in crude oil). EnviroOrg software was used to assign molecular formulae [40,41]. Molecular formulae were classified based on their stoichiometry and modified aromaticity indices (AImod) [42] into condensed aromatic (AI_{mod} \geq 0.67), aromatic (0.67 \geq AI_{mod} < 0.5), unsaturated, low oxygen $(ULO) = AI_{mod} < 0.5, H/C < 1.5, O/C < 0.5; unsaturated, high oxygen =$ $AI_{mod} < 0.5, H/C < 1.5, O/C > 0.5; aliphatic = H/C \ge 1.5-2.0$ [43,44]. Although we report these classes as % Relative Abundance (%RA) throughout the manuscript for brevity, only compounds amenable to (-) ESI are considered. The reproducibility of ultrahigh-resolution mass spectrometry data is described by Hawkes et al., 2020 [45].

2.6. Statistical analyses

Parallel factor analysis was conducted using drEEM 5.0 toolbox on two EEMs datasets (oil and HOPs) produced from this study. Parallel factor (PARAFAC) analysis of HOPs-WOD and HOPs-WD produced a five-component model [46,47]. A four-component model was validated for the oil-WD and oil-WOD samples (n = 22). Principle component analysis examined potential variations between oil-WD and oil-WOD samples. Microsoft Excel 2016 data analysis add-in feature was used to run Anova and t-Test analyses. Shapiro Wilk test for normality was performed on all variables, and the null hypothesis was accepted ($\rho >$ 0.05). Although we report % Relative Contribution throughout the manuscript for brevity, only compounds in crude oil that fluoresce are considered.

3. Results and discussion

3.1. Dispersant enhanced photodissolution produces elevated NVDOC

Fig. 1 shows Δ NVDOC plotted as a function of irradiation period for HOPs-WOD (red), HOPs-WD (black) and with % oil photodissolution on a secondary axis [27]. NVDOC concentrations for D₂₄₀ show a 4–5x increase in NVDOC for the sample with dispersant kept in the dark for 240 h (32.3 mgC L⁻¹) relative to the sample without dispersant kept in the dark for 240 h (7.16 mgC L⁻¹). This result shows the expected result for dispersant-enhanced dissolution without sunlight. NVDOC concentrations ranged from 7.16 to 234 mgC L⁻¹ (Δ NVDOC 227 mgC L⁻¹) for dissolved HOPs produced from oil films without dispersant (Table S1). The percent oil-WOD photodissolution ranges from 0.8% at 24 h to 3.5% at 240 h, with a maximum of 3.8% at 216 h. These values fall within the



Fig. 1. Change in non-volatile dissolved organic carbon (Δ NVDOC) concentrations and percentage of thin film oil photodissolution as a function of time for HOPs-WOD (red); HOPs-WD (black). Note that samples labeled as D₂₄₀ are 240 h darks in the absence and presence of dispersant, respectively.

range (~0.5–4.0% oil photodissolution) of other laboratory/controlled field studies in the absence of dispersant report by Roman-Hubers et al., 2022 (Fig. 1) [27]. A significant increase in NVDOC produced from the oil-WD relative to the oil-WOD and control-WD ($\rho < 0.001$) was observed. Photoirradiation of the oil-WD had NVDOC concentrations ranging from 32.3 mgC L⁻¹ at D₂₄₀ to 499 mgC L⁻¹ (Δ NVDOC 467 mgC L⁻¹) at 240 h (Table S1). The NVDOC concentration for the HOPs-WD produced after 240 h of irradiation is appears to be greater than twice the amount of NVDOC produced HOPs-WOD. Moreover, the percent photodissolution of oil-WD ranges from 0.5% at 24 h to 7.2% at 240 h, an apparent increase of more than twice that of oil-WOD (Fig. 1). This result is likely due to increased light interaction with dispersed oil droplets with a higher surface area than an intact film.

3.2. Excitation-emission matrix spectroscopy (Oil)

3.2.1. Enhanced loss of fluorescence in dispersed oil

Fig. 2 shows raw EEM spectra for the dark and irradiated oil films in the absence (left) and presence (right) of dispersant before and after 240 h of irradiation. The EEM spectra for both dark samples are nearly identical, with the same excitation/emission maxima (Ex_{max} / Em_{max}) 260 nm/360 nm. However, after extended irradiation to simulated



Fig. 2. EEMs spectra of oil in the dark for 240 h (D₂₄₀) (top) and 240 h (bottom) in non-dispersed (left) and dispersed (right) thin oil films.

sunlight, a loss of fluorescence is observed with a concurrent blue shift (decrease in maximum wavelength) in emission for the oil-WOD (255 nm/357 nm) and oil-WD (260 nm/282 nm) similar to previous reports [32,48]. We attribute this fluorescence loss to the photodegradation of the main chromophores, polyaromatic hydrocarbons, in the oil, as reported in previous laboratory studies [17,21]. The loss of fluorescence in the oil correlates with increased NVDOC concentrations (i.e., photodissolution) because of the enhanced oxygenation of petroleum. These data show that dispersants can enhance photodegradation in the presence of oil. As stated previously, the enhancement is likely due to greater accessibility to oil compounds in the dispersed system compared to an intact thin film. Although Corexit was previously shown to scavenge free radicals in the presence of a sensitizer [49], that effect appears less critical than other effects that yield a net enhancement in oil photodegradation rates in the presence of the dispersant. More experiments are needed to understand the role of reactive oxygen species in oil photodegradation in the presence of dispersants.

