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Molecular Comparison of Solid-Phase Extraction and Liquid/Liquid Extraction of Water-Soluble Petroleum Compounds Produced through Photodegradation and Biodegradation by FT-ICR Mass Spectrometry

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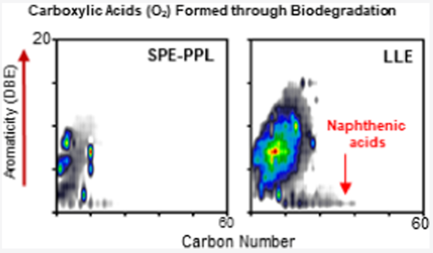
ABSTRACT: We apply two widely used extraction techniques, liquid/liquid extraction and solid-phase extraction with styrene−divinylbenzene polymer with a proprietary nonpolar surface priority pollutant (PPL) to water-soluble compounds generated through photodegradation and biodegradation of petroleum. We compare the molecular composition of bio- and photodegraded water-soluble organic (WSO) acids by 21 T negative-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). We highlight the compositional differences between the two extraction techniques for abiotic and biotic degradation processes and identify known toxic species (naphthenic acids) produced through hydrocarbon biodegradation identified by liquid/liquid extraction (LLE) that are not detected with solid-phase extraction (SPE) of the same sample. Photodegraded WSO compounds extracted by SPE-PPL correspond to species with higher O/C ratio and carbon number compared to LLE extracted compounds. Naphthenic acids, a recalcitrant class of nonaromatic carboxylic acids and known acute toxicants formed through biodegradation of oil, are detected in LLE extracts (up to C_{30} and double-bond equivalents, DBE < 3) but are not detected in SPE-PPL extracts. This suggests that LLE and SPE-PPL retain different water-soluble oil species based on the dominant type of oil weathering process.



INTRODUCTION

Changes in chemical composition and physical properties directly and indirectly affect the partitioning, fate, and toxicity of petroleum compounds released into the environment.[1−4] Understanding these weathering processes and the effects on different chemical classes is instrumental to a rigorous identification of spilled oil residues and migration into marine ecosystems.[5−11] Furthermore, tracking the alterations in the chemical composition of oil residues relative to the freshly released oil is crucial for conducting chemical fingerprinting and toxicological risk assessment.[12−19] Advanced analytical techniques have been applied to understand the impact of biotic and abiotic degradation of oil in the environment and its water-soluble transformation products in response to anthropogenic releases, oil production, and natural seepage.[20−29] Biodegradation and photodegradation are the two dominant degradation processes responsible for increased water solubility, and thus toxicity of hydrocarbons in the environment.[30−45]

Liquid/liquid extraction (LLE) is the primary method used to isolate petroleum-derived compounds from oil-impacted waters, produced water, and aqueous byproducts of oil production.[46−48] Liu and Kujawinski applied LLE to identify compounds derived from petroleum that partition into water through dissolution and identify unique distributions of compounds across a range of hydrophobicity.[49] Importantly, this work utilized LLE extraction coupled with ESI FT-ICR MS to estimate the environmental impacts of different crude oil compounds. Another study applied LLE to catalog hydrocarbons isolated from water associated with *Deepwater Horizon* oil spill-impacted sediments between 2010 and 2013 to track aliphatic hydrocarbons in deep sea sediments.[50] Produced water extraction often applies liquid/liquid extraction to catalog compounds that transition from oil-soluble to water-soluble in oil production.[51]

The recent application of the solid-phase extraction of dissolved organic matter from aqueous samples has extended the application of ultra-high-resolution Fourier transform ion cyclotron resonance mass spectrometry to a wide range of applications, including marine and terrestrial carbon cycling.[20,52−68] Solid-phase extraction with styrene−divinylbenzene polymer with a proprietary nonpolar surface (Bond Elut, Agilent Technologies, Priority PolLutant, PPL) is fast,

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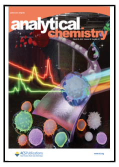

