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Article

Chemical Analysis of Wastewater from Unconventional Drilling Operations

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Abstract: Trillions of liters of wastewater from oil and gas extraction are generated annually in the US. The contribution from unconventional drilling operations (UDO), such as hydraulic fracturing, to this volume will likely continue to increase in the foreseeable future. The chemical content of wastewater from UDO varies with region, operator, and elapsed time after production begins. Detailed chemical analyses may be used to determine its content, select appropriate treatment options, and identify its source in cases of environmental contamination. In this study, one wastewater sample each from direct effluent, a disposal well, and a waste pit, all in West Texas, were analyzed by gas chromatography-mass spectrometry, inductively coupled plasma-optical emission spectroscopy, high performance liquid chromatography-high resolution mass spectrometry, high performance ion chromatography, total organic carbon/total nitrogen analysis, and pH and conductivity analysis. Several compounds known to compose hydraulic fracturing fluid were detected among two of the wastewater samples including 2-butoxyethanol, alkyl amines, and cocamide

diethanolamines, toluene, and *o*-xylene. Due both to its quantity and quality, proper management of wastewater from UDO will be essential.

Keywords: wastewater; hydraulic fracturing; analytical chemistry; chromatography; mass spectrometry; total organic carbon; unconventional drilling

1. Introduction

Public concern about the potential impacts of hydraulic fracturing (HF) is often focused more on the fluids injected into the ground than the fate of the large volume of resulting wastewater, even though the latter may be more important in preventing environmental contamination [1]. Wastewater from oil and gas production consists of formation water as well as fluids injected into the well for various purposes. When HF is used, particularly large volumes of wastewater are generated due to the injection of up to more than 10 million liters of HF fluid into the well for stimulation [2]. After HF is completed, the wastewater generated initially reflects the chemical characteristics of HF fluid, having relatively high total organic carbon (TOC) content without a concomitantly high conductivity. Later, as the well begins to produce hydrocarbons, the wastewater bares a closer resemblance to the formation water, having relatively low TOC content and high conductivity [3], though it may still have a moderate TOC content when it is in contact with oil.

Clark and Veil [4] published one of the most comprehensive studies estimating the volume of wastewater generated annually in the US using data from 2007. They estimated that about 3.3 trillion liters of wastewater from both conventional and unconventional drilling operations are generated annually in the US; the present value is likely higher. The potential environmental impact of such a large volume of waste, if not properly handled, cannot be overstated, though this is not a new problem in many areas across the country. Options for handling wastewater include disposal and treatment for reuse or other industrial applications. Disposal of wastewater in disposal wells (DWs) can have high associated transportation costs, may induce seismic activity [5], can contaminate nearby aquifers [6], and is not always compatible with the regional geology. In the US, wastewater management practices vary regionally depending on local resources. For example, in Pennsylvania, a state where only a few DWs can provide satisfactory containment, most of the wastewater generated from HF is reused as HF fluid [7]. In contrast, in the Barnett Shale of North Texas, the wastewater is mostly disposed of in DWs [8]. In general, the use of DWs is often the least expensive wastewater management option. The cost of treatment as well as the optimum management strategy is governed of course by the wastewater composition [9].

High total dissolved solids, radioactivity, and the proprietary nature of fracturing fluids present challenges in the treatment and reuse of wastewater. The chemical content of the waste is highly variable and depends both on geological factors and the composition of the HF fluid used, which varies regionally and across operators. Analytical methods to assess the composition/quality of wastewater can allow the best management practices and the selection/development of best treatment methods.

Characterization of wastewater from HF operations has been reported in the literature in various degrees of detail [3,10–13]. Orem *et al.* [3] characterized produced water and formation water samples

from various shale and coalbed methane plays using TOC analysis, high-performance liquid chromatography (HPLC) for volatile fatty acids, and gas chromatography-mass spectrometry (GC-MS) for extractable hydrocarbons. Maguire-Boyle and Barron [10] analyzed produced water from the Marcellus (PA), Eagle Ford (TX), and Barnett (NM) shale plays using TOC analysis, GC-MS for organic acids and volatile organic compounds, inductively coupled plasma-optical emission spectroscopy (ICP-OES) for metals, and conductivity and pH analysis. Thurman *et al.* [11] analyzed ethoxylated surfactants in flowback water and produced water using liquid chromatography-quadrupole-time-of-flight-mass spectrometry (LC-QTOF-MS). Lester *et al.*, characterized a single composite HF flowback water sample from the Denver-Julesburg basin of Colorado using a suite of analytical techniques including TOC analysis, ion chromatography, inductively coupled plasma-mass spectrometry (ICP-MS), GC-MS, LC-QTOF-MS and spectrofluorometry [13].