3.2.2. Parallel factor analysis (PARAFAC)

To further examine the effect of dispersant on the optical composition of irradiated oil, parallel factor analysis was applied, and a fourcomponent model was validated (Fig. 3). The PARAFAC model loadings from the oil samples were uploaded into OpenFluor with a similarity score > 0.97 (Tucker congruence coefficient). The shortest wavelengths are reported for C4, with Ex/Em maxima at 285 and 325 nm, respectively. A total of four entries matched C4 in the database. Three of the models were created from natural water samples. These papers called this component a "protein-like" fluorescence signature [50–52]. However, the other model was generated from a laboratory study of petroleum photodissolution [25]. As noted by Zito et al., 2019 proteins and amino acids (i.e., tryptophan (Peak T) and tyrosine (Peak B)) are not present in petroleum. Instead, these fluorescence signatures are associated with relatively aliphatic hydrocarbons with low heteroatom content (i.e., reduced) like fluorene, naphthalene, 1-methyl naphthalene, and their O-containing/alkyl-substituted derivatives [4, 25,29,53–56].

C1 is slightly red-shifted relative to C4 with Ex/Em maxima at 260 and 373 nm, respectively. This component matched two entries in OpenFluor. Darrien et al., 2019 describe this component as "protein-like" with microbial origins [57]. However, Gonsior et al., 2016 and Podgorski et al., 2018 more precisely describe compounds associated with C1 fluorescence as low molecular weight, relatively aromatic (H/C > 1), and high O/C [54,58]. Moreover, C1 shares similar features to EEM spectra reported for 3-ring polycyclic aromatic hydrocarbons (PAH) structures like phenanthrene and dibenzothiophene [55,56,59].

The Ex/Em maxima of C2, 270/414 nm, respectively, are red-shifted relative to C4 and C1. Like C1, C2 only matched two entries in the database. Both papers describe the respective component reported in their models as "humic-like." Interestingly, both these models were created from samples collected from unique environments influenced by thermal sources (submarine mud volcanoes and effluent from a hot spring) [60,61]. Furthermore, Cabrera et al., 2020 indicate that the C2 component in their model is like one reported by Gonsior et al., 2018 for dissolved organic matter derived from hot springs in Yellowstone National Park, USA [60,62]. Similar to "protein-like" fluorescence, the common link of thermogenic-derived organic matter in those three studies and ours indicate that C2 fluorescence is likely from a mixture of oxidized/alkyl-substituted PAHs with 3–4 ring core structures like chrysene and pyrene [4,56,59].

Finally, C3 is the most red-shifted component with Ex/Em maxima 260/504 nm, respectively. This component returned the most entries from the OpenFluor database with 37. Fluorescence in this region is commonly called "terrestrially-derived humic/fulvic-like" [63–65]. However, the compounds associated with this fluorescence region are likely from relatively large 5–6 ring (alky-substituted) PAHs like perylene and their O-containing derivatives [56,59]. This red-shifted fluorescence has been previously observed for photooxidized oil and corresponds to the onset of oxygenation that occurs with



Fig. 3. Change in relative contribution of PARAFAC components (a) C1, (b) C2, (c) C3, (d) C4 generated from the oil samples. Each component's Ex/Em spectrum is included in its respective panel with Ex/Em maxima in white. Note that% Relative Contribution only considers the compounds in crude oil that fluoresce.

photodegradation. This shift is further enhanced with the application of Corexit [32,66].

3.2.3. Oil fluorescence blue-shifts with time

Changes in the % relative contribution (i.e., only of the fluorescent compounds in crude oil) of each component as a function of the irradiation period for oil-WOD (black) and oil-WD (red) are shown in Fig. 3 and Table S2. The molecular composition of the oil-WD is significantly different for each component when compared with the oil-WOD ($\rho < 0.001$). Component 3 has the longest wavelength of the four components, indicating fluorescence from relatively large 5-6 ring (alkylsubstituted) PAHs (Fig. 3c). The relative contribution of C3 ranges from 15.9% at D_{240} to 6.8% at 240 h for the oil-WOD and 14.7% at D_{240} to 3.8% at 240 h for the oil-WD (Fig. 3c). The most notable change in the relative contribution of C3 for both oil-WOD/WD occurs between D₂₄₀-24 h of irradiation. Here, there is an approximately 3-fold decrease in the relative contribution of C3. The contribution of C3 plateau to a range of 3.8-6.9% after the initial 24 h of irradiation with no discernable difference between oil-WOD/WD. The decrease in the contribution of C3 is likely due to the relatively rapid photodegradation of the large PAHs. The residual C3 signature may be from the oil-soluble equivalent of carboxy-rich alicyclic molecules (CRAM) (e.g., fully degraded (refractory) asphaltenes) [67].

The relative contribution of C2, the component with the second longest wavelength, ranges from 51.1% at D₂₄₀ to 42.8 at 240 h for the oil-WOD and 48.8% at D₂₄₀ to 24.8% at 240 h for the oil-WD (Fig. 3b). Although both samples exhibit a decrease in the relative contribution of C2 as a function of time, there is a greater decrease in C2 with the oil-WD relative to oil-WOD. The discernable onset in the deviation of C2 between sample types begins at approximately 48-72 h of simulated sunlight, corresponding to the approximate time when the divergence in Δ NVDOC concentration is observed between treatment types (Fig. 1). As mentioned previously, the EEM spectrum of C2 is like those reported for 3-4 ring PAH core structures. A previous study showed that EC9500A (dispersant used in this study) accelerated the degradation of anthracene and 9,10-dimethylanthracene (3-ring aromatics) by a factor of 3.8 and 9.1, respectively [68]. The increased degradation rate for the alkylated analog relative to the parent is attributed to the alkyl bonds acting as electron-donating groups, making it more prone to oxidation [69]. Another report indicates that dispersant increases the first-order photodegradation rate of pyrene (4-ring PAH) by 5.5% and 16.7%, respectively, and reduces or ceases pyrene volatilization [70].

Moreover, previous mechanistic studies show that in the absence of a dispersant, singlet oxygen, and superoxide radicals play a critical role in the photodegradation of pyrene [71,72]. With the addition of EC9500A, the singlet oxygen degradation pathway for pyrene is inhibited [71]. However, it was shown that EC9500A enhances the role of superoxide radicals because it can transform into peroxide radical and hydrogen peroxide, which efficiently degrade pyrene [71]. Fu et al., 2017 conclude, "accelerated photodegradation of larger oil compounds by the Corexit dispersants may also enhance the dissolution and decomposition of persistent oil compounds," which corroborates the results presented in this study.

Components C1 and C4 are the most blue-shifted (shortest wavelength) of the four components (Fig. 3a,d). The relative contribution of C1, the component associated with 3-ring PAHs like phenanthrene and dibenzothiophene, ranges from 30.0% at D₂₄₀ to 45.3% at 240 h for the oil-WOD and 33.6% at D₂₄₀ to 66.0% at 240 h for the oil-WD. The increase in the contribution of this component can be attributed to the degradation products of larger aromatic compounds like those associated with C2 and C3 and/or the oxidation of smaller compounds into low molecular weight, relatively aromatic (H/C > 1), and high O/C. Although both pathways are likely to occur simultaneously, the fluorescence data suggest the latter may be the most prominent. The onset of the deviation between oil-WOD/WD (oil-WD increase) begins at approximately 72–96 h of irradiation, like the deviation onset for C2 (oil-WD decrease).

The range in relative contribution for C4, the component with the shortest wavelength, is from 3.1% at D_{240} to 5.1% at 240 h for the oil-WOD and 3.0% at D_{240} to 5.4% at 240 h for the oil-WD (Fig. 3d). This fluorescence signature is associated with compounds on the cusp of the analytical window for fluorescence analyses, like fluorene, naphthalene, and 1-methyl naphthalene. Like C1, the compounds with C1 fluorescence are formed from the oxidation of small compounds and/or products of large photodegraded (cracked) compounds. Unlike C1, the relative contribution of C4 for oil-WOD/WD begins at the onset of irradiation between D_{240} -24 h. The data imply that compounds associated with C4 are (oxy-) hydrocarbons native to the oil and/or degradation products from larger compounds related to C2 and C3. The relative blue-shift observed in this study corroborates findings that dispersant enhanced the photo-degradation of low-molecular-weight hydrocarbons in the Macondo oil [73].

3.3. Ultrahigh resolution mass spectrometry (Oil)

3.3.1. Molecular-level composition of dispersed oil shifts to paraffin wax Fig. S2 shows a panel of van Krevelen diagrams separated by compositional classes (red) for the dark (top) and irradiated (bottom) oil-WD and oil-WOD. Anova analyses revealed significant changes were observed in molecular formulae containing aliphatic ($\rho < 0.01$), unsaturated low oxygen (ULO) ($\rho < 0.001$), unsaturated high oxygen (UHO) ($\rho < 0.001$), aromatic ($\rho < 0.001$) and condensed aromatic (CA) ($\rho < 0.001$), and carboxyl-rich alicyclic molecules (CRAM) ($\rho < 0.001$) compound classes for the dispersed oil relative to the non-dispersed oil.

The relative abundance of the molecular formula classes (i.e., compounds in crude oil that ionize by (-) ESI) for aliphatics, unsaturated, low oxygen (ULO), aromatics, and condensed aromatics are shown in Fig. 4 and Table S2. The % relative abundance (%RA) of the aliphatic class range from 69.4% at D_{240} to 65.1% at 240 h for the oil-WOD and 33.6% at D₂₄₀ to 66.0% at 240 h for the oil-WD (Fig. 4a). The perceived enrichment of aliphatic compounds in both samples is likely a result of both dissolution of more conjugated aromatic compounds and the formation of oxy-PAHs and cracked products from photochemical degradation processes. The %RA of the aliphatic class is elevated throughout the entire incubation process, indicating that the oil-WD is consistently more enriched in O-containing aliphatics. These results corroborate the fluorescence data. Together, these results prove that the oil phase is enriched in compounds like oxidized relatively small PAHs that are highly alkylated and/or aliphatic acids. The latter are outside the analytical window of EEMS but inside the window for negative ion ESI-MS (more details below).

The %RA of the aromatics, condensed aromatics, and ULO exhibit a general decrease in %RA as a function of the irradiation period. The % RA of the ULO class range from 28.3% at D_{240} to 24.6% at 240 h for the oil-WOD and 22.9% at D₂₄₀ to 13.7% at 240 h for the oil-WD (Fig. 4d). Generally, the oxygen-containing compounds reported in this class are moderately aromatic and/or less alkylated relative to the aliphatics. The compound classes that decrease are most likely partitioning into the aqueous phase. This result provides evidence that compounds in the ULO class are leaving the oil through dissolution. As mentioned in Section 3.2.3, the EEMs spectrum for C2 matches those reported for 3-4 ring aromatics which we may expect to find in the ULO class of compounds. Studies show that dispersant accelerates the photodegradation of 3-4 ring (alkyl-substituted) aromatic compounds like anthracene, 9,10-dimethylanthace, and pyrene, facilitating dissolution [68,70,71]. Although we cannot determine the structure, it is plausible that highly alkylated analogs of these parent PAH fall into the ULO class (H/C < 1.5, AI_{mod} < 0.5). The implication is that the decrease in ULO as a function of time can be attributed to the dissolution of these compounds after they are photooxidized, and the dispersant accelerates the process.

Both the aromatic and condensed aromatic exhibit similar trends in both sample types. The %RA of the aromatic class range from a high of



Fig. 4. Molecular formula classes: (a) aliphatics, (b) aromatics, (c) condensed aromatics, (d) unsaturated, low oxygen (ULO), and (e) carboxyl-rich alicyclic molecules (CRAM) in the oil as a function of irradiation period. Note that% Relative Abundance only considers the compounds in crude oil that are ionizable by (-) ESI.

4.4% at 24 h to a low of 2.2% at 240 h for the oil-WOD and 1.5% at D_{240} to 0.5% at 240 h for the oil-WD (Fig. 4c). Meanwhile, the %RA of the condensed aromatic class is 0.1% at D_{240} to 0.3% at 240 h for the oil-WOD and 0.4% at D_{240} to 0.1% at 240 h for the oil-WD (Fig. 4d). The relative decrease in both samples' aromatic and condensed aromatic classes is attributed to the photodegradation of aromatic compounds, as expected [74]. At extended exposure periods, compounds in these classes will either be photobleached into relatively aliphatic compounds and/or oxidized into water-soluble compounds that will dissolve into the aqueous phase. The differences in the relative abundances between oil-WOD/WD for both classes are prevalent at D₂₄₀. Taken together with the increase in NVDOC concentration as a function of time, this information indicates that these aromatic classes of compounds are photo-oxidizing and partitioning from the oil into the aqueous phase, and the addition of dispersant facilitates the photo-oxidation process and their subsequent dissolution into the aqueous phase.

When exposed to light, the oil CRAM class of compounds exhibits a sharp increase in both treatments. The CRAM class is 0.1% at D₂₄₀ and 7.8% at 240 h, with a maximum of 10.1% at 144 h for oil-WOD and 2.6% at D₂₄₀ to 8.5% at 240 h for the oil-WD. The identification of CRAM is interesting because, to our knowledge, this is the first time CRAM has been reported in the oil phase of photodegraded petroleum. However, the detection of CRAM is not surprising because the Boduszysnki-Altgelt model of petroleum composition indicated that many alicyclic ring structures in petroleum could oxidize through indirect photochemical processes to form CRAM [75-78]. Compounds classified as CRAM are known to be some of the most refractory in marine ecosystems [67]. However, these compounds are apparently enriched as a function of time. Unfortunately, UHR-MS is not quantitative. However, we know that NVDOC concentrations increase with time. Collectively, that information leads us to conclude that either CRAM (and aliphatics) persists in the oil phase relative to the aromatics, CA, and ULO, or these compounds are intermediate between degraded oil products in the oil phase before partitioning into the aqueous phase.

3.3.2. Principal component analysis highlights shift in oil composition to paraffin wax

Principal component analysis (PCA) was completed on the oil samples to assess the variability in the PARAFAC loadings (C1-C4), aliphatics, CRAM, ULO, aromatics, and CA. Additional variables calculated

from the UHR-MS data that are significantly different were added to the PCA plot ($\rho < 0.001$) (Table S2). These variables include weighted average, molecular weight (MWw), nominal oxidation state of carbon (NOSC_w), hydrogen/oxygen to carbon ratio (H/C_w, O/C_w), and modified aromaticity index (AImod_w) for the oil-WOD (red) and oil-WD (black) as a function of time (Fig. 5) [42,79-81]. The plus symbols denote different variables (i.e., C1, C2, aliphatic, etc.), and the shading represents an increasing irradiation period. PCA 1 and PCA 2 account for 84% of the variance. Positive correlations are observed between the condensed aromatics, aromatics, unsaturated, low oxygen compositional classes, $\ensuremath{\text{NOSC}}_w$, and C2 in PCA 1 (Fig. 5). This group of variables is negatively correlated along the PCA1 (54% of variance) axis with another group of positively correlated variables, including C1, C4, the aliphatic class of compounds, H/C_w , and MW_w (Fig. 5). The main drivers of variance along the PCA2 axis (34%) are two positively correlated variables, O/C_w and CRAM class, negatively correlated with C3.

Collectively, the variables in the PCA plot highlight the differences in the oil-WOD/WD as a function of time. The composition of both sample types at D₂₄₀ are slightly shifted from each other but in relative proximity in PCA space closely correlated with C3. When exposed to simulated sunlight, the oils take different compositional paths. The composition of oil-WOD shifts to a grouping of positively correlated variables, including C2, ULO, aromatics, CA, AImodw, and NOSCw. Notably, the chemical composition of the degraded oil remains in the quadrant associated with those variables. Conversely, the chemical composition of oil-WD trends to the group of variables consisting of aliphatics, C1, C4, H/Cw, and MWw along the PCA1 axis. However, both sample types are influenced by the CRAM and O/C_w variables along the PCA2 axis. These results suggest that oxygenated, relatively aromatic compounds readily partition into the aqueous phase in the presence of dispersant, leaving the oil relatively depleted in those aromatic compounds. Conversely, oxygen-containing aromatic compounds are retained in the oil-WOD. It is likely that with enough irradiation time, the oxygenated aromatic compounds in the oil-WOD would partition into the aqueous phase. However, these results (along with NVDOC) prove that dispersant accelerates this process. In the presence of dispersants and sunlight, the composition of the crude oil is rapidly driven towards a paraffinic wax. This process is likely responsible for forming (or seeding) opaque or "clear" tar balls reported after the DWH spill. Although there are many reasons for the accelerated change in the



Fig. 5. Principal component analysis for oil-WOD (red) and oil-WD (Black). The darkest shades are D₂₄₀, and the lightest shades are 240 h. Variables are indicated by (+).

composition of the oil-WOD relative to the oil-WD that are beyond the scope of this study, one noticeable difference is the increased surface area of oil droplets as opposed to a completely intact film. Regardless, the molecular perspective of oil composition with and without dispersant corroborates dispersant-enhanced photodissolution.

3.4. Fluorescence spectroscopy (Dissolved Hydrocarbon Oxidation Products)

3.4.1. Parallel factor analysis

A five-component model was validated from the EEM spectra collected from HOPs-WD and HOPs-WOD (Fig. 6). The PARAFAC model loadings from the water samples were uploaded into OpenFluor with a similarity score > 0.97 (Tucker congruence coefficient). There were matches for each component to a total of 101 entries. The shortest



Fig. 6. Percent relative contribution of a) C1, b) C2, c) C3, d) C4, and e) C5 in HOPs-WOD/WD.

wavelengths are found in C5, with Ex/Em maxima at 207 and 309 nm, respectively. A total of 14 entries matched C5 in the database. PARAFAC components with this signature are commonly called "tryptophan-", "tyrosine-", and "phenylalanine-like" (i.e., "protein-like") fluorescence [82-84]. However, as described in Section 3.2.2, petroleum has no amino acids. Rather, this signature is derived from relatively small, reduced aliphatic compounds. C3 is red-shifted relative to C5 with Ex/Em maxima at 250/375 nm. There was only one match for this component in the database. The matched component was generated from a model that only included dissolved photo-produced HOPs [25]. The component reported there did not match any in the database using a 0.95 similarity score and is attributed to an abundance of structural motifs in C3 that are not present in modern (non-petrogenic) dissolved organic matter [25]. Although not matched in the database, fluorescence with these Ex/Em maxima is described as naphthalene-like [4,85]. Moreover, other studies report unique (relative to modern dissolved organic matter) fluorescence signatures with relatively low Ex/Em maxima for photo-solubilized HOPs, which are likely associated with oxidized degradation products of relatively small, aliphatic, hydrocarbons [2,86]. The Ex/Em maxima of C1, 250, and 352 nm, respectively, are red-shifted relative to C3 and C5. C1 matched 15 entries in the database that reported it as "terrestrial humic-like" and "protein-like" fluorescence [87–89]. The Em maximum shifts to longer wavelengths by adding aromatic rings in a PAH core structure. Therefore, this fluorescence region observed in C1 is likely from "mid-size" (alkyl-substituted) aromatic hydrocarbons and their O-containing derivatives. C2 is the second longest wavelength component with Ex/Em maxima at 250/414 nm. Thirty entries matched C2 in the database. This component is reported as "microbial humic-like" [90-92]. HOPs associated with these long wavelength signatures are associated with relatively large (alkyl-substituted) aromatic core structures (3-4 ring) containing oxygen heteroatoms. Finally, C4 is the most red-shifted component with Ex/Em maxima at 255/472 nm. This component matched 41 entries in the OpenFluor database, the most of all components. The long wavelength Ex/Em maxima of this component is commonly called "humic-/fulvic-like" fluorescence [93-95]. Again, this fluorescence signature is derived from highly aromatic (5–6 + ring PAH cores) and highly oxidized HOPs (see Section 3.3.3).