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inexpensive, and has been reported to concentrate ∼40 to 65% of organic carbon from marine aqueous systems.[57] In addition, rinsing with hydrochloric acid removes salt compounds that challenge ionization with minimal cost and equipment requirement.[57,69,70] The application of FT-ICR MS to molecular characterization of dissolved organic matter in environmental systems has exploded due to the application of the SPE-PPL method initially proposed by Dittmar et al.,[57] who report the highest recovery of organic carbon with PPL sorbent compared to other commercially available cartridges based on the dissolved organic carbon concentration (DOC) of the water. The large particle size and high surface area and capacity of the modified styrene−divinylbenzene polymer (PPL) enables fast extraction speeds and retains highly polar, polyfunctional species inherent to dissolved organic matter while capturing and recovering polyfunctional, polar species functionalities for subsequent characterization.[55,61,70,71] Therefore, SPE-PPL has become one sample preparation routinely applied to isolate dissolved organic matter in marine and terrestrial water systems, and has expanded the application of FT-ICR MS to characterize natural organic matter systems.[2,30,55−63,68−73]

Recent studies focused on characterization of water-soluble, polar transformation products of oil degradation apply SPE-PPL and FT-ICR MS to differentiate impacts of biotic and abiotic weathering processes on *Deepwater Horizon* oil residues.[74−78] The molecular composition of the water-soluble photoproducts of *Deepwater Horizon* oil from the Mississippi Canyon Block 252 and Arabian heavy oil extracted by SPE-PPL has been cataloged by (-ESI) FT-ICR MS,[75] and LLE extraction followed by FT-ICR MS.[79] Recent studies have compared the quantitative extraction efficiency of oil compounds in groundwater plumes in field samples and report similar yields based on the total petroleum hydrocarbons determined by gas chromatography.[77] To the best of our knowledge, there has not been a direct comparison of the molecular composition of WSO species isolated through LLE and SPE-PPL, and the impact of abiotic or biotic weathering processes on the composition detected by FT-ICR MS.

Here, we apply two extraction techniques, liquid/liquid extraction and solid-phase extraction (PPL) to water-soluble oil compounds generated through photodegradation and biodegradation of MC252 oil to identify compositional differences in acidic species derived from negative-ion ESI 21 T FT-ICR MS. We highlight the compositional differences between two extraction techniques (SPE-PPL and LLE) and identify specific compositional classes produced through biodegradation not detected by negative-ESI FTICR MS after SPE extraction. Importantly, one of the most toxic compound classes in petroleum formed through biodegradation, the naphthenic acids, is only detected when extracted with LLE.[80−91]

■ EXPERIMENTAL METHODS

Oil Sample. The Gulf of Mexico crude oil (NIST SRM 2779) from the Mississippi Canyon Block 252 (MC252) was purchased from the National Institute of Standards and Technology (NIST, Gaithersburg, MD). All solvents were of HPLC grade from JT Baker Chemical Company (Phillipsburg, PA) and used as received. Bond Elut PPL solid-phase extraction cartridges (1 mg, 1 mL) were obtained from Agilent Technologies (Santa Clara, CA) and biodegraded or photodegraded water-soluble organics were derived from *Deepwater Horizon* oil as previously reported.[76,92]

Biodegradation Microcosm. Biodegradation experiments were conducted with a microbial population isolated from live seawater collected from the Gulf of Mexico (29.91 N, 84.51 W) (temperature: 23.1 °C; salinity: 30.8 parts per thousand; pH 7.6; dissolved oxygen: 5.21 mg L^{-1}) as previously reported.[1] Water samples were stored on ice. Filtration was performed with a 0.8 μm membrane filter to remove debris and large organisms. Additional filtration with a 0.2 μm membrane filter allowed for the isolation of the microbial population. The microbial population was then added to sterile artificial seawater (Instant Ocean Aquarium Systems, Inc. Mentor, OH). Crude oil (325 mg) was then added to the bio-microcosm to generate an oil film of the same thickness as for the photo-oxidation microcosm. The bio-microcosm was wrapped in aluminum foil to prevent photo-oxidation and incubated (Thermo Scientific MaxQ 4000 orbital shaker) with shaking at 110 rpm at 23 °C for 30 days. After 30 days, the aqueous layer of the microcosm was transferred to a sterile container with a sterile glass pipette and subsequently filtered through a 0.2 μm membrane filter to remove the microbial population prior to extraction. The sample was subsequently dried under a nitrogen gas and stored in the dark at 4 °C to prevent further oxidation of samples prior to mass analysis.

Photodegradation Microcosm. A thin oil film (120 μm) generated with 325 mg (385 μL) of oil was layered onto 50 mL of autoclaved 70% artificial seawater (Instant Ocean Aquarium Systems, Inc., Mentor, OH) in a jacketed beaker attached to a water chiller. Samples were subsequently placed in an ATLAS Suntest CPS solar simulator, where they were irradiated by artificial sunlight for 24 h (equivalent to 6 days of natural sunlight[22]) at 27 °C. After irradiation, water was removed by pipette and the oil layer was isolated and dried under nitrogen gas.

Solid-Phase Extraction with PPL (SPE-PPL). Water-soluble organics derived from microcosms were subjected to an SPE priority pollutant (SPE-PPL) extraction method as previously described.[46,48]

Liquid/Liquid Extraction of Water-Soluble Organics (WSO). WSO species were isolated from microcosm samples according to a modified EPA method 3500C as previously reported.[46]

21 T FT-ICR MS. Ions were generated at atmospheric pressure via negative-ion micro-electrospray and analyzed by negative-ion electrospray 21 T FT-ICR MS.[93,94]

Complete experimental methods for dissolved organic carbon analysis, liquid/liquid extraction, and 21 T FT-ICR MS data acquisition and data processing can be found in the Supporting Information.

■ RESULTS AND DISCUSSION

Formation of Water-Soluble Organic Compounds through Bio- and Photodegradation Microcosms Increases DOC. Table 1 shows the DOC (ppm) for both laboratory-generated water-soluble compounds from both microcosms compared as previously reported.[75,79,92,93] Photo-oxidation of oil on water for 24 h (equivalent to 6 days of natural sunlight)[95] results in a nearly 10-fold increase in the amount of water-soluble organics compared to bio-oxidation for 30 days. The baseline DOC values correspond to dark controls for the same time and indicate a 3-fold increase in WSO formed through bio-oxidation and approx-

Table 1. DOC Concentration for Water-Soluble Organics Generated from Bio-Oxidation and Photo-Oxidation Microcosms

	DOC (ppm)
Dark control 30 days	3.19 (±1.21)
Dark control 24 h	1.81 (±0.06)
Bio-Ox 30 days	9.64 (±0.34)
Photo-Ox 24 h (6 days equiv)	95.95 (±3.47)

imately 50-fold increase in WSO through photodegradation. Due to limitations for microbial growth, we limit the microcosm to 30 days, which is the maximum time possible without deleterious effects.[96,97]

Heteroatom Class Distribution Comparison of SPE-PPL and LLE: WSO Formed through Photodegradation. Photodegradation transforms polycyclic aromatics (PAHs) in crude oil into more polar compounds with increased water solubility and thus increases the dissolution rate of oil compounds.[43,98−110] Figure 1 shows the heteroatom class distribution for acidic water-soluble photoproducts after 24 h irradiation (6 days solar equivalence) isolated by SPE-PPL and LLE derived from negative-ESI FT-ICR MS. WSO photoproducts extracted by both SPE-PPL and LLE after 24 h irradiation reveal increased relative abundance of highly polar acidic compounds that contain up to $O_{20\text{-}22}$ oxygens per molecule. Unlike bio-oxidation, WSO photoproducts isolated by SPE-PPL contain O_1 compounds (phenols or alcohols) that are not detected in the LLE sample. This suggests a structural difference between O_1 intermediates formed through photodegradation compared to biodegradation, in agreement with previous reports on field samples derived from the *Deepwater Horizon* oil spill.[16,23,33,92,111−116]

