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Examining the Compositional Selectivity of Hydrocarbon Oxidation Products Using Liquid–Liquid Extraction and Solid-Phase Extraction Techniques

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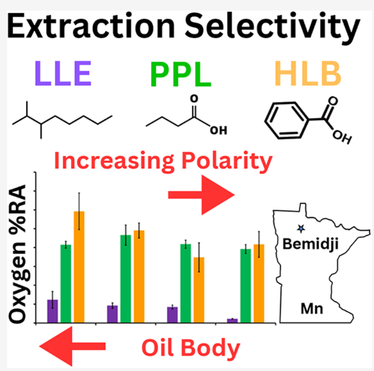
ABSTRACT: The effect of extraction methods on detecting hydrocarbon oxidation products (HOPs) in groundwater remains unclear. HOPs are polar, water-soluble byproducts of petroleum biodegradation. Our previous work showed that liquid–liquid extraction (LLE), a method commonly used in regulatory monitoring, has a significantly lower extraction efficiency for HOPs compared to solid-phase extraction (SPE). In this study, we evaluate the analytical limitations and compositional selectivity of LLE and SPE using groundwater samples from the Bemidji, MN, crude oil spill site. Optical properties were characterized using excitation–emission matrix spectroscopy (EEMs), and a three-component PARAFAC model was validated, showing consistent trends across both extracts and whole water samples. Ultrahigh-resolution mass spectrometry (UHR-MS) revealed that LLE selectively recovered aliphatic-like compounds but underrepresented more polar oxygenated HOPs. In contrast, SPE methods were more effective at isolating highly oxidized compound classes. These differences were consistent across a gradient of contamination. Overall, the LLE was less precise and less representative of polar HOPs, introducing bias in the characterization of HOPs. This study is the first to quantitatively demonstrate the compositional selectivity and analytical bias of LLE versus SPE for HOPs using combined EEM-PARAFAC and UHR-MS techniques, with implications for long-term monitoring and site assessment protocols.



KEYWORDS: *dichloromethane, high resolution mass spectrometry, oil spill, petroleum, fluorescence, EEMs, green extraction, green chemistry*

INTRODUCTION

Anthropogenic activities can threaten groundwater resources, causing short- and long-term impacts to aquatic and terrestrial life. Releases of crude oil and petroleum fuels to the environment occur during production, transport, processing, storage, and use.[1] These releases have the potential to contaminate soil and infiltrate into aquifers, as previously observed for past spills.[2,3] Depending on the type of oil or fuel and the conditions of the environment (anoxic and/or oxic), abiotic and biotic degradation processes can occur, adding oxygen to the oil compounds and rendering them water-soluble, forming hydrocarbon oxidation products (HOPs).[4−8] The most well-studied terrestrial oil spill is in a remote location near Bemidji, Minnesota, where oil infiltrated the soil and aquifer over 45 years ago. The National Crude Oil Spill Fate and Natural Attenuation Research Site is an interdisciplinary research project started in 1983 dedicated to monitoring the natural attenuation of oil in an aquifer. It is also used as a site for industry and private sector companies to study and examine the potential toxicity of petroleum degradation products, specifically, HOPs. The method used to test for the presence of hydrocarbons and HOPs in aquifers is total petroleum hydrocarbon analysis in the diesel range (TPHd), which uses a liquid–liquid extraction (LLE) technique to quantify petroleum compounds in the water.[9−11]

Recently, much debate has been on how effective TPHd testing is for HOPs in aqueous systems.[2,12−15] Generally, the EPA test Method 8015B for TPHd monitoring requires water samples to be extracted with a nonpolar solvent and analyzed using gas chromatography.[16] Previous studies have demonstrated that only a portion of HOPs are quantified using the TPHd method.[2,12,13] More advanced analytical instrumentation and methods are required to identify and detect HOPs, such as ultrahigh-resolution mass spectrometry (UHR-MS). The extraction techniques for HOPs analysis may include solid-phase and liquid–liquid extraction methods.

Although solid-phase extraction (SPE) is a widely used extraction technique for DOM,[17] little is known about the compositional selectivity of HOPs when using SPE versus LLE

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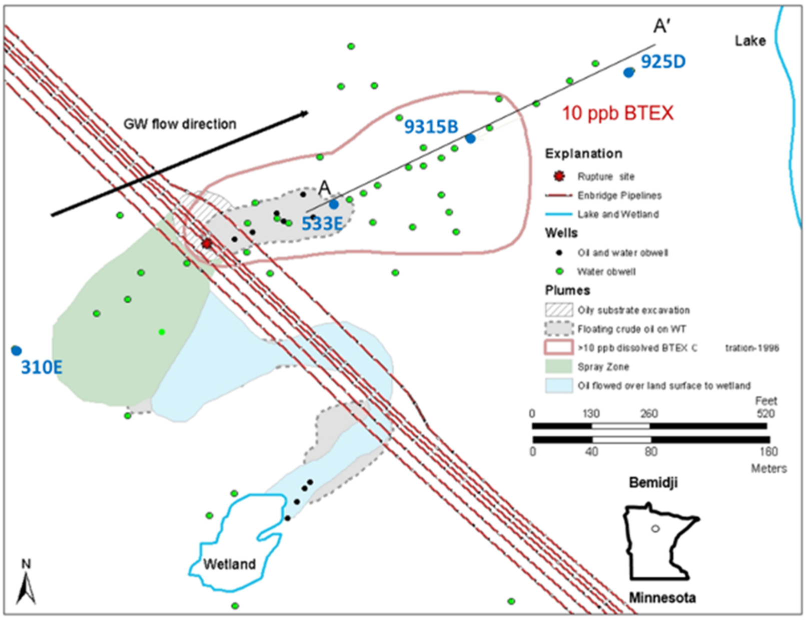

Figure 1. A map of the Bemidji site. The blue wells are the focus of this study. Image reproduced from [15]. Copyright [2025] American Chemical Society.

techniques. This study builds upon Zito et al. (2019)[13] using the same extraction techniques and wells to assess if current analytical methods—spectroscopy and UHR-MS—exhibit a compositional selectivity in identifying HOPs.

The objective of this study is to (1) extract HOPs using LLE and SPE for samples collected at a range of distances from the oil body source zone at the Bemidji site; (2) utilize excitation–emission matrix spectroscopy and UHR-MS to identify the optical and molecular level composition of each extract; and (3) compare samples from a compositional gradient of most contaminated to least contaminated to understand the selectivity of each extraction method and assess any bias between them.

■ MATERIALS AND METHODS

Sample Site. The samples were collected from the clean background and a transect downgradient of the oil source zone in the direction of groundwater flow at the National Crude Oil Spill Fate and Natural Attenuation Research Site (Figure 1) near Bemidji, MN (herein referred to as the Bemidji site; https://mn.water.usgs.gov/projects/bemidji/). The site was contaminated in August 1979, when a pressurized oil pipeline ruptured, spraying 440,000 gallons of crude oil over 10 acres of land in a remote location near Bemidji, MN.[3,18] About 75% of the oil was removed by burning, excavation, and pumping, and the remaining oil was left to degrade through natural attenuation. In 1983, the United States Geological Survey (USGS) established a long-term study of the fate of spilled oil. By 1998, 370 wells and test holes had been installed to evaluate the migration of hydrocarbons in the subsurface aquifer. The water table is 6–8 m below the land surface, and the groundwater flows east-northeast at an average velocity of 22 m y^{-1} toward an Unnamed Lake.[18] The degradation of hydrocarbons has led to groundwater plumes of elevated nonvolatile dissolved organic carbon (NVDOC) concentrations within and downgradient from the oil source zone.[2,19,20]

Water Collection. Water samples were collected from one background well (310E) and three wells in the groundwater plume (533E, 9315B, and 925D) at the Bemidji site along the centerline of the north oil pool plume during the 2019–2020 field seasons (Figure 1).[21] Well 310 E is about 200 m upgradient from the north oil pool source zone, as previously shown in Podgorski et al. (2021).[20] The water collected from 310E is representative of the native DOM in the background. Prior to collection, each well was purged with more than three well volumes, and samples were collected after a series of field measurements were stabilized. All samples were filtered through an ADVANTEC 0.27 μm glass fiber filter (previously combusted at 450 °C) and stored in acid-washed (Hydrochloric acid 34–37%, ARISTAR PLUS, VWR Chemicals BDH) HDPE bottles at 4 °C and shipped overnight to UNO.

Extraction Procedure. Dissolved organic carbon analyses and extraction procedures for solid-phase (SPE) and liquid–liquid (LLE) extraction were previously reported by Zito et al. (2019).[13] A brief description of each extraction method is provided here. Each filtered sample was acidified to pH 2 with HCl and then loaded onto a 100 mg PPL SPE cartridge (Agilent Bond Elut Priority Pollutant, a styrene-divinylbenzene polymer modified with a proprietary nonpolar surface; Agilent Technologies, Santa Clara, CA). Each sample was then desalted with pH 2 nanopure water and eluted with one cartridge volume of methanol (Methanol (HPLC), Fisher Chemical).[22] For the Waters Oasis Hydrophilic–Lipophilic Balanced (HLB) (a monodisperse divinylbenzene and *N*-vinylpyrrolidone copolymer, Waters Corporation, Milford, Massachusetts), each sample was loaded onto a 300 mg stationary phase cartridge. Each sample was then eluted with two cartridge volumes of methanol and two cartridge volumes of 1:1 (v/v) methanol:dichloromethane (DCM) (Dichloromethane ≥ 99.5% stabilized ACS, VWR Chemicals BDH). For LLE, samples and pure water were extracted following the EPA method 3510C.[23] Briefly, filtered water samples were pH adjusted to 10 using 10 M sodium hydroxide (NaOH Fisher Chemical ACS Certified). The bases and neutrals were extracted using 1 part DCM to 4 parts sample (v/v). Each DCM fraction was collected and combined into a round-bottom flask. The water sample was then adjusted to pH 2 with 10 M sulfuric acid (Sulfuric Acid ACS grade EMD Chemical), and the acidic species were extracted using a 1:4 DCM sample. Each fraction was combined, and the DCM was evaporated to a small volume and transferred to a 40 mL vial. The round-bottom flask was rinsed with three 5 mL aliquots of DCM to ensure that all residues were transferred and added to the 40 mL vials. The DCM fraction was evaporated to dryness to prepare it for nonvolatile DOC analysis. Sample and pure water (blank) extractions were performed in triplicate for each method (Table S1). The final concentrations of all extracts were 50 μgC mL^{-1}, and the extracts were stored at 4 °C before analysis.

Instrumental. *Spectroscopic Measurements.* Fluorescence measurements were performed on a Horiba Aqualog fluorometer with a 10 mm quartz cuvette. The fluorescence excitation range was measured at 250−600 at 5 nm increments, and the emission range was fixed at 230−800 nm with 2 nm increments. Prior to EEMs, absorbance was measured using an Agilent Cary 60 spectrophotometer, and any signals above 0.1 absorbance at A254 nm were diluted to 0.1 by using nanopure water to reduce any inner filter effects during the EEMs measurements. The instrument's accuracy was validated weekly using a Starna Raman Water Fluorescence Reference, and daily Raman scattering units (RSU) were validated before use. DrEEM Toolbox version 0.6.5 was used to apply Parallel Factor Analysis (PARAFAC) to 40 samples (triplicate for each sorbent per well and whole water samples (4 total)), and a three-component model was validated by random split-half analysis.[24,25] Prior to validation, Raman scattering removal was performed and the PARAFAC model was computed with nonnegativity constraints on all modes.

Ultrahigh-Resolution Mass Spectrometry. PPL, LLE, and HLB sample extracts were analyzed on a 21T Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS). Direct infusion negative-ion electrospray ionization (ESI) at a flow rate of 700 nL min^{-1} with a custom-built FT-ICR mass spectrometer equipped with a 21-T superconducting magnet was utilized for DOM analyses.[26] The reproducibility of ESI ultrahigh-resolution mass spectrometry (UHR-MS) for individual samples on multiple instruments is reported in detail elsewhere.[27] Molecular formulas were assigned to signals >6σ RMS baseline noise with EnviroOrg software developed at the National High Magnetic Field Laboratory (NHMFL)[28] and by Hemingway (2017).[29] A mass resolving power of 1,200,000 ($m/\Delta m$ 50%) was achieved at m/z 400, and the mass measurement accuracy was less than 200 ppb. Each molecular formula was classified based on stoichiometry according to condensed aromatic (CA) (modified aromaticity index) (AI_{mod} $\geq$ 0.67), aromatic (0.67 > AI_{mod} > 0.5), unsaturated, low oxygen (ULO) (AI_{mod} < 0.5, H/C < 1.5, O/C < 0.5), unsaturated, high oxygen (UHO) (AI_{mod} < 0.5, H/C < 1.5, O/C $\geq$ 0.5), aliphatic (H/C $\geq$ 1.5, $N = 0$) (Figure S1).[30−32] The abundance-weighted nominal oxidation state of carbon (NOSCw), H/Cw, O/Cw, and molecular weight (M_w) were calculated based on methods described elsewhere.[33,34] One of the triplicates for Well 925D was spilled prior to UHR-MS analysis; therefore, statistical analyses could not be performed on these data.

Description of Compositional Trends from Previous Results. Podgorski (2021) used a combination of excitation−emission matrix spectroscopy (EEMS), ultrahigh-resolution mass spectrometry (UHR-MS), nuclear magnetic resonance (NMR) spectroscopy, and the benzene carboxylic acid (BCA) method to characterize uncontaminated wells and a transect along the centerline of the contamination plume at the Bemidji oil spill site. Background wells contained nonvolatile dissolved organic carbon (NVDOC) concentrations of <2 ppm, consistent with typical groundwater. The chemical composition of these background samples was dominated by unsaturated, oxygen-rich compounds, as expected for groundwater.

Well 533E, located adjacent to and downgradient from the oil body in the direction of groundwater flow, had NVDOC concentrations 15−20 times higher than the background. The composition in this well closely resembled that of the oil with relatively reduced aliphatic and aromatic compounds (i.e., low O/C ratios). Measurements from 19 wells across the plume showed that well 925D, the farthest downgradient in the transect, receives water that takes ~11.5 years to travel from the source. Across the transect, NVDOC concentrations decreased exponentially with selective removal of aliphatic and aromatic compounds.

Although NVDOC levels were lower downgradient, they did not return to background values. Furthermore, the compounds in well 925D were, on average, larger and more aromatic than those in the background wells. These results suggest that labile, reduced compounds are preferentially degraded by microbial processes, whereas larger, more aromatic constituents, while partially oxidized, persist downgradient.

Limitations and Nomenclature. Analysis of the nonvolatile, unresolved complex mixture (UCM) is inherently nontargeted, and no single analytical method can fully characterize its composition. Furthermore, no authentic standards exist for UCM compounds. Consequently, classification must be based on stoichiometric relationships using van Krevelen diagrams (O/C; H/C), for UHR-MS (Figure S1) and on correlations between EEM components and chemical composition previously established in the literature.[35−37]

The terminology used in this study is relative rather than absolute. For example, when fluorescence results are described, the term "aliphatic" does not refer to pure alkanes but rather to compounds shifted toward the relatively aliphatic region within the fluorescence analytical window. Similarly, not all compounds in our samples can be detected by negative-ion electrospray ionization (ESI); only those with at least one acidic functional group can be ionized under these conditions. Thus, all compounds classified in the UHR-MS data contain acidic oxygenated functionalities. For instance, a compound categorized as "aliphatic" in our data set is not a neutral alkane, which would not ionize by negative-ion ESI, but could be an alkane derivative such as a naphthenic acid that readily ionizes due to its carboxylic acid group.

Although no single analytical method can fully characterize a complex mixture, combining complementary techniques such as ultrahigh-resolution mass spectrometry UHR-MS and EEMS provides a more comprehensive, albeit still incomplete, representation of its composition. The integration of these data sets captures different but overlapping fractions of the mixture, enabling a broader and more informative characterization than either technique alone.

RESULTS AND DISCUSSION

Isolation of HOPs after Extraction Using SPE and LLE. A previous study by our group examined the extraction efficiency of HOPs by comparing LLE and three SPE methods

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(PPL,C18 (not shown) and HLB).[13] From this 2019 study, we concluded that LLE extracted only 16–24% of the NVDOC for HOPs in contaminated samples from the Bemidji site.[13] The PPL had an extraction efficiency of 74–93% for NVDOC and the HLB was 70–119% (Figure 2).[13] The high extraction efficiency calculated for the HLB sorbent may have been due to the sorbent's leaching, as Li et al. reported elsewhere.[38]

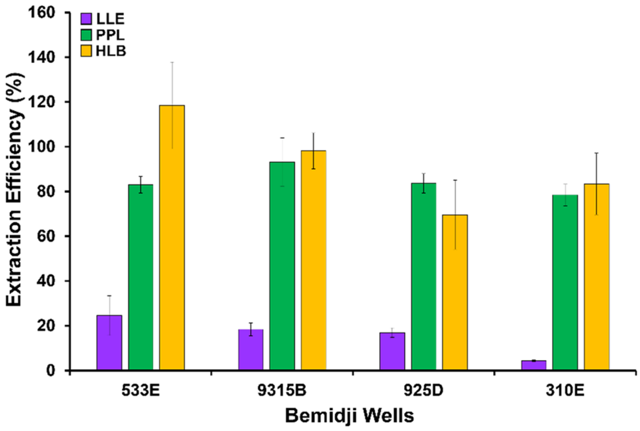

Figure 2. Percent extraction efficiency comparing LLE (purple), PPL (green), and HLB (gold) techniques. Error bars reflect the 95% confidence interval of the mean ($n = 3$). Adapted from [13]. Available under CC-BY 4.0. Copyright [2025][NGWA].

Assessing Extraction Bias Using Optical Spectroscopy. Optical spectroscopy was used to evaluate changes in chromophoric and fluorophoric dissolved organic matter (C/FDOM) across different extraction methods. A three-component model was validated from the excitation–emission matrix (EEM) spectra using parallel factor analysis (PARAFAC),[24] which identified the dominant fluorophores in each sample. Figure 3 shows the percent relative contribution (% RC) of the three PARAFAC components. C1 (3a), C2 (3b), and C3 (3c), derived from EEM analysis. For each component, bar graphs compare results from liquid–liquid extraction (LLE, purple), PPL solid-phase extraction (green), and HLB solid-phase extraction (gold), displayed alongside corresponding EEM-PARAFAC contour plots. The model was uploaded to the OpenFluor database,[39] where 45 matches were found with a Tucker's congruence coefficient (TCC) above 0.97. Most components aligned with petroleum-derived fluorophores previously reported in the literature.[20,40,41] Component 1 (C1) corresponds to low molecular weight (M_W) aromatic compounds, with an excitation maximum at 240 nm and emission maxima between 360–378 nm.[40] Component 2 (C2) reflects small, reduced aliphatic compounds, showing excitation at 265 nm and emission at 310 nm.[42,43] Component 3 (C3) is associated with high MW, alicyclic/aromatic compounds, with an excitation maximum at 250 nm[40,41] and emission maximum at 441 nm. These C3-type fluorophores are generally linked to oxidized, high-MW degradation products of hydrocarbons, consistent with reduced or aged hydrocarbon oxidation products (HOPs).[41] For Component 1 (C1), LLE extracts from petroleum-contaminated wells 533E, 9315B, and 925D were not statistically different from PPL and HLB extracts ($\rho > 0.05$), which aligns with expectations since HOPs are typically rich in aromatic compounds. However, PPL and HLB extracts showed significant differences from each other in % RC at wells 533E, 925D, and 310E, likely due to HLB's broader polarity range and higher NVDOC recovery, particularly for acids, bases, and neutrals.[13] At the background well 310E—characterized by more polar NVDOC and no known HOPs—the LLE extract differed significantly from both PPL ($\rho < 0.05$) and HLB ($\rho < 0.004$). Component 2 (C2) exhibited similar trends: no significant differences between LLE and SPE methods at contaminated wells, but notable differences at 310E, and between PPL and HLB at 533E ($\rho < 0.05$). For Component 3 (C3), all LLE extracts were statistically different from PPL and HLB across the contaminated wells ($\rho < 0.05$). LLE and HLB were similar at 310E. When comparing all extracts to whole water, two key observations emerged: (i) extractable C/FDOM patterns were consistent with whole water despite preconcentration, and (ii) global trends across C1–C3 were preserved, supporting direct compositional comparisons.

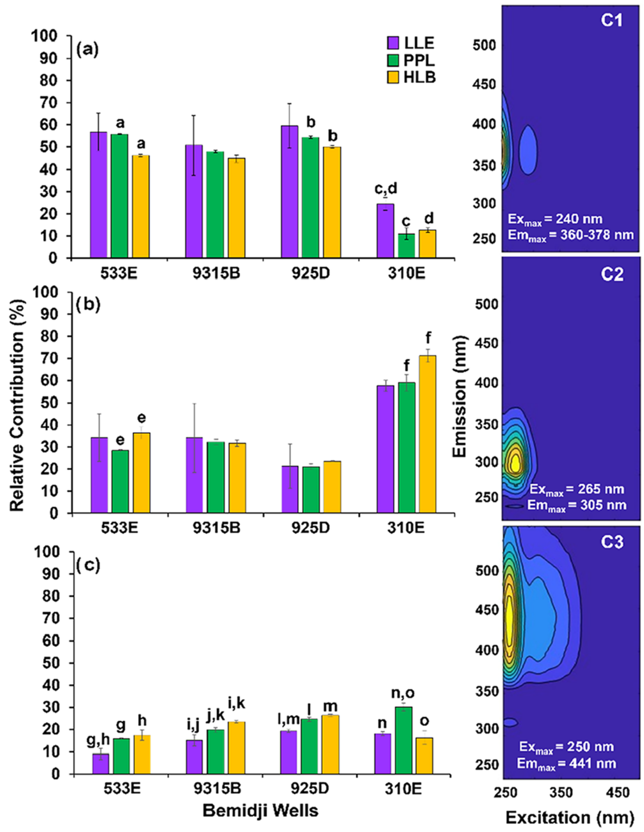

Figure 3. Percent relative contribution of PARAFAC components to fluorescence intensity: (a) C1, (b) C2, and (c) C3, in extracts prepared using LLE (purple), PPL (green), and HLB (gold) from groundwater wells impacted by petroleum contamination. Contour plots on the right illustrate the spectral signatures of each component. Error bars represent one standard deviation from the mean ($n = 3$), and letters indicate statistically significant differences between samples ($\rho < 0.05$). All ρ values are reported in Supporting Information Table S4.

Ultrahigh-Resolution Mass Spectrometry Reveals Compositional Selectivity of Extraction Techniques as a Function of Polarity. Figure 4 presents the percent relative abundance of compositional classes (aliphatic, unsaturated low oxygen, unsaturated high oxygen, and aromatic) identified by ultrahigh-resolution mass spectrometry (UHR-MS) for groundwater samples extracted using three different methods: liquid–liquid extraction (LLE, purple), PPL (green), and HLB

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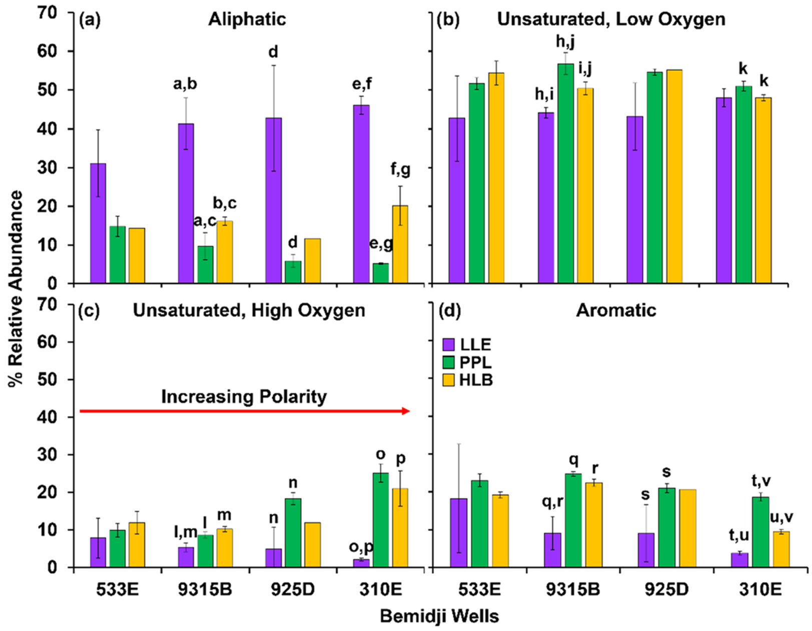

Figure 4. (a) Aliphatic, (b) unsaturated low oxygen, (c) unsaturated high oxygen, and (d) aromatic compositional classes for groundwater wells extracted with LLE (purple), PPL (green), and HLB (gold). The red arrow illustrates the direction of increasing polarity or distance from the oil body. The letters denote statistically different compound classes (ρ < 0.05) for all samples. Error bars represent one standard deviation from the mean (n = 3), and letters indicate statistically significant differences between samples (ρ < 0.05). Actual ρ values are reported in Supporting Information Table S5.

(gold) solid-phase extraction. LLE consistently recovered higher proportions of aliphatic compounds (panel a), particularly in wells closest to the oil body, reflecting this method's affinity for nonpolar constituents. In contrast, HLB preferentially extracted more polar compounds such as unsaturated high oxygen and aromatic species (panels c and d), especially from wells farther from the contamination source (e.g., 925D) and the background well, as indicated by the red arrow denoting increasing polarity. Statistically significant differences (p < 0.05, denoted by letters) were observed between most extraction methods for all compound classes in wells 9315B, 925D, 310E, and 533E (ULO only) underscoring the influence of extraction chemistry on compositional profiles. These results highlight the importance of extraction method selection when characterizing dissolved organic matter from petroleum-contaminated sites using UHR-MS.

Extraction Technique and Source Composition Drive Variance between Extraction Techniques. Principal component analysis (PCA) of the combined ultrahigh-resolution mass spectrometry (UHR-MS) and excitation−emission matrix (EEM) fluorescence data revealed distinct compositional groupings based on the extraction method (Figure 5). LLE-derived samples exhibited the greatest dispersion across the PCA space but were clearly separated from PPL- and HLB-derived samples along PC1, indicating substantial chemical diversity and compositional dissimilarity from samples extracted with solid-phase methods.[40] In contrast, PPL and HLB extracts formed more compact and overlapping clusters in the upper right quadrant, suggesting that these methods recover chemically similar, polar compound classes. The orientation and length of the loading vectors further support this differentiation, with variables associated with aromatic and oxygen-rich species aligning closely with the PPL and HLB clusters, while those corresponding to aliphatic or less oxygenated constituents

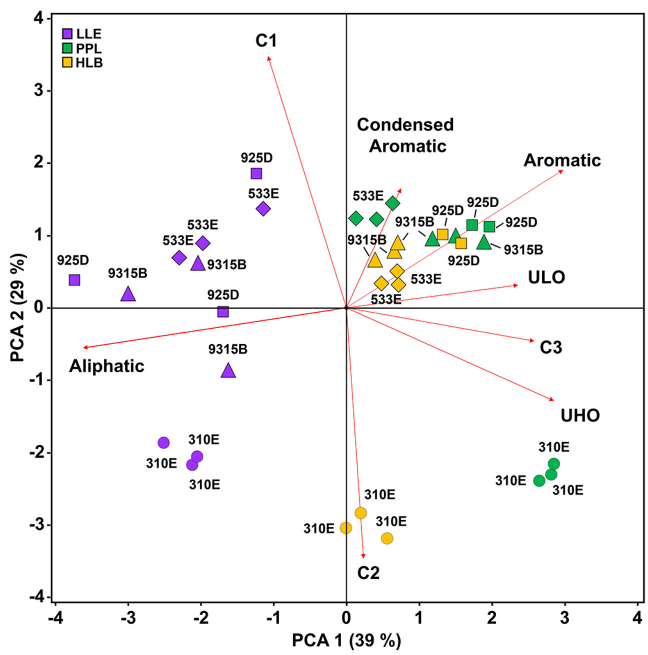

Figure 5. PCA illustrates the variance between extraction techniques for EEMs and UHR-MS for LLE (purple), PPL (green), and HLB (gold) samples collected from Bemidji. The shapes correspond to each well: 533E (diamonds), 9315B (triangles), 925D (squares), and 310E (circles). Unsaturated Low Oxygen (ULO); Unsaturated High Oxygen (UHO) from UHR-MS measurements.

pointed toward the LLE group. These results underscore the influence of extraction chemistry on observed compositional trends in DOM. In particular, LLE appears to recover a broader range of hydrophobic or nonpolar compounds not effectively captured by solid-phase resins, which may bias molecular level interpretations of oil-derived DOM if only a single extraction method is applied.

Few studies have examined how compositional and fluorescent dissolved organic matter (C/FDOM) characteristics of hydrocarbon oxidation products (HOPs) are altered by solid-phase extraction (SPE) and liquid−liquid extraction (LLE) in environmental samples.[44] Most existing literature focuses on DOM from nonpetroleum sources.[17,45,46] For example, Wunsch et al. (2018) reported extraction bias when comparing pure water samples to PPL resin extracts from Arctic fjord environments, finding that the extracts did not accurately represent the original water composition.[47] In our study, we observed relatively minor differences in C/FDOM between whole water samples and extracts from contaminated sites, likely because oil-derived chromophores and fluorophores generate strong signals at shorter wavelengths, complicating their spectral interpretation. However, when samples are separated based on polarity, the spectroscopic differences among chromophores and fluorophores become more pronounced in polar fractions, especially in samples farther from the oil body. Complementary UHR-MS analysis supported these findings, showing that LLE recovered a more compositionally diverse set of compounds, including aliphatic and low-oxygen species, while PPL and HLB preferentially extracted more polar, oxygen-rich, and aromatic constituents. Together, these results demonstrate that the extraction method exerts a strong influence on both the molecular and optical characterizations of oil-derived DOM, with implications for interpreting compositional shifts across petroleum-impacted gradients.

The most important implication of the compositional bias we have documented for LLE toward aliphatic and low-oxygen species is that compounds in these classes are relatively biodegradable. Podgorski et al. (2021) showed that aliphatic and low-oxygen species decrease with distance from the source more rapidly than the more polar, oxygen-rich, and aromatic constituents prevalent in extracts obtained using PPL and HLB methods. The result is that TPH_d analyses provide a picture of relatively rapidly decreasing HOP concentrations with distance from the source, in contrast to concentrations obtained from other extraction methods (Bekins et al. 2020). This picture obscures the true effect of the crude oil source zone on concentrations of HOPs in the downgradient groundwater.

Green Extraction Considerations. Dichloromethane (DCM) is a common solvent in extractions, synthesis, and chromatography, but is classified as a Group 2A carcinogen.[48−50] Following its 2022 risk determination, the U.S. EPA issued an April 2024 rule under the Toxic Substances Control Act (TSCA) prohibiting most consumer, industrial, and academic uses to protect human health.[51−53] Chronic inhalation or dermal exposure causes cancer and noncancer effects, including central nervous system depression and liver damage, as DCM is metabolized into formaldehyde, formyl chloride, and carbon monoxide.[54] Even small accidental injections cause acute injury, and 85 fatalities were reported from 1980−2018, primarily in occupational settings.[55]

Limited workplace uses remain, such as chemical production, solvent welding, and some laboratory work, under the Workplace Chemical Protection Program, which requires frequent breathing-zone air monitoring to meet exposure limits.[51−53,56] These mandates impose substantial technical and financial burdens, especially on smaller institutions, prompting many to consider eliminating DCM entirely by May 5, 2025.[57]

Although the conception, experimental work, data acquisition, and analysis for this project were completed in 2018−2019, we obtained serendipitous results relevant to recent EPA regulations on DCM. Both the HLB and LLE methods employ DCM in their procedures. The LLE method (EPA 3510C) requires comparatively large volumes, typically hundreds of milliliters per extraction, when replication is considered. For example, the most common sample volume of 1 L necessitates 200 mL of DCM. In contrast, the HLB method requires only milliliter-scale volumes. However, the new EPA regulations on DCM are not volume-dependent; the use of any quantity is subject to restriction. In comparison, the PPL extraction method requires only acidified water and methanol, making it a greener alternative with a high extraction efficiency. Ongoing work in our group is focused on developing greener protocols for both LLE and HLB extractions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.5c07016.

Blank DOC concentrations for LLE, PPL, and HLB (Table S1); openFluor matches and reference (Table S2); summary of Openfluor matches for C1−C3 (Table S3); generic vanKrevelen diagram of defined UHR-MS compositional classes (Figure S1); ρ values for Figure 3 (Table S4), and ρ values for Figure 4 (Table S5)(PDF)

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Notes

The authors declare no competing financial interest.

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