3.4.2. Dissolved HOPs shift to longer wavelength with time

Changes in the relative contribution of each PARAFAC component s as a function of the irradiation period for HOPs-WOD (red circles) and HOPs-WD (black diamonds) are shown in Fig. 6 and Table S1. Component 4 has the longest wavelength of the five components, which indicates fluorescence from relatively large 5–6 ring (alkyl-substituted) PAH core structures. The relative contribution of C4 ranges from 4.0% at D₂₄₀ to 19.2% at 240 h in the HOPs-WOD and 7.5% at D₂₄₀ to 23.6% at 240 h for the HOPs-WD. As such, the relative contribution of C4 in both the HOPs WD/WOD indicates that relatively larger, more aromatic compounds are photosolubilized as a function of the irradiation period.

Component 2 has the second longest wavelength of the HOPs model. The relative contribution of C2 ranges from 3.6% at $D_{\rm 240}$ to 35.8% at 240 h for the HOPs-WOD and 6.0% at $D_{\rm 240,}$ and 45.4% at 240 h for the HOPs-WD (Fig. 6). The deviation between the relative contribution of C2 for the HOPs WOD/WD begins at approximately 96 h of simulated sunlight. As stated above, fluorescence in this region is attributed to relatively large aromatic cores (3-4 rings) with alky-substitutions and oxygen heteroatoms. The 96 h mark is also the approximate time the ∆NVDOC concentrations between the HOPs-WD start to deviate (increase) relative to the HOPs-WOD. One plausible explanation for this result is that relatively "more" highly fluorescent 3-4 ring aromatic compounds partition into the aqueous phase in the presence of a dispersant. The ability of the dispersant to break the oil into small droplets increases the surface area for solar irradiation. This process results in an increase in photooxidation and subsequent dissolution of relatively large aromatic compounds. This concept is observed in the

bottom panels of Fig. 2 (240 h oil-WOD/WD). There, we observe an abundance of fluorophores with emission wavelengths > 350 nm in the oil phase without dispersant after 240 h of irradiation. Conversely, those same fluorophores are mostly absent in the sample with dispersant, indicating that the compounds associated with fluorescence in that region are partitioned into the aqueous phase (i.e., the relative increase in aqueous phase C2).

C1, associated with mid-size aromatics and their derivatives, ranges from 26.8% at D₂₄₀ to 8.7% at 240 h for the HOPs-WOD and 29.2% at D₂₄₀ and 7.8% at 240 h for the HOPs-WD (Fig. 6). The decrease in the relative abundance of compounds associated with fluorescence in this region is the same for both samples, with nearly identical values at each time point. Similarly, the trends in the relative contribution of C3, the component identified in previous petroleum photodissolution studies, are almost identical for both HOPs WOD/WD. The relative contribution of D₂₄₀ is low for both HOPs-WOD (7.5%) and HOPs-WD (6.4%). There is a noticeable increase in those values once the films are exposed to simulated sunlight. The range for HOPs-WOD is 38.72% at 24 h to 0% at 240 h and 44.2–0% for HOPs-WD. Although there are slight deviations in the relative contributions of C3 at 24–48 h, the trend and values at later time points are nearly identical between the HOPs-WOD and HOPs-WD.

Finally, C5 is the component with the shortest wavelength. This component corresponds with relatively small, reduced aliphatic compounds. The relative contribution of C5 ranges from 3.96% at D₂₄₀ to 19.2% at 240 h in the HOPs-WOD and 7.47% at $D_{\rm 240}$ to 23.59% at 240 h for the HOPs-WD. The relative contribution of C5 at D_{240} is 58.10% in HOPs-WOD and 50.86% for HOPs-WD. The values for both sample types drastically decrease at 24 h and then steadily increase to 240 h. The range of C5 values for the HOPs-WOD is 14.7% at 24 h to 36.3% at 240 h and 10.1% at 24 h to 23.2% at 240 h for the HOPs-WD. There is a discontinuity between the HOPs-WOD/WD at approximately 96 h. This discontinuity (and timepoint) is like that observed for C2 and Δ NVDOC concentrations. The difference in the trends between C2 and C5 is that the relative contribution of C2 is highest in HOPs-WD, while the relative contribution of C5 is highest in the HOPs-WOD. Taken with the increased Δ NVDOC concentration of HOPs-WD, this result supports the idea that the increased surface area of droplets formed by the dispersant facilitates photooxidation and subsequent dissolution of 3-4 ring aromatic compounds (and derivatives).

3.5. Ultrahigh resolution mass spectrometry (Dissolved Hydrocarbon Oxidation Products)

3.5.1. Molecular-level composition of photochemically produced HOPs

Detailed discussion about the chemical composition of photochemically mobilized dissolved HOPs in the absence of dispersant is described elsewhere [25]. A > 2x increase in Δ NVDOC concentration produced from the two different treatments at 240 h corresponded with significant changes in the aliphatic ($\rho < 0.001$), aromatic ($\rho < 0.001$), condensed aromatic ($\rho < 0.001$), ULO ($\rho < 0.001$), CRAM ($\rho < 0.005$), and UHO ($\rho < 0.001$) classes of HOPs WOD/WD are significantly different. The relative abundance of the aliphatics at D₂₄₀ - 240 h in the HOPs-WOD ranged from 16.1% to 12.6% and 84.9–22.5% in the HOPs-WD. The %RA of the aliphatic class in the HOPs-WOD remains relatively steady, with a slight decrease at later time points (Fig. 7a and Table S1). However, the same class in the HOPs-WD exhibits a sharp decrease from \sim D_{240} (84.9%)- 48 h (26.9%) before reaching a relative plateau that remains higher than the HOPs-WOD. One major limitation of ultrahigh resolution mass spectrometry is that it is not quantitative. However, using complementary analytical techniques shows that the general trends observed in the aliphatic classes are like the shortest wavelength components measured by EEMS. Moreover, comparing samples is relative and shows differences in compositional classes between the HOPs samples. However, this can be attributed to the photosensitization of aliphatic compounds from radical oxygen species produced by the



Fig. 7. Percent relative abundance of compound classes in HOPs obtained by ultrahigh resolution mass spectrometry a) aliphatics, b) aromatics, c) condensed aromatics, d) unsaturated, low oxygen (ULO), e) carboxyl rich alicyclic molecules (CRAM), and e) unsaturated, high oxygen (UHO).

degradation of aromatics [96]. The major differences between HOPs-WOD and HOPs-WD indicate that the dispersant facilitates the dissolution of relatively aliphatic compounds relative to the sample without dispersant.

The trends in %RA of the aromatics and condensed aromatics are similar for the HOPs-WOD compared with the HOPs-WD (Fig. 7b,c). The percent relative abundance of photoproduced condensed aromatics in the HOPs-WOD is 0.2% at D_{240} to 0.9% at 240 h, with a maximum of 1.4% at 96 h. The HOPs-WD are 0.0-0.6%, with a maximum of 1.0% at 120 h. This result shows a slight but significant ($\rho < 0.001$) difference in the percent relative abundance of the condensed aromatics in the HOPs-WD relative to the HOPs-WOD. The percent relative abundance of photoproduced aromatics in the HOPs-WOD is 1.8-8.1% at D₂₄₀-240 h with a maximum of 10.0% at 144 h and 1.0-5.1% with a maximum of 7.5% at 48 h in the HOPs-WD. The sharp increase in the relative abundance of both classes when the oil film is exposed to simulated sunlight indicates that these compounds are rapidly oxygenated and partition into the aqueous phase. It is likely that a higher concentration of (condensed) aromatics in the HOPs-WD relative to the HOPs-WOD. However, the data from UHR-MS cannot provide that information because it is not quantitative. Future studies will focus on quantitative measurement of the amount of water-soluble (condensed) aromatics to better understand the compositional mass balance [29,97].

The %RA of the CRAM class is 53.7-59.5% in the HOPs-WOD and 9.4-57.0% for HOPs-WD. There is only a slight increase in the %RA of the CRAM class for the HOPs-WOD from $D_{240} - 240$ h. However, there is a sharp increase in the %RA of the same class from $\sim D_{240}\text{-}48$ h. There is an increase from 9.4% at D_{240} to 51.4% at 48 h. A notable inverse relationship exists between the aliphatic and CRAM classes ($r^2 = 0.97$). The increase of CRAM-like compounds formed in the oil phase and the subsequent increase of these compounds in the aqueous phase indicate that oil films serve as a CRAM pump when exposed to sunlight with extended exposure periods. Together with the Δ NVDOC data and oil CRAM class (Fig. 4e), these results prove that the composition of the additional NVDOC produced from the WD samples relative to those WOD is CRAM-like. It is suggested that these compounds are refractory and relatively benign. However, more research is required to answer this question definitively [27,67]. Similarly, the percent relative abundance of photoproduced unsaturated, high oxygen classes in HOPs-WOD ranges from 3.8% at 24 h to 13.3% at 240 h. The initial value of 23.3% at D_{240} in HOPs-WOD is likely due to overprinting of background DOM in the seawater [98]. The unsaturated, high oxygen class ranged from 0.7% to 7.9% in the HOPs-WD. The increase in the %RA of the UHO class further indicates the production of water-soluble compounds that are likely to be refractory. The results from the UHR-MS portion of this work suggest that the initial composition of the HOPs is relatively aliphatic and that they become more highly oxygenated and CRAM-like with an extended exposure period. The composition of the compounds partitioning into the aqueous phase is similar for the HOPs-WOD/WD. However, the increase in NVDOC concentration tells us that "more" of these compounds are being produced in the HOPs-WD relative to the HOPs-WOD.

3.5.2. Slightly different compositional pathways of HOPs to similar end products

Principal component analysis (PCA) was completed on the HOPs samples to assess the variability in the PARAFAC loadings (C1-C5), aliphatics, CRAM, UHO, ULO, aromatics, CA, and other variable that were significantly ($\rho < 0.001$) different between treatments including, weighted average, molecular weight (MWw), nominal oxidation state of carbon (NOSC_w), hydrogen/oxygen to carbon ratio (H/C_w, O/C_w), and modified aromaticity index (AImod_w) for the HOPs-WOD (red) and HOPs-WD (black) as a function of time (Fig. 8 and Table S1). The plus symbols denote different variables (i.e., C1, C2, aliphatic, etc.), and the shading represents an increasing irradiation period. PCA 1 and PCA 2 account for 74% of the variance. Positive correlations are observed between the condensed aromatics, aromatics, ULO, UHO, CRAM compositional classes, NOSCw, O/Cw, MWw, AImodw, C2, and C4 in PCA 1 (Fig. 8). This group of variables is negatively correlated along the PCA1 (50% of variance) axis with another group of positively correlated variables, including C1, C4, H/Cw, and the aliphatic class. The main drivers of variance along the PCA2 axis (20% of variance) are positively correlated variables, UHO class, O/Cw, C5, and C4, that are negatively correlated with ULO, CA, and aromatic classes, C3, C1, and AImod_w.

Collectively, the variables in the PCA plot highlight the different compositional pathways for the HOPs-WOD/WD as a function of time. The composition of both sample types at D_{240} is correlated with ULO, CA, and aromatic classes, C3, C1, and AImod_w. When exposed to simulated sunlight, the HOPs-WOD/WD take slightly different compositional paths. Most notably, the HOP-WD takes a track skewed to



Fig. 8. Principal component analysis for HOPs-WOD (red) and HOPs-WD (Black). The darkest shades are D₂₄₀, and the lightest shades are 240 h. Variables are indicated by (+).

relatively more aliphatic, while HOPs-WOD is relatively more aromatic. Both sample types trend to the bottom-right quadrant of the PCA plot associated with UHO, O/C_w, NOSC_w, and relatively long wavelength components C2 and C4. Most interestingly, the chemical composition of 240 h for the HOPs-WOD/WD is tightly correlated. This is another indication that the chemical composition of the HOPs is similar in the absence and presence of a dispersant. However, adding dispersant to a fresh oil film produces significantly ($\rho < 0.01$) more of this material with time.

4. Conclusion

Like previous laboratory experiments that provided evidence of petroleum photodissolution, the results from these laboratory experiments indicate that oil in the presence of a dispersant enhances photodissolution relative to oil in the absence of a dispersant. We show that adding dispersant to relatively fresh surface oil appeared to enhance the percent photodissolution of light, sweet, aliphatic crude oil from approximately 4-7%. These results indicate that regarding surface oil dissolution, dispersant + sunlight > sunlight only > dispersant no sunlight > no dispersant or sunlight, and the information is essential for calculating oil spill mass balances and response. Moreover, these experiments show the need for rapid application of dispersants if photodissolution of surface oil is a goal in response to an oil spill. Ultimately, the results from this laboratory study inform "environmentally relevant" research and modeling [99-103]. Variables including temperature, salinity, and oil composition will change rates of photodissolution. However, these experiments were completed with a light, aliphatic crude, in ideal systems to control for those variables. The next step is to perform these experiments on a mesocosm scale to introduce variables not included in this laboratory study, like temperature, salinity, oil composition, water column depth, and film thickness.

Environmental implication

Dissolved hydrocarbon oxidation products (HOPs) are of emerging concern. HOPs can be formed when surface oil undergoes photooxidation in sunlight. Once sufficiently oxidized, polar HOPs are mobilized into the aqueous phase, where they can travel great distances from the source. Recent studies quantified the percent photodissolution of surface oil. However, they did not consider how the addition of dispersant to surface oil affects the photodissolution of HOPs into the aqueous phase. We provide evidence from laboratory experiments that adding dispersant accelerates and enhances the photodissolution process.

CRediT authorship contribution statement

David Podgorski: Methodology, Validation, Formal analysis, Data Curation, Resources. Investigation, Writing - Original Draft, Visualization, Supervision, Project administration Jacob. Walley: Investigation Matthew P. Shields: Investigation Deja Hebert: Investigation Maxwell L. Harsha: Software Robert G. M. Spencer: Resources Matthew A. Tarr: Conceptualization, Methodology, Resources, Data Curation, Primary funding acquisition Phoebe Zito: Conceptualization, Methodology, Validation, Formal analysis, Resources, Data Curation, Writing - Original Draft, Visualization, Supervision, Project administration. All authors contributed to Review & Editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2023.132558.

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