We aimed in this pilot study to develop and apply a broad suite of modern analytical techniques to characterize selected wastewater samples from HF operations in West Texas, a region in which there exists little to no literature of detailed chemical analyses of wastewater from UDO, as thoroughly as possible. Three wastewater samples, obtained from various sources, were analyzed for volatile and semi-volatile compounds with GC-MS, for metals with ICP-OES, for non-volatile organic compounds with high performance liquid chromatography–high resolution mass spectrometry (HPLC-HRMS), and high performance ion chromatography (IC). Nonspecific measurements included TOC/total nitrogen (TN) content, conductivity, and pH. Several compounds identified among the wastewater samples are known common components of HF fluid, including 2-butoxyethanol, cocamide diethanolamines, and *o*-xylene [14].

2. Materials and Methods

2.1. Sampling

Samples were collected in amber high-density polyethylene bottles with limited headspace, stored and shipped to the University of Texas at Arlington on ice, and refrigerated in the laboratory at 4 °C prior to analyses. Sample 1 was taken directly from effluent of an HF well in Odessa, Texas. Sample 2 was obtained from a DW near Reagan County, Texas, taken about 3 months after disposal began in the well. Sample 3 was taken from a waste pit in Nolan County, Texas, within weeks of the pit being filled. To the best of our knowledge, Samples 2 and 3 only contain wastewater from wells that had been stimulated by HF.

2.2. Reagents and Standards

Ammonium acetate (99.999%) (SKU No. 372331) and HPLC grade ethyl acetate (SKU No. 34858) were purchased from Sigma-Aldrich Corp. (St. Louis, MO, USA) LC-MS grade water (cat. No. LC-365), isopropanol (cat. No. 9827), and acetonitrile (cat. No. zh30000LCMS) were purchased from Honeywell International, Inc. (Morristown, NJ, USA), Avantor Performance Materials, and PHARMCO-AAPER, respectively. Deionized (DI) water was supplied by a model 1102D High-Purity deionized water system using a continuously recirculating loop (Aries Filterworks, West Berlin, NJ, USA). Nitric acid (OmniTrace®) (cat. No. NX0407-2) was purchased from EMD Millipore (Darmstadt, Germany). The

metals standard solution containing all metals with the exceptions of Sr and Zr for ICP-OES (cat. No. QCS-26) was purchased from High-Purity Standards, Inc. (Charleston, SC, USA). The Sr and Zr standard solution used for ICP-OES consisted of strontium chloride hexahydrate (cat. No. AC31508-1000) and zirconium (IV) oxychloride octahydrate (cat. No. AC20837), purchased from Thermo Fisher Scientific, Inc. (Waltham, MA, USA) in 2% nitric acid in DI water. The following chemicals used to prepare the standard solution for IC: potassium nitrate (cat. No. A14527) from Alfa Aesar; potassium perchlorate (cat. No. 7053) and sodium chloride (cat. No. 7581-06) from Mallinckrodt Pharmaceuticals; potassium sulfate (cat. No. P-305) and sodium acetate (cat. No. S-210) from Fisher Scientific Co. (Hampton, NH, USA); and potassium formate (cat. No. S-5044) from Merck and Co., Inc. (Kenilworth, NJ, USA).

2.3. Gas Chromatography-Mass Spectrometry

The GC-MS analysis protocol was adapted from Fontenot *et al.* [15]. A GCMS-TQ8030 gas chromatograph-mass spectrometer equipped with an SHRXI-5MS (30 m × 0.25 mm × 0.25 μm) column and an AOC-20i/s autoinjector/autosampler (all from Shimadzu Scientific Instruments, Inc., Columbia MD, USA; hereinafter SSI) was used to identify volatile and semi-volatile organic compounds. Liquid-liquid extraction was used to separate organics from the samples. Five milliliters of sample (or DI water blank) were vortexed for 30 s with 2 mL ethyl acetate. Sample 1 was available in limited volume and was diluted 10x before extraction. Operