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High-Resolution Mass Spectrometry Identification of Novel Surfactant-Derived Sulfur-Containing Disinfection Byproducts from Gas Extraction Wastewater

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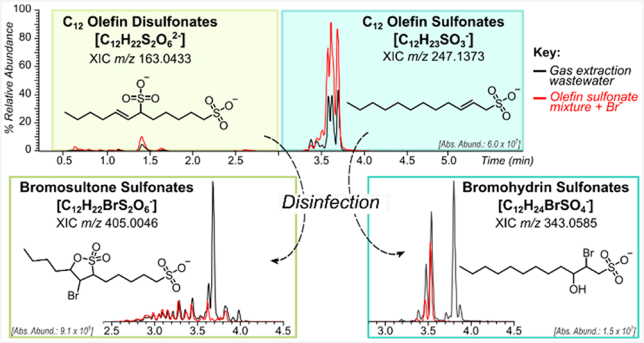
ABSTRACT: Introduction of oil and gas extraction wastewaters (OGWs) to surface water leads to elevated halide levels from geogenic bromide and iodide, as well as enhanced formation of brominated and iodinated disinfection byproducts (DBPs) when treated. OGWs contain high levels of chemical additives used to optimize extraction activities, such as surfactants, which have the potential to serve as organic DBP precursors in OGW-impacted water sources. We report the first identification of olefin sulfonate surfactant-derived DBPs from laboratory-disinfected gas extraction wastewater. Over 300 sulfur-containing DBPs, with 43 unique molecular formulas, were found by high-resolution mass spectrometry, following bench-scale chlor(am)ination. DBPs consisted of mostly brominated species, including bromohydrin sulfonates, dihalo-bromosulfonates, and bromosultone sulfonates, with chlorinated/iodinated analogues formed to a lesser extent. Disinfection of a commercial C_{12}-olefin sulfonate surfactant mixture revealed dodecene sulfonate as a likely precursor for most detected DBPs; disulfur-containing DBPs, like bromosultone sulfonate and bromohydrin disulfonate, originated from olefin disulfonate species, present as side-products of olefin sulfonate production. Disinfection of wastewaters increased mammalian cytotoxicity several orders of magnitude, with chloraminated water being more toxic. This finding is important to OGW-impacted source waters because drinking water plants with high-bromide source waters may switch to chloramination to meet DBP regulations.



INTRODUCTION

Oil and gas extraction activities have become increasingly common due to enhanced gas extraction from shale. Millions of liters of water are injected per well, which return to the surface containing components released from the shale, including bromide and iodide. With the large volumes of wastewater being created, transported, and disposed, concerns have been raised about the potential for contamination of drinking water sources.[1,2] In most source waters, the major organic disinfection byproduct (DBP) precursor is natural organic matter (NOM), which is composed of fulvic and humic acids.[3] However, disinfectants can also react with organic contaminants to form DBPs,[3−5] and oil and gas extraction wastewaters (OGWs) tend to be highly concentrated with dissolved organic matter (DOM) contributed by both anthropogenic and geogenic constituents.[5,6] DBP speciation and concentrations depend on organic precursor species, bromide/iodide concentration, and the type of disinfectant used. In general, chlorine- and chloramine-disinfection of halide-rich waters, including saline[7−9] and oil/gas extraction wastewaters,[1,2,5] enhance the formation of brominated (and iodinated, especially with chloramination) DBPs, which are more toxic than their chlorinated analogues that predominantly form during chlor(am)ination of low-salinity waters.[10−14] Flowback and produced waters from oil and gas activities have been reported to contain tens to thousands of parts-per-million (ppm) bromide and tens of ppm iodide from shale,[1,5,15] as well as up to thousands of ppm total organic carbon (TOC), mostly from fluid additives.[6,15]

Oil and gas extraction fluids (and their wastewaters) contain chemical additives (biocides, friction reducers, corrosion

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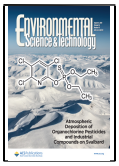

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inhibitors, surfactants, etc.) to optimize the efficiency of shale fracturing and oil/gas extraction processes. Although additives make up a small portion of the fluid on a percentage basis (<1% additives), their concentrations (hundreds to thousands of parts-per-million [ppm; mg/L]) are relevant from an environmental contaminant perspective. There are thousands of chemicals used in the oil and gas industry, and the unique combinations employed for different wells are determined by the optimum conditions for a given geological formation.

As disclosure of additives has become increasingly common through the FracFocus registry and researchers continue to evaluate fluid compositions,[16−20] some chemicals are still known generically or as "proprietary", but many are fully disclosed, including CAS registry numbers.[16] Unfortunately, the *exact* structures and/or isomeric distributions of many disclosed chemicals remain unknown, as classes are often lumped together under one chemical identifier. Many surfactants fall into this category of compounds of unknown or variable composition, with mixtures documented as a single item; for example a FracFocus registry of "sodium C_{14-16} olefin sulfonate" (CAS# 68439−57−6) is a mixture of C_{14-16}-alkane hydroxy- and -alkene sulfonic acids.[21] Surfactant mixtures constitute almost a part-per-thousand of the fluid injected during the extraction process.[19] At these levels, surfactants have the potential to persist at ppm levels in OGW-impacted source waters after release.

The interrogation of chemical mixtures has been greatly aided in recent years by advances in nontargeted analysis (NTA) supported by high-resolution mass spectrometry (HRMS).[22] Nontargeted analysis approaches samples with no preconceptions about the nature of the chemicals to be detected, typically using HRMS to generate potential formulas for molecular ions and fragment ions, examining isotopic patterns, and interpreting the unknown compound's mass spectrum to assign a potential chemical structure. A variety of HRMS instruments have been developed, including quadrupole time-of-flight (Q-TOF), Orbitrap, and ion cyclotron resonance (FT−ICR) platforms, which possess the ability to determine molecular composition on the basis of accurate mass and isotope information, and to determine chemical structural information via fragmentation.[23] This approach has been previously applied in the identification of oil and gas extraction fluid additives[19,24,25] and wastewater components,[5,26] as well as to the discovery of novel DBPs in numerous water sources.[27−30] Most of the literature discussing nontargeted identification of oil- and gas-related surfactants have focused on nonionic ethoxylate-based surfactants.[19,24,25]

Previous related DBP studies have focused primarily on quantifying select, known DBPs formed during chlor(am)-ination from the reaction of disinfectant with bromide and iodide from OGW and NOM in impacted surface waters,[1,2,31−35] and a recent study reported the formation of iodinated halomethanes during biological treatment of OGW.[36] A previous study of shale wastewater reported unintended halogenated byproducts formed during the extraction process,[37] and further simulation-based studies have been conducted to assess transformation products resulting from interactions between common fluid additives and natural shale brines.[38−40] To the best of our knowledge, no studies have examined the role of OGW anthropogenic constituents on DBP formation during *in situ* or simulated wastewater/drinking water disinfection; however, in previous subsurface simulation experiments, NaOCl was one of several oxidants ("breakers") studied, resulting in transformation products analogous to DBPs.[38−40] To date, the only surfactants that have previously been characterized as DBP precursors are alkylphenol ethoxylates studied after chlorination at municipal wastewater treatment plants[41,42] and linear alkyl benzenesulfonates (LAS) in treated saline wastewater.[43] Although these studies were not OGW-focused, alkylphenol ethoxylates and LAS are common surfactants used as fluid additives in oil/gas extraction processes.[20,44] This study reports the first nontargeted identification of olefin sulfonate surfactant-derived DBPs identified from chlorine- and chloramine-disinfected gas extraction wastewater, along with the comparative quantitative cytotoxicity of these wastewaters in mammalian cells *in vitro*.

MATERIALS AND METHODS

Standards and Reagents. Sodium hypochlorite solution (NaOCl, 5.65−6%) and anhydrous dibasic potassium phosphate, hydrogen peroxide solution (H_2O_2, 30%) hydrochloric acid, sulfuric acid, and sodium hydroxide were obtained from Fisher Scientific (Hampton, NH). Ammonium chloride (NH_4Cl), anhydrous granular sodium sulfate, and sodium halide salts (i.e., NaCl, NaBr, and NaI) were purchased from Sigma-Aldrich (St. Louis, MO). GC^2 ethyl acetate and methanol were obtained from Burdick & Jackson (Muskegon, MI). A commercial C_{12}-olefin sulfonate standard, which was a mixture of sodium dodecene sulfonate (20−30%) and hydroxydodecylsulfonate (20−30%), was obtained from Stepan Company (Northfield, IL).

Inorganic reagents, i.e., halides, NH_4Cl, and buffer stock solutions, were prepared at least monthly in purified water (18 MΩ-cm) from a Barnstead E-Pure system (Lake Balboa, CA). NaOCl reagent was standardized (λ_{max} = 292 nm, ε = 350 M^{-1} cm^{-1})[45] within a week prior to each disinfection experiment using a Molecular Devices SpectraMax M5 spectrophotometer (Sunnyvale, CA). Monochloramine reagent was prepared fresh for each reaction with new solutions of NaOCl and NH_4Cl. Briefly, 100 mL of 0.05-M NH_4Cl was adjusted to pH 8.5 with 1-M NaOH. While stirring and maintaining pH between 8.4 and 8.7 with HCl and NaOH, 77 mL of 0.05-M NaOCl was added to the NH_4Cl solution, a few mL at a time, to satisfy a 1:1.3 NaOCl/NH_4Cl molar ratio. Resulting monochloramine concentration was determined spectrophotometrically (λ_{max} = 243 nm, ε = 461 M^{-1} cm^{-1}).[45]

Sample Collection and Characterization. Produced water samples from a Texas gas-charged reservoir were collected headspace-free in 2-L high-density polyethylene (HDPE) containers (Fisher Scientific). Prior to two-day shipment on ice, a portion of the produced water was subjected to pretreatment methods that included bag filtration (20 μm) and gas/hydrocarbon removal. The two types of samples were thereafter deemed "raw feed (RF)" and "pretreated (PT)". HPLC grade water was shipped, unopened, to the sample collection site, where it was transferred to HDPE bottles headspace-free and shipped alongside samples as a travel/field blank (FB).

Total organic carbon (TOC) analyses were performed using a Sievers InnovOx TOC Analyzer (GE Analytical Instruments, Boulder, CO).[5] Prior to halide analysis, samples were filtered through 0.45-μm poly(ether sulfone) membrane syringe filters (VWR International, Radnor, PA) that were prerinsed with 10 mL of purified water to remove iodide interferent. Calibration standards for chloride (10−750 μg/L), bromide (1−750 μg/L), and iodide (10−750 μg/L) were prepared in purified

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water. Standards and filtered samples were analyzed by a Dionex 1600 ion chromatograph (IC) with conductivity detector (Sunnyvale, CA) using an IonPac AS9-HC column and AERS-500 carbonate suppressor at a 1.5 mL/min flow rate. Although the pretreatment process reduced TOC (RF = 575 vs PT = 435 mg/L as C), halide levels were not impacted, with 29 mg/L bromide and 14 mg/L iodide in both RF and PT.

Simulated Disinfection Experiments. RF, PT, and FB waters were each mixed separately with purified water (10% sample + 90% purified water). Large-scale reactions (18 L for PT and RF; 21 L for FB) were performed in covered stoppered-glass jugs to minimize light exposure. Chlorination and chloramination reactions were performed for 24 and 72 h, respectively, with disinfectant doses to achieve a 1.0−2.0 mg/L chlorine residual at the end of the allotted reaction times. Each reactor was buffered at pH 7.5 with 10-mM phosphate. Controls of each sample, with no disinfectant applied, were analyzed in the same manner for comparison.

A portion of the reaction mixture was quenched with ascorbic acid (1.3:1 quench/chlorine molar ratio, assuming a 2.5 mg/L residual) and analyzed directly by liquid chromatography (LC)-high resolution mass spectrometry (MS) with electrospray ionization (ESI). A 250 mL aliquot of the quenched mixture was used for duplicate measurements of speciated total organic halogen (TOX). The remainder of the water was extracted using XAD resins (see below) for high-concentration factor, high-sensitivity MS analyses, and mammalian cell cytotoxicity studies.

Total Organic Halogen (TOX). Total organic chlorine, bromine, and iodine (TOCl, TOBr, TOI) were measured in duplicate according to a method published previously using a TOX analyzer (Mitsubishi Chemical Analytech, Chigasaki, Japan; Cosa Xentaur, Yaphank, NY, U.S.A.) followed by ion chromatography (IC).[46,47] For each replicate, approximately 50 mL of quenched, acidified (pH < 2) sample was passed through two activated carbon (AC) columns on a Mitsubishi TXA-04 adsorption unit to isolate organic components. Residual inorganic species were removed from the AC columns with a 10 mL KNO_3 wash (5 mg NO_3^-/mL).

The two AC columns for each sample were combusted in separate ceramic boats, and combustion products from both were collected into the same centrifuge tube. An autosampler (Mitsubishi ASC-240S) loaded boats containing AC columns into the combustion unit (AQF-2100H), where carbons were pyrolyzed at 1000 °C for 4 min in the presence of oxygen and argon. Combustion products of halo-organic compounds (HCl, HBr, HI gases) were collected in 5 mL of 0.003% H_2O_2 and 0.01-mM phosphate sorption solution, followed by an additional 5 mL of sorption solution to rinse the gas line from the furnace to the sorption unit (AU-250). TOCl, TOBr, and TOI were quantified as Cl^-, Br^-, and I^- using the IC halide method described above.

For accurate TOX determination, each of the lines on the adsorption unit was calibrated within two months of analysis to determine the exact volume of each, which ranged from 45 to 47 mL. In addition, centrifuge tubes containing the sorption solution were weighed before and after the sorption process to gravimetrically determine the method dilution factor.

XAD Resin Extraction. We modified a method published previously[48−50] to extract and concentrate the organic material and DBPs from the reactors. Using XAD resin extraction, the recovery of organics from different water types was between 64.6% and 69.5%.[51] Briefly, 30 mL each of XAD-2 and DAX-8 resins (Sigma-Aldrich) were conditioned with successive rinses of purified water, 0.1-M HCl, and 0.1-M NaOH. Sample was acidified in 2-L aliquots with concentrated H_2SO_4 to a pH of 0−2 and poured over resin. Adsorbed analytes were eluted with 200 mL of ethyl acetate, subsequently dried with sodium sulfate, and concentrated to 2 mL under nitrogen gas. A portion of each extract was solvent exchanged in methanol prior to LC−ESI−MS analysis.

Biological and Chemical Reagents, Chinese Hamster Ovary (CHO) Cells. CHO K1 cell line AS52, clone 11−4−8 was used to assess toxicity end points.[52−54] Cells were kept at 37 °C in a mammalian cell incubator with a humidified atmosphere of 5% CO_2, and were maintained in Hams F12 medium with 5% fetal bovine serum (FBS), 1% L-glutamine, and 1% antibiotics (0.25 μg/mL amphotericin B, 100 μg/mL streptomycin sulfate, and 100 units/mL sodium penicillin G in 0.85% saline).

CHO Cell Chronic Cytotoxicity Analyses. The majority (85%) of the ethyl acetate XAD extracts were used for cytotoxic evaluation in CHO cells based on a method published previously.[55,56] Each XAD ethyl acetate extract was solvent exchanged into dimethyl sulfoxide and diluted with F12 plus FBS cell culture medium. A variety of concentration factors (CFs) were analyzed (with replicates) in a 96-well microplate. After 72 h of cell exposure to each sample, i.e., RF, PT, FB; disinfected and raw, the viable cell density was recorded and used to construct concentration−response curves. In general, triplicate experiments were conducted for each water sample, a range-finding experiment followed by two independent experiments within a focused concentration range. The number of independent replicates (independent clones) per sample concentration ranged from 4 to 24. The CF that induced 50% cell density compared to a negative control (CHO cells plus culture medium) and the cytotoxicity index values (CTI = $[LC_{50}]^{-1}[10^3]$) were determined from concentration−response curves. Both LC_{50} and CTI values were expressed in terms of the CF associated with induction of cytotoxic effects.

Statistical Analyses of Biological Data. We conducted statistical analyses on each data set. The process followed the generation of a concentration−response curve from combined replicate experiments with a test for significance using a one-way analysis of variance (ANOVA) test. If a significant F value of $P \leq 0.05$ was obtained, then we performed a Holm-Sidak multiple comparison versus the control group analysis with the power $(1-\beta) > 0.8$ at $\alpha = 0.05$ to identify the lowest concentration that induced an adverse biological impact.[57] After nonlinear regression analyses, we determined a LC_{50} value for the CHO cell cytotoxicity assay. A bootstrap statistic was conducted on the CHO cell cytotoxicity data, and a mean CTI value (±standard error [SE]) was calculated.[58,59] Using these index values, we conducted an ANOVA test to identify significant differences among specific treatment groups.

LC−QTOF MS. We performed a preliminary nontargeted DBP screening with an Agilent (Santa Clara, CA) liquid chromatograph (LC)−quadrupole-time-of-flight (QTOF) mass spectrometer (MS) with resolving power (RP) around 30 000. LC (1290 Infinity II UHPLC) and MS (6545 QTOF) parameters are provided in the Supporting Information (SI) Tables S1 and S2, respectively. Briefly, quenched water samples were diluted 10-fold, 10 μL was injected onto an Agilent InfinityLab Poroshell C18 column (2.1 mm × 150 mm

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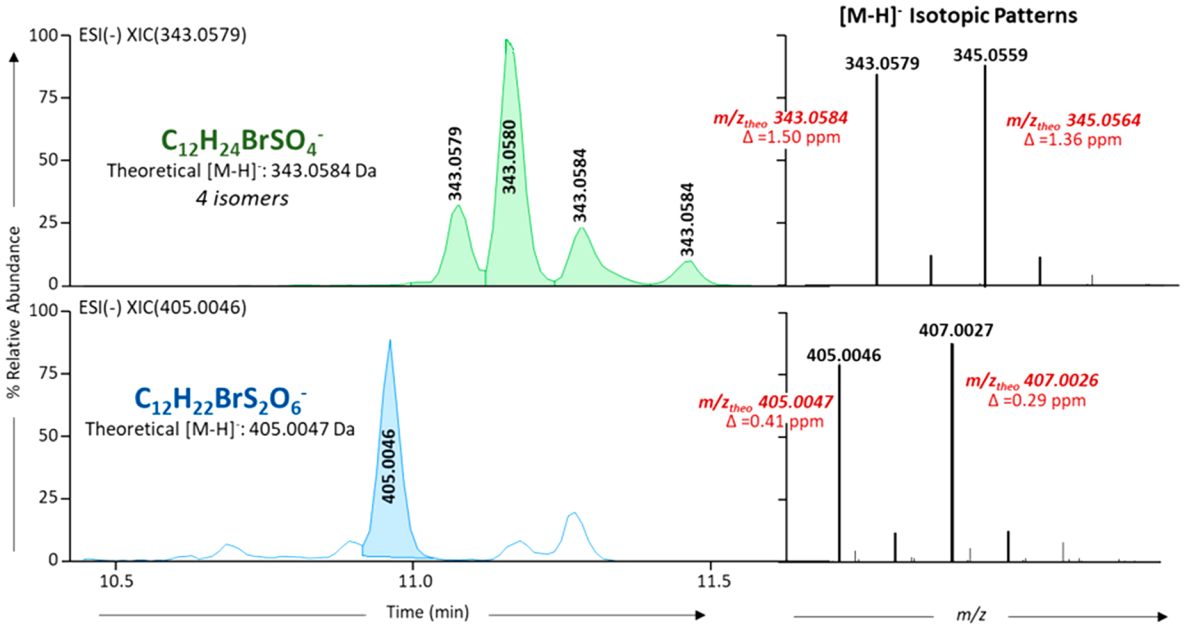

Figure 1. LC−QTOF extracted ion chromatograms (XICs) and ESI mass spectra of two brominated sulfur-containing DBPs in chlorinated RF.

× 2.7 μm), and a linear gradient elution program with water and methanol (both with 0.1% formic acid) was used that ramped from 5% to 95% methanol over 10 min, with a 2 min hold at 95% methanol (Table S1). Negative electrospray ionization (ESI−) MS and MS/MS spectra were obtained simultaneously, allowing for correlation of precursor and product ions during data processing.[60] We processed the "All Ions" data independent acquisition (DIA) data files in MassHunter Qual software using molecular feature extraction (small organic molecule) and molecular formula generation software tools.

Fourier Transform-Ion Cyclotron Resonance MS. Ultrahigh resolution (RP ≥ 1 000 000), molecular identification and structural elucidation (MS/MS, and MS^3) of DBPs was performed on a 21 T Fourier transform ion cyclotron resonance (FT−ICR) mass spectrometer with ESI− at the National High Magnetic Field Laboratory (Tallahassee, FL).[61,62] Prior to analysis, an aliquot of the XAD ethyl acetate extracts (equivalent to approximately 2 L of aqueous sample) was solvent exchanged into 200 μL of methanol, followed by a 2-fold dilution prior to FT−ICR MS analysis. Direct-infusion ESI− analysis allowed for longer acquisition and, thus, higher sensitivity MS and MS^n analysis of whole-sample components. We applied 10-min data-dependent acquisition (DDA) methods with optimization of parameters for both abundance-based and hydrogen halide neutral loss (-HCl, -HBr, -HI) to initiate MS^3 from MS/MS fragments (Tables S3 and S4).

LC−Orbitrap MS. Subsequent analyses for isomer-specific MS, MS/MS, and MS^3 data were performed using an LC-Orbitrap Fusion Tribrid MS (Thermo Scientific, Waltham, MA). LC and MS parameters for both MS scan and MS^n analyses are outlined in Tables S5−S7. Briefly, 10 μL of quenched water samples were injected onto a Waters Acquity BEH C18 column (2.1 mm × 50 mm × 1.7 μm). A gradient elution program consisted of (A) 95:5 water/acetonitrile (ACN) and (B) 95:5 ACN/water (both with 0.4-mM ammonium formate) ramped from 10% to 100% B over a 5 min period and held at 100% B for 3 min. Separate methods were used for the acquisition of high-resolution (RP 120 000 at m/z 200) MS scan data and targeted-mass MS^3 (RP 30 000); details of each are provided in Tables S6 and S7, respectively. Thermo Compound Discoverer software was used for nontargeted analytical comparisons between Orbitrap MS (120 000 resolution) data for raw, chlorinated, and chloraminated gas extraction wastewaters and bromide-spiked surfactant mixture.

RESULTS AND DISCUSSION

A variety of high-resolution MS techniques were utilized to investigate the molecular structure and composition of DBPs formed in chlorinated and chloraminated gas extraction wastewater. First, LC−QTOF−MS provided preliminary high-resolution information with DIA to quickly acquire associated accurate-mass MS and MS/MS data for quenched samples.[60] Although QTOF−MS provided sufficient mass accuracy for molecular formula assignments, fragmentation beyond MS/MS was necessary for structural elucidation. Next, we applied FT−ICR−MS to obtain high-sensitivity, ultrahigh-resolution MS^3 data of concentrated XAD resin extracts. Lastly, isomer-specific structural information on compounds in aqueous samples was provided through data-dependent MS^3 scans of selected MS/MS transitions (i.e., MS^1 and MS^2 ions fixed) with an Orbitrap Fusion Tribrid instrument.

Preliminary Identification of Two Br−S-DBPs by LC−QTOF−MS. Molecular formula results were initially filtered to locate Br-containing formulas, given that brominated DBPs would be expected during disinfection of halide-rich waters.[12,63] Four major isomers of $C_{12}H_{24}BrSO_4^-$ and one isomer of $C_{12}H_{22}BrS_2O_6^-$ were observed (Figure 1). Although previous studies have reported sulfur-containing DBPs,[4,50] this was the first identification of these brominated sulfur-containing DBPs. MS/MS data (Figures S1 and S2) provided little structural information, aside from the existence of Br and S in the structures and product ions indicative of SO_4 or SO_3.

In the undisinfected control, the presence of several isomers of $C_{12}H_{25}SO_4^-$ (m/z 265.1474) at high abundance seemed to be candidates for precursors to the $C_{12}H_{24}BrSO_4^-$ DBPs

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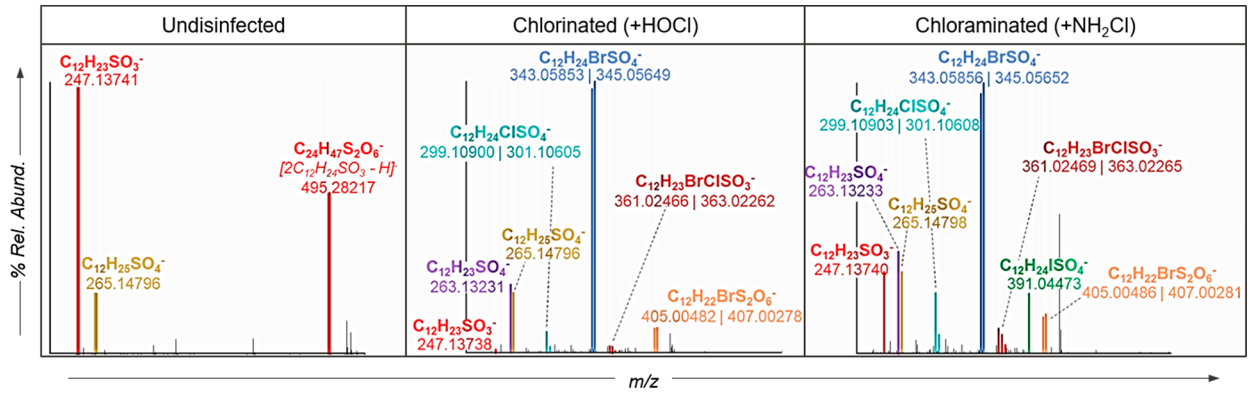

Figure 2. FT−ICR−ESI−MS scan of undisinfected (left), chlorinated (middle), and chloraminated (right) RF wastewater.

because they differed by only the addition of a bromine. This corresponds to the molecular formula of lauryl sulfate, a widely used surfactant.[19,20] However, the structure of lauryl sulfate, i.e., linear, saturated, with no rings or double bonds, is not conducive to halogenation, and because no significant decrease in $C_{12}H_{25}SO_4^-$ isomer abundance was observed after disinfection, this indicated that this compound was nonreactive with chlorine and monochloramine.

Given that high-purity surfactants are not necessary for most industrial uses, we inferred that an impurity, perhaps an unsaturated analogue, in industrial-grade lauryl sulfate could have served as the DBP precursor instead. Therefore, we obtained industrial-grade sodium lauryl sulfate and subjected it to chlorine disinfection in the presence of bromide. No significant differences in mixture components were observed for chlorinated vs undisinfected (data not shown), which further confirmed the nonreactivity of lauryl sulfate with chlorine and indicated that unsaturated analogues were not present in the industrial-grade lauryl sulfate. It was, therefore, unlikely that lauryl sulfate products were involved in the formation of these DBPs.

Direct Infusion FT−ICR−MS and MS^3. Further analysis by ESI− direct infusion FT−ICR−MS of XAD extracts enabled the identification of lower abundance chloro- and iodo- analogs of these compounds and facilitated rapid comparison of prominent spectral features between disinfected and undisinfected samples (Figure 2). MS^3 experiments provided structural elucidation and revealed that the most abundant compounds corresponded to *sulfonate* compounds, likely halohydrin sulfonates. After MS/MS loss of HX, the major MS^3 transitions (Figure 3) were variations of SO_3- and SO_2-containing fragments/losses and loss of carbon monoxide (−CO). This type of variation associated with SO_x losses and fragments is not uncommon for sulfonate compounds because gas-phase rearrangements can occur during collision-induced dissociation.[64−67]

The high sensitivity provided by FT−ICR direct infusion analysis was crucial to the isolation and MS/MS (and MS^3) elucidation of the iodohydrin sulfonate and bromochlorosulfonate. In addition to increased sensitivity, ICR−MS achieved resolving power sufficient to separate two distinct *A*+2 peaks in the molecular ion (Figures 4 and S4) resulting from the natural abundance of heavy halogens (^{81}Br, ^{37}Cl) and sulfur (^{34}S). ICR−MS achieved resolving power to separate $^{81}Br^{35}Cl$ and $^{79}Br^{37}Cl$ isotopes of the bromochlorosulfonate $[M-H]^-$, both with nominal mass of 361 Da but differing in exact mass by 900 μDa, which is less than the mass of two electrons.

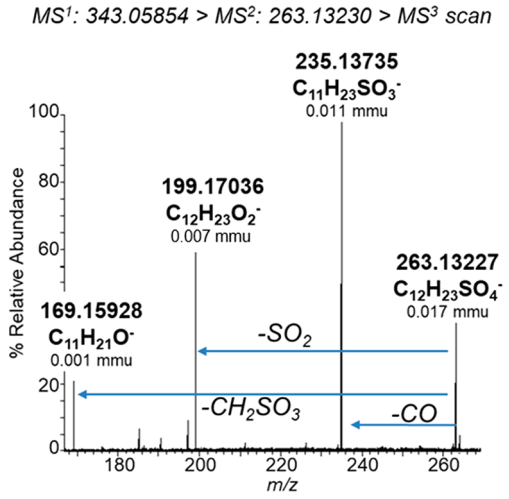

Figure 3. FT−ICR−MS^3 mass spectrum of $C_{12}H_{24}BrSO_4^-$ (m/z 343.05854) after loss of HBr (m/z 263.13230), including difference (mmu) between observed and theoretical m/z for each fragment formula.

In the undisinfected RF and PT samples, the most abundant peaks detected were m/z 247.13741 and 495.28217, corresponding to formulas of $C_{12}H_{23}SO_3^-$ and $C_{24}H_{47}S_2O_6^-$ (Figure 2). As shown in Table 1, compounds decreased substantially after both chlorine and chloramine disinfection, indicating that these compounds were likely transformed into the observed halohydrin- and dihalo-sulfonate DBPs.

DBP Precursor Confirmation. On the basis of observed FT−ICR−MS results, it became apparent that the likely precursor was olefin sulfonate, another commonly used surfactant in oil and gas extraction.[20] Figure S5 shows the extracted ion chromatograms of olefin sulfonate precursor and DBP transformation products formed during disinfection. The 12-carbon variation of these surfactants (C_{12}-olefin sulfonate) agreed with the formula derived experimentally for the unknown compounds in the undisinfected RF and PT samples with high mass accuracy, which differed by only 70 μDa. At high concentrations, proton dimers ($[2M-H]^-$) of sulfonates can form in-source during electrospray ionization.[67] This phenomenon is responsible for the presence of the $C_{24}H_{47}S_2O_6^-$ (m/z 495.28217) spectral feature observed in the undisinfected samples.

Many commercial olefin sulfonate products also contain hydroxysulfonate compounds, formed as byproducts during olefin sulfonate production.[68] These compounds are functional

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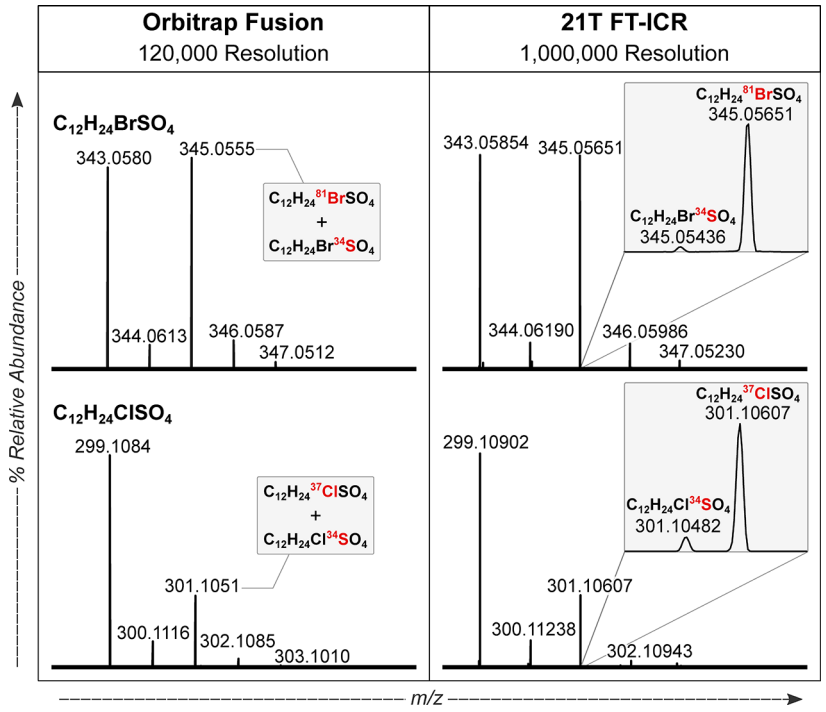

Figure 4. Mass spectra of molecular ion ($[M-H]^-$) for the bromo- and chloro-hydrin sulfonate byproducts obtained from different high-resolution MS systems. Note: Insets depict a zoomed-in view of the $A+2$ m/z to show the resolved peaks pertaining to the heavy halogen vs sulfur atoms.

Table 1. Precursor Compounds in Raw Feed Samples and C_{12} Olefin Sulfonate "Standard"[a,b]

compound-identifying ions	isomer number	RT (min)	standard % consumed by HOCl	RF sample % consumed by HOCl	RF sample % consumed by NH_2Cl
base peak $C_{12}H_{23}SO_3^-$	1	3.38	94	100	99
$[M-H]^-$247.1373 ± 0.0001 m/z	2	3.44	100	100	100
	3	3.51	96	90	94
secondary ion $C_{24}H_{47}S_2O_6^-$	4	3.58	100	100	100
$[2M-H]^-$495.2820 ± 0.0003m/z	5	3.62	90	100	100
	6	3.69	21	100	97
	1	0.58	–	100	100
base peak $C_{12}H_{22}S_2O_6^{2-}$	2	0.62	81	100	100
$[M-2H]^{2-}$163.0434 ± 0.0001 m/z	3	0.76	16	100	100
	4	0.88	31	100	100
secondary ion $C_{12}H_{23}S_2O_6^-$	5	0.97	−140[c]	100	100
$[M-H]^-$327.0942 ± 0.0001 m/z	6	1.05	46	100	100
	7	1.29	17	100	100
	8	1.48	21	100	100
	1	3.11	–	100	100
base peak $C_{12}H_{21}SO_3^-$	2	3.27	94	100	100
$[M-H]^-$245.1217 ± 0.0002 m/z	3	3.54	76	100	100
	4	3.65	32	100	100

[a]Data from Orbitrap LC−ESI−MS analysis. [b]% consumption calculated using base peak area. [c]Negative % consumption for a single isomer of $C_{12}H_{22}S_2O_6^{2-}$, as this specific isomer was *formed* in the standard, while other isomers were consumed.

isomers of alkylsulfate compounds, having the same mass and formula but with a sulfonate (SO_3) and a hydroxy (OH) group in lieu of sulfate (SO_4). The presence of m/z 265.14796 ($C_{12}H_{25}SO_4^-$) in both undisinfected and chlorinated/chloraminated samples was not lauryl sulfate but several isomers of hydroxydodecanesulfonate.

For further high-resolution-MS, MS/MS, and MS^3 analyses with isomeric information, an LC-Orbitrap Fusion MS was used. Several isomers of dodecene sulfonate (C_{12} olefin sulfonate) found in the undisinfected samples were hypothesized to be the likely precursors to the observed halohydrin sulfonate byproducts. Figure S3 shows the formation of halohydrins after disinfection, where the suspected precursor isomers were removed almost entirely during disinfection.

For confirmation, we obtained a surfactant mixture of sodium dodecene sulfonate (20−30%) and hydroxydodecylsulfonate (20−30%). This commercial product was diluted (~50 ppm) in pH 7.2 phosphate-buffered purified water and

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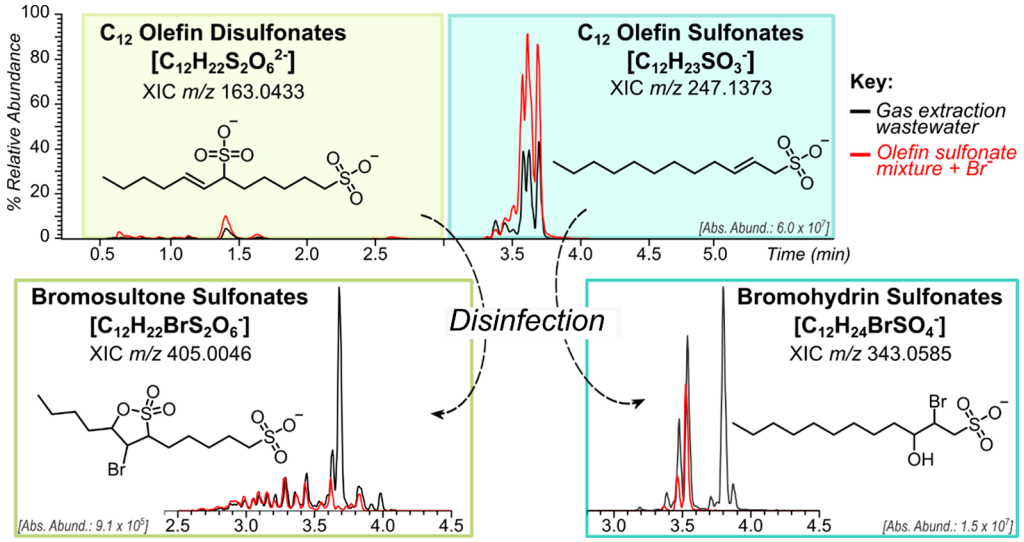

Figure 5. LC−Orbitrap extracted ion chromatogram (XIC) comparisons of DBPs and their suspected precursors in gas extraction wastewater to the commercial olefin sulfonate surfactant mixture. Top: olefin disulfonates (XIC m/z 163.0433) and sulfonates (m/z 247.1374) in undisinfected wastewater and surfactant mixture; Bottom: major chlorination disinfection byproducts, bromosultone sulfonates (m/z 405.0046), and bromohydrin sulfonates (m/z 343.0585). Note: Structures shown are representative.

subjected to 18 h of chlorination (100 ppm as Cl_2) in the presence of bromide (10 ppm). We identified three suspected DBP-precursors based on percent consumed (≥50%) during disinfection in both RF and bromide-containing surfactant mixture samples (Table 1).

Two of these compounds, $C_{12}H_{23}SO_3^-$ (olefin sulfonate) and $C_{12}H_{21}SO_3^-$ (diolefin sulfonate impurity) were suspected to be precursors to the identified singly sulfonated DBPs. The major component of the RF and commercial surfactants was olefin sulfonate, and thus it is not surprising that the majority of the singly sulfonated DBPs derived from the various isomers of $C_{12}H_{23}SO_3^-$. As shown in Figure 5, this proof-of-concept chlorination of olefin sulfonate "standard" led to the formation of three of the same bromohydrin sulfonate isomers identified in the gas extraction wastewater chlorination/chloramination reactions.

Collectively, a single compound, $C_{12}H_{23}S_2O_6^-$, was the sole precursor to all disulfur-containing DBPs detected, and it generated many of the disulfur containing isomers shown in Figure 5. As demonstrated in Figure S6, these doubly charged $[M-2H]^{2-}$ ions are unmistakable, given that their isotopic pattern is the same as the singly charged but with half the m/z difference between isotopes, e.g., 163.0435/163.5439 [^{13}C]/164.0406[^{34}S], varying by approximately half of one Dalton between each isotope. This precursor was also not identified in the processing of the LC−QTOF−MS data because our data processing workflow did not incorporate doubly charged species identification, and the singly charged species was low in abundance. The S_2O_6 precursor was also not detected by FT−ICR−MS because the organic XAD extract did not recover the doubly charged precursor.

C_{12}-Olefin Sulfonate-Derived DBP Speciation. Thousands of features were identified in the Orbitrap−MS spectra for raw, chlorinated, and chloraminated gas wastewaters and the bromide-spiked surfactant mixture. Results were filtered using the Thermo Compound Discoverer software to include only those with assigned formulas containing "C_{12}", "S", and "O". With these three collective filters, 92 molecular formulas were identified for C_{12} sulfur oxide-containing components. From these, 43 formulas were determined to be DBPs, based on at least a doubling in signal from undisinfected to disinfected, indicating significant formation during disinfection, and a minimum extracted ion area of 5000. Almost all of these had multiple isomers, with as many as 24 visible isomers. Tentatively identified compound details are provided in Table S8, including the number of isomers identified for each molecular formula in each sample. A total of 330 C_{12}-sulfonate DBPs were tentatively identified in chlorinated RF, 289 in chloraminated RF, and 158 in the chlorinated olefin sulfonate mixture with bromide. Many DBPs shared the same isomeric distribution between samples, but others, e.g., $C_{12}H_{24}ClSO_4^-$, favored the formation of one or two specific isomers via chloramination that were at much lower abundance in chlorinated samples.

Assuming similar ionization efficiency across sulfonated compounds in this study, the halohydrin sulfonates ($C_{12}H_{24}XSO_4^-$) were by far the most abundantly formed DBPs in both chlorinated and chloraminated waters. This finding is similar to that of Gong et al.'s chlorination of linear alkylbenzenesulfonates (LAS) in fresh and saline waters, where dihalo-dihydroxy-alkylbenzenesulfonates were the dominant DBPs formed.[43] Although chlor(am)inated RF formed mostly bromohydrin sulfonates, the chlorinated Br-spiked surfactant mixture favored the formation of one chlorohydrin isomer over the other chloro- and bromo-hydrins. This is likely due to a difference between the surfactant-to-Br^- ratios of the gas extraction wastewater samples vs the controlled reactions with the surfactant mixture, or due to failure to meet the chlorine demand in this proof-of-concept chlorination reaction setup for the surfactant mixture.

There was a vast difference observed for chlorohydrin byproducts between disinfection types that was not observed for the analogous bromo- and iodohydrin DBPs. This is because the elevated levels of bromide and iodide in the gas extraction wastewaters drive bromo- and iodo-DBP formation much more so than the disinfectant type; however, the chlorine in chloro-DBPs is contributed by the chlorine or chloramine disinfectant itself and is not dependent on chloride

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concentration.[12,13,63] The difference in reactivity of chlorine vs chloramine was demonstrated most by the chlorohydrin (and other chloro-DBP) formation. In general, chloramine-disinfection favored the production of a few specific isomers, whereas chlorination produced a wider range of isomers, all at roughly equal abundance. For example, chloramination favored a single chlorohydrin species (3.8 min) over the others, which was 100-fold more abundant than in the chlorinated water, whereas chlorine had a more equal distribution to form many other isomers (Figures S3 and S5).

Like the gas extraction wastewater, the chlorinated Br-spiked surfactant mixture yielded many chlorohydrin isomers, but favored one isomer, which was different (3.5 min) than that favored by chloramine disinfection of RF. Although not as extreme as chlorohydrin, the dominant bromohydrin species did differ slightly between the two disinfectants. There was also lower formation of the iodohydrin from chlorine than chloramine, which was expected due to the tendency of chlorine to form iodate rather than organic iodo-DBPs from iodide.

Examination of the apparent "disulfonate" ($C_{12}H_{22}XS_2O_6^-$) byproducts revealed they were no longer disulfonates; the characteristic double charge was no longer present post-disinfection. Unlike the olefin disulfonate precursors, the two-sulfur-containing halo-DBPs were observed in the organic extracts analyzed by direct infusion FT−ICR, meaning they were effectively extracted from the aqueous phase, which is unlikely if both sulfonate groups were left intact. In addition, it is uncommon to observe DBPs that have the same number of double bond equivalents (DBE) as their precursor compound because double bonds are usually eliminated in the halogen addition reactions of olefins.[69,70] Both the precursor ($C_{12}H_{23}S_2O_6^-$) and the halogenated S_2O_6 DBPs (e.g., $C_{12}H_{22}BrS_2O_6^-$) ions had the same DBE of 1.5 (1.0 for the neutral molecules), which indicated that the halogenation of double bonds initiated a reaction to form cyclic sulfur groups (sultones).

Various isomers were observed, likely due to differences in sultone ring size as a result of varying double bond placement in olefin disulfonate precursor isomers (Figure S6).[71] The hypothesized sultone formation was further supported by the large difference in retention time and chromatographic peak shape between the precursor (early eluting with tailing) and Br−S_2O_6 byproducts (later-eluting, symmetric peaks). Along with cyclic DBPs, lower-abundance di-S DBPs, halohydrin disulfonates ($C_{12}H_{24}XS_2O_7^-$; Table S8), were also tentatively identified in the aqueous chlor(am)inated gas extraction wastewater samples. As shown in Figure S6, these byproducts were early eluting, with broad, tailing chromatography, and possessed a prominent $[M-2H]^{2-}$, similar to the precursor compound.

Other lower-abundance, halogenated DBP series were identified in both the chlorinated/chloraminated gas extraction wastewater samples and the chlorinated Br-spiked surfactant mixture (Table S8, Figure S5), including mono- and dihalogenated sulfonates formed from the same suspected olefin sulfonate precursors. A variety of DBPs were formed that could have resulted from both the olefin sulfonate or from impurities, such as diolefin sulfonates, resulting in multiply unsaturated and/or oxidized byproducts. For example, DBPs of the generic formula $C_{12}H_{23-n}X_nSO_4^-$, including the mono-chlorinated species, $C_{12}H_{22}ClSO_4^-$, have the same DBE as olefin sulfonate (1.5), indicating either halohydrination of diolefin sulfonate (DBE 2.5) to form halohydroxy-dodecene sulfonates, or the formation of halo-carbonyl sulfonates from olefin sulfonate precursors. Both olefin and diolefin sulfonates were completely consumed in chlor(am)ination of RF (Table 1), indicating that both species were likely precursors, with olefin sulfonate having a larger contribution than diolefin sulfonate. The formation of dihalogenated variations of this same DBP class (e.g., $C_{12}H_{21}Cl_2SO_4^-$) supports the idea of ketone and aldehyde formation because it is common for multiple α-substitutions to occur, resulting in multiply halogenated carbonyl compounds.[69]

In addition to halogenated DBPs, many nonhalogenated products were observed postdisinfection, including higher degrees of unsaturation, i.e., more double bonds, as well as mono- and multihydroxy- and carbonyl-sulfonates (Table S8). In general, chlorination and chloramination both resulted in these byproducts, but they tended to vary in which major isomers formed. Nitrogen-containing DBPs (both halogenated and nonhalogenated) were also formed, but only in the chloraminated samples. N-DBPs with DBE of 2.5, e.g., $C_{12}H_{22}NSO_3^-$ and $C_{12}H_{22}NSO_4^-$, were likely nitriles or heterorings containing a double bond, whereas those with DBE of 1.5 were likely amides formed through the hydrolysis of nitrile intermediates in disinfected water.[72,73]

Importance of High-Resolution MS. High-resolution MS was crucial to the identification of DBPs in this mixture, given its extreme complexity. Figure S7 shows a single LC−MS spectrum from the chlorinated RF sample that alone has several examples where low resolution may have led to misidentification of components as halo-DBPs from the appearance of characteristic halogen isotope patterns. With the high level of coelution that is present in these complex mixtures, in the absence of high-resolution, accurate mass capabilities, m/z series of $A/A+2/A+4/A+6$, like that of 313/315/317/319 shown in Figure S7 could be mistaken for a tribromo-compound based on its pattern. However, enhanced mass resolution revealed that, in fact, only two of these peaks belonged to the same compound (315/317), which contained only one bromine. Similarly, the ions at m/z 261/263/265 could have been indicative of a dibrominated compound, when in fact, each m/z belonged to a different compound.

There are thousands of chemicals used in oil/gas extraction, and these vary from well to well based on geological conditions.[19] Complexity of mixtures and absence of proprietary chemical details make the identification of additives, much less DBPs resulting from these additives, extremely difficult. In the absence of information and high-quality standards, high-resolution MS (with MS^n capability) is a crucial tool in the generic structural elucidation of unknowns. Although specific isomers are unknown, new classes of DBPs can still be identified through high-resolution accurate mass analyses.

Cytotoxicity and Total Organic Halogen (TOX). Mammalian cell cytotoxicity of both RF and PT gas wastewaters was greatly enhanced by chlorine and chloramine disinfection. Disinfected samples required dilution beyond their initial concentration (concentration factor [CF] < 1) for determination of the cytotoxic potency (Figure 6, Table S9). Chlorinated and chloraminated wastewaters were 14- and 26-fold, respectively, more toxic than undisinfected controls for both PT and RF samples. Employing an ANOVA all-pairwise test of the CTI values for each of the RF and PT wastewaters and field blanks, the descending rank order cytotoxicity of the

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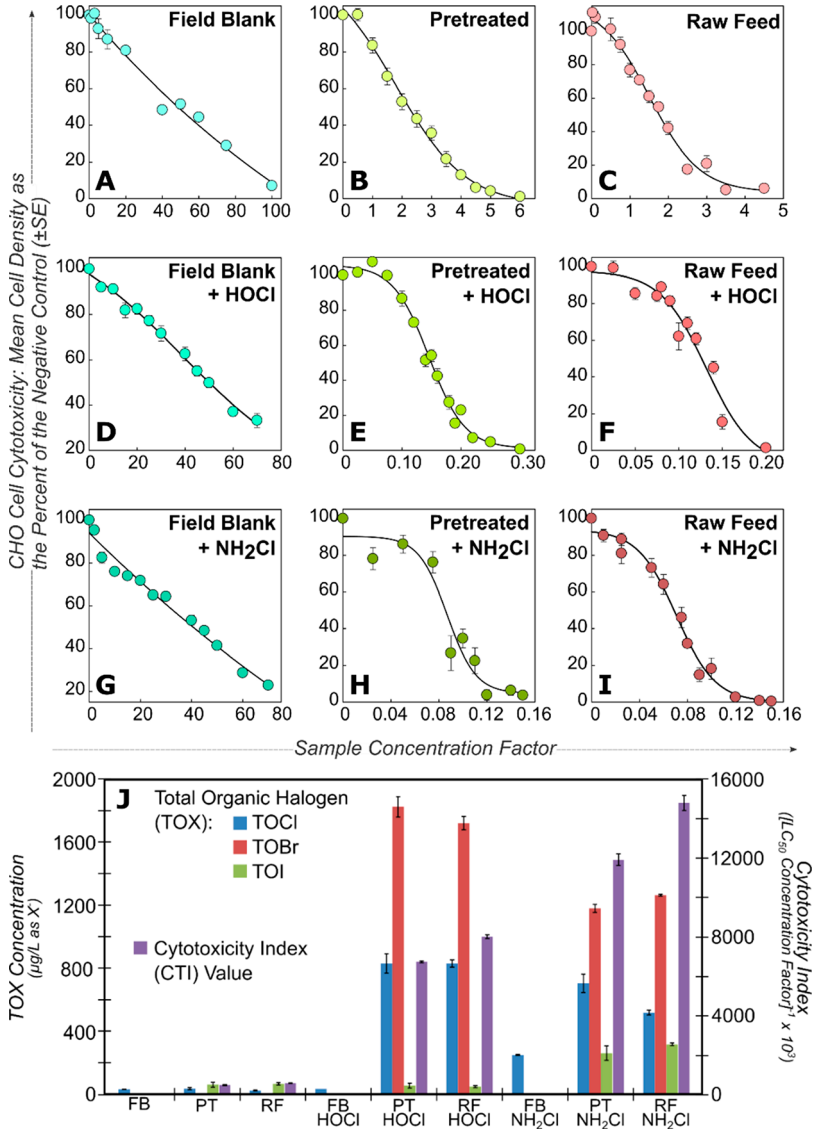

Figure 6. A–I: Concentration–response curves for mammalian cell cytotoxicity of undisinfected (A, B, C), chlorinated (HOCl; D, E, F), and chloraminated (NH_2Cl; G, H, I) field blank (A, D, G), pretreated (B, E, H), and raw feed (C, F, I) samples. J: Total organic halogen concentrations (left *y*-axis; ± SE [n = 2]) and cytotoxicity index values (right *y*-axis) for field blank (FB), pretreated (PT), and raw feed (RF) undisinfected, chlorinated (HOCl), and chloraminated (NH_2Cl) reactors. Notes: Concentration factors incorporate the 10-fold dilution performed and, thus, represent concentration factor of the *undiluted* sample. Concentration factors <1 indicate that samples required dilution, rather than further concentration, to induce quantifiable cytotoxic effects.

water samples was NH_2Cl RF > NH_2Cl PT > HOCl RF > HOCl PT > RF > PT > NH_2Cl FB ≈ FB ≈ HOCl FB (the > symbol indicated a significant difference, whereas the ≈ indicated no significant difference between adjacent water samples [$F_{9,90}$ = 1217; $P \leq 0.001$]). A Pearson Product Moment Correlation analysis of cytotoxicity and TOX (r = 0.78; $P \leq 0.02$), TOCl (r = 0.81; $P \leq 0.009$), TOBr (r = 0.88; $P \leq 0.002$), and TOI (r = 0.82; $P \leq 0.007$) revealed that the CTI and these TOX measurements were significantly correlated (Table S10). The previously mentioned study by Gong et al. that evaluated LAS as precursors to DBPs during chlorination in fresh and saline waters reported similar results: disinfected LAS-containing waters were significantly more toxic in marine polychaete embryo assays than raw, undisinfected waters, with the bromide-rich, chlorinated saline water being the highest in TOBr and the most toxic.[43]

Although chloraminated PT and RF wastewaters exhibited lower formation in overall total organic halogen (TOX), chloraminated waters were more cytotoxic than chlorinated waters. Statistical analysis of only the disinfected samples revealed an explanation (Table S11). In the disinfected samples, CTI was highly and significantly correlated only with TOI (r = 0.913; $P \leq 0.011$), and TOX was highly and significantly correlated with TOCl (r = 0.985; $P \leq 0.001$) and TOBr (r = 0.99; $P \leq 0.002$) but was not significantly correlated with TOI (r = 0.404; p = 0.427). Therefore, although CTI overall was significantly correlated with treatment (and TOX), the difference between treated samples was correlated with TOI. This enhanced toxicity is likely due to the formation during chloramination of iodinated and nitrogenous DBPs, which are more cytotoxic than non-iodinated or non-nitrogenous DBPs.[3,10,56,74−77]

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Assuming the various compounds ionized similarly, we used the fraction of total ion abundance to estimate the concentration of bromohydrin sulfonate DBPs as a function of the 50-ppm "standard" olefin sulfonate concentration. From the contribution of Br^-, we estimated that they constituted approximately 10% of the quantified total organic bromine (TOBr) in the chlor(am)inated gas extraction wastewaters. Nothing is known about the toxicity of these newly identified sulfonate DBPs, and it is unclear whether their formation contributed significantly to the observed increase in toxicity with disinfection. It is possible that the observed toxicity could be due to the formation of other DBPs not identified in this study.

Further Environmental Implications. The surfactants discussed here are utilized by far more industries, e.g., personal care products and detergents, than just oil and gas extraction, meaning that these organic DBP precursors could enter drinking water sources through a variety of wastewater introduction pathways, including municipal wastewater,[41,42,44,78] and advanced oxidative treatment of wastewaters may generate toxic byproducts.[79] It may be important to continue to study these surfactants, especially how they degrade/transform in natural waters during drinking water treatment. Although it is possible that these surfactants could biodegrade[44,68,80] or be outcompeted by NOM to form DBPs in natural waters, it is also likely that their high concentrations could result in the formation of the newly identified DBPs reported here. Given the impact of bromide and iodide levels on the speciation of DBPs, and that OGW-impacted waters exhibit the combination of uniquely high halide levels and high surfactant loads, the ultimate toxicological impact of these DBPs for impacted water sources should be a subject of future study. Unfortunately, no standards were available for identity-confirmation of the DBPs reported in this study. If standards were synthesized or commercially available, then individual DBPs could be further assessed for toxicity and formation potential.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.0c01997.

Additional tables and figures pertaining to instrumental parameters, mass spectral and chromatographic data, compound identification, biological analyses, and total organic halogen analyses (PDF)

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Notes

The authors declare no competing financial interest.

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