Heteroatom Class Distribution Comparison of SPE-PPL and LLE: WSO Formed through Biodegradation. Figure 2 shows the heteroatom-compound class distribution for WSO formed through biodegradation. Both SPE and LLE extracted compounds above 0.1% relative abundance span a wide range of O_x, N_1O_x, and S_1O_x classes. The most abundant acidic class in the SPE-PPL corresponds to highly polar O_4−O_6, S_1O_4−O_6, and N_1O_4−O_6, which are also abundant in the LLE sample, and corresponds to compounds that contain at least one carboxylic acid functionality. Importantly, LLE extraction of the same water sample extracts and identifies less polar O1 compounds, which correspond to alcohols or aldehyde intermediates formed by oxidation of hydrocarbons that are further oxidized into carboxylic acids through biodegradation, and are not detected in the SPE-PPL extract.[100,102,104] These compounds have been observed in oil residues extracted from field samples extracted from *Deepwater Horizon*-contaminated sediments, detected up to 41 months postspill, an indication of active in situ biodegradation.[16] WSO extracted by SPE-PPL contains higher oxygens per molecule compared to LLE across O_x, N_1O_x, and S_1O_x classes, which indicates that more polar compounds are extracted by SPE-PPL compared to LLE.

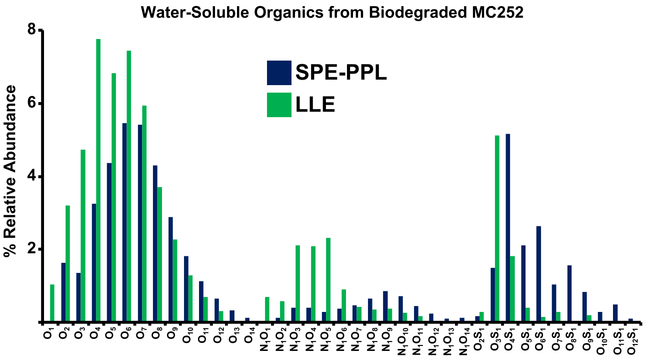

Figure 2. Heteroatom-compound class distribution for biodegraded acidic water-soluble organics extracted by solid-phase extraction with PPL (blue) and liquid/liquid extraction (green) derived from negative-ion electrospray ionization FT-ICR MS, showing O_x, NO_x, and SO_X compounds for both fractionation techniques. Species that contain only carbon and hydrogen (HC) and are detected in negative-ion ESI correspond to five-member ring hydrocarbons.

Compositional Comparison: DBE versus Carbon Number Images. *WSO Formed through Photodegradation.* The plots for DBE versus carbon number for the O*x* class for the WSO acidic photoproducts are shown in Figure 3 for SPE-PPL (top) and LLE (bottom). Each image shows the relative abundance weighted average carbon number and DBE, calculated from neutral elemental compositions. Across the same heteroatom class, LLE extraction yields slightly more aromatic (1−4 DBE) species with two to three more carbons per molecule. Lower oxygen species (O_1 and O_2) are not

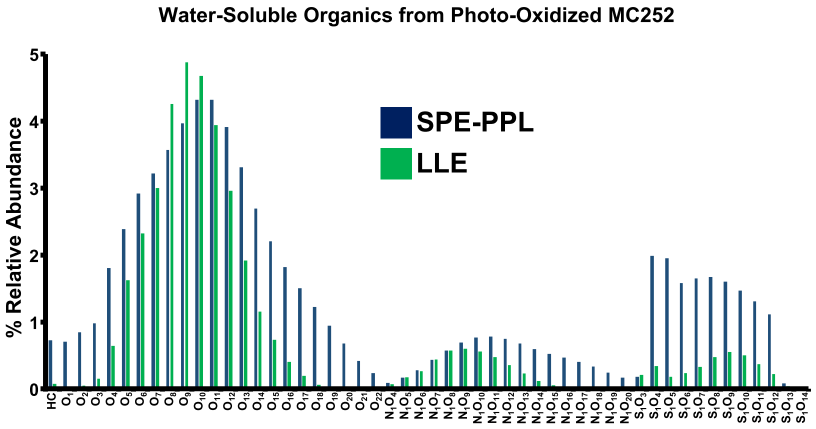

Figure 1. Heteroatom-compound class distribution for photodegraded acidic water-soluble organics extracted by solid-phase extraction with PPL sorbent (SPE-PPL, blue) and liquid/liquid extraction (green) derived from negative-ion electrospray ionization FT-ICR MS, showing O_x, NO_x, and SO_x compounds for both fractionation techniques.

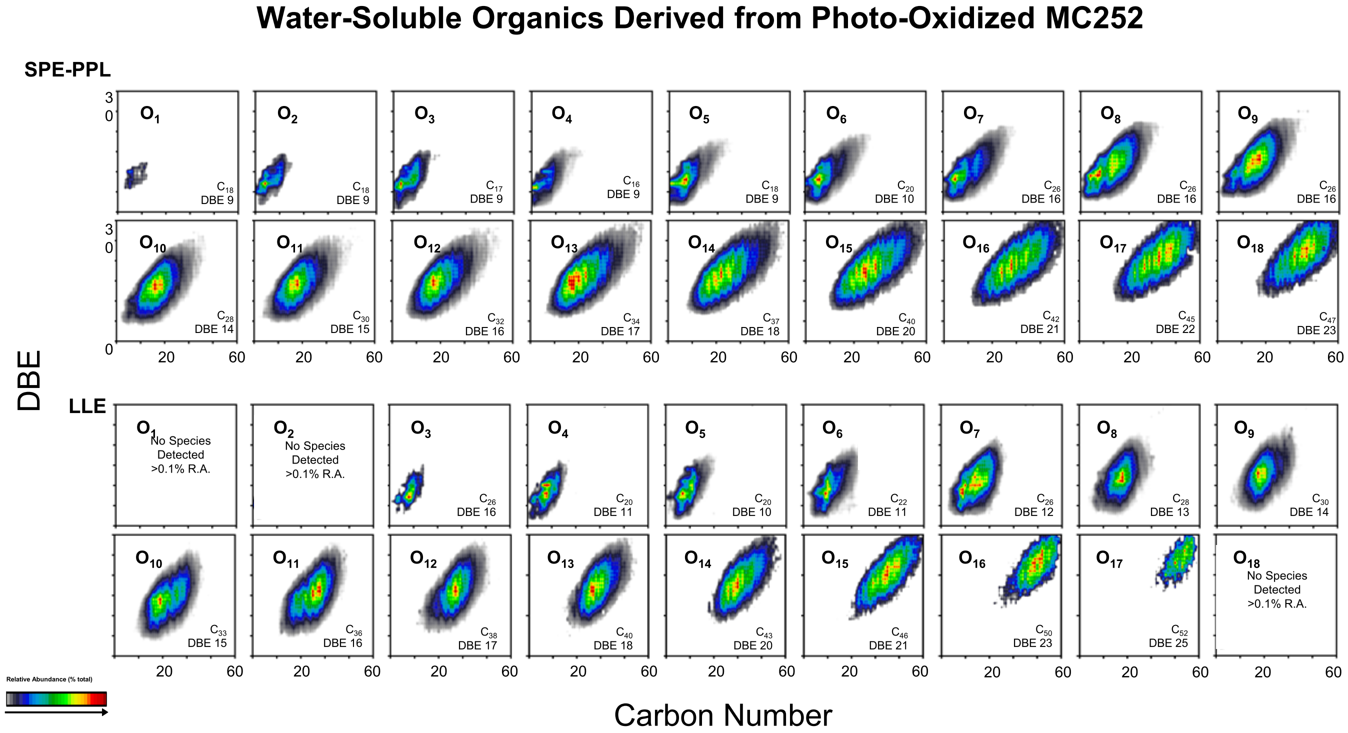

Figure 3. Isoabundance color-coded contoured plots of double-bond equivalents (DBE = number of rings plus double bonds to carbon, DBE = $C - h/2 - n/2 + 1$, calculated from the elemental composition for neutral species $C_cH_hN_nO_oS_s$) versus carbon number for water-soluble O_x species generated by photodegradation isolated by SPE-PPL (top) and liquid/liquid extraction (bottom) derived from negative-ion electrospray ionization FT-ICR MS. Each image is scaled to the most abundant species within each heteroatom class, where red equals 100% and the black equals some fraction of a percent. Relative abundance-weight-average DBE and carbon numbers are included on each image for all species detected with signal magnitude greater than 0.1% relative abundance.

detected above 0.1% relative abundance with liquid/liquid extraction, whereas SPE-PPL detects O_1 and O_2 species (C_{18} and DBE 9). However, LLE acids correspond to higher carbon number and aromaticity compared to SPE acids with the same number of oxygens (e.g., O_{16} and O_{17} SPE species averaging C_{42} and C_{45} and DBE 21 and 22; with LLE acids averaging C_{50} and C_{52} and DBE 23 and 25). Although O_1 and O_2 classes are not detected by LLE, the compositional space between the O_3 and O_{15} span similar aromaticity (DBE) and carbon number range for both extraction methods.

WSO Formed through Biodegradation. Isoabundance color-coded contoured plots of double-bond equivalents (DBEs = number of rings plus double bonds to carbon) versus carbon number provide rapid visualization of compositional space within a heteroatom class. The plots for the O_x class for the WSO acidic photoproducts are shown in Figure 4 for SPE-PPL (top) and LLE (bottom). Extraction of WSO formed through biodegradation with LLE yields abundant naphthenic acids that are not detected in the SPE-PPL. Nonaromatic acidic oxygen species (DBE < 3) are detected in O_1−O_5 classes by LLE that are not observed in the SPE-PPL extract. This suggests that SPE-PPL is more selective for highly polar, higher oxygen compounds, whereas more nonpolar compounds are extracted with LLE. These compounds, naphthenic acids, are highly toxic and recalcitrant compounds that remain undetected with SPE-LLE. Microorganisms can biodegrade hydrocarbons to produce polar compounds in crude oil, specifically acidic compounds that efficiently ionized by negative-ion ESI FT-ICR MS.[117−130] Naphthenic acids identified as the primary source of acute toxicity in oil process affected water are a highly recalcitrant complex mixture of carboxylic acids ($C_nH_{2n+Z}O_2$, where n is the carbon number and Z the number of rings) widely used to indicate oil biodegradation.[124,131,132] Organic acids indicate evidence of microbial degradation, and 1−2 ring naphthenic acids (DBE 2 or 3) are indicators for active, ongoing biodegradation in oil reservoirs.[127,133−140]

O_2 compounds extracted by SPE-PPL highlight several "hot spots" that correspond to highly abundant acidic compounds ($C_{20}H_{28}O_2$, DBE 7), which could correspond to a polycyclic monoaromatic previously detected in Alaska North Slope oils.[141] The most abundant carboxylic acid in the O_2 class, $C_{11}H_{14}O_2$ DBE 5, could correspond to 4-*tert*-butylbenzoic acid, a commonly use petroleum oil[142] and $C_{13}H_{12}O_2$ (DBE 8), which could correspond to 3′,5′-dihydroxybiphenyl-4-carboxylic acid methyl ester, previously detected in the heavily biodegraded oil from South America and used to trace *Exxon Valdez* oil in Alaska[39,143] These compounds have also been implicated as organic contaminants in lunar samples.[144]

Van Krevelen Diagrams for Unique Elemental Compositions. FT-ICR MS analysis results in tens of thousands of elemental compositions within a single mass spectrum and van Krevelen diagrams that highlight global shifts in H/C and O/C ratios for all oxygen species.[71,145] Each dot on the graphs represents H/C and O/C ratios assigned for elemental compositions assigned from negative-ESI FT-ICR MS from each mass spectrum. Figure 5 is composed of the van Krevelen diagrams of the molecular formulae that are unique to each fractionation technique for water-soluble phototransformation (top) and biotransformation (bottom) products derived from negative-ESI FT-ICR MS. Figure 5 highlights the photo-oxidation products unique to the LLE

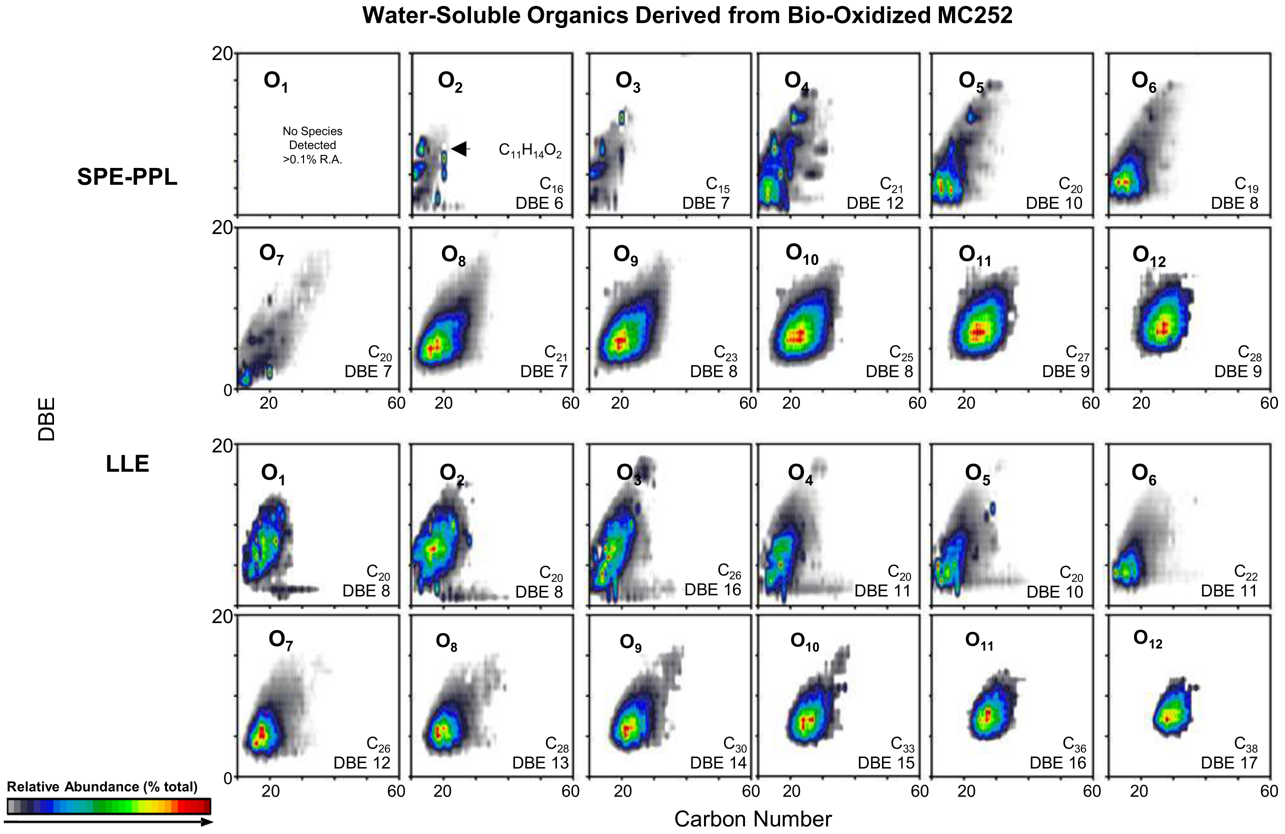

Figure 4. Isoabundance color-coded contoured plots of double-bond equivalents versus carbon number for water-soluble Ox species formed through biodegradation and subsequently isolated by SPE-PPL (top) and liquid/liquid extraction (bottom) by (−) ESI FT-ICR MS. Relative abundance-weight-average DBE and carbon numbers are included on each image for all species detected with signal magnitude greater than 0.1% relative abundance.

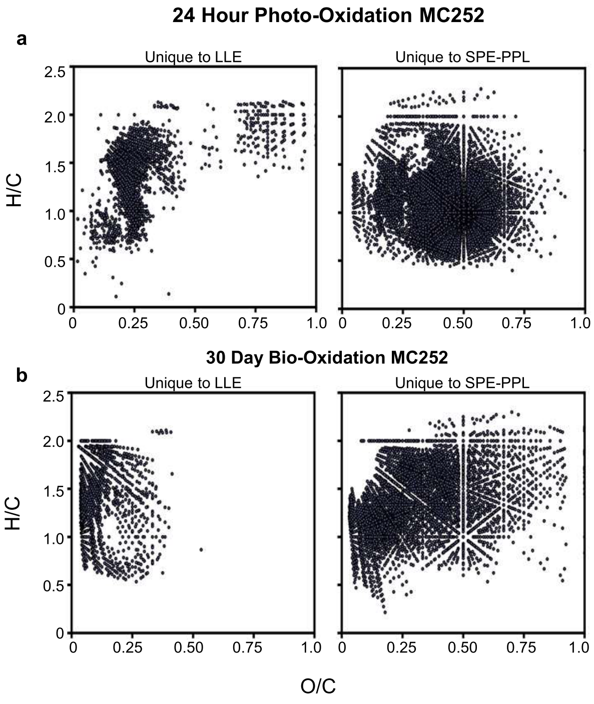

Figure 5. Van Krevelen diagrams for molecular formula of species generated through photodegradation (a) and biodegradation (b) unique to LLE and unique to SPE-PPL extraction. Assigned elemental compositions derived from mass-to-charge ratios that are detected in both samples have been discarded.

(left) and SPE-PPL (right) and shows the increased O/C ratio for SPE-LLE compared to LLE. Biodegradation products unique to LLE are lower in O/C ratio, with species between H/C 1.5−2.0 and O/C of 0.125 only detected in LLE-extracted compounds. These species correspond to naphthenic acids (O_2) and O_3−O_5 that span a range of carbon numbers across DBE < 3, formed through biodegradation and are linked to increased toxicity. For both photodegraded and biodegraded WSOs, SPE-PL isolates higher O/C compounds compared to LLE.

■ CONCLUSIONS

We compare the molecular composition of MC252-derived water-soluble species isolated by liquid/liquid extraction and solid-phase extraction from two independent microcosms of biodegraded and photodegraded oil, and analyze acidic species by negative-ion ESI FT-ICR MS. For photodegraded and biodegraded WSO, LLE isolates more nonpolar compounds, and when present, efficiently isolates compounds known to be toxic (naphthenic acids) that remain undetected by SPE-PPL. Although fast and easy, SPE-PPL isolates more polar compounds and is highly effective and useful for DOM isolation, and isolation of petroleum-derived WSO does not encompass nonpolar and less aromatic acidic compounds.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.analchem.0c05230.

Oil sample; dissolved organic carbon analysis; solid-phase extraction with PPL (SPE-PPL); liquid/liquid extraction (LLE); and FT-ICR mass spectrometry and data analysis (PDF)

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Notes

The authors declare no competing financial interest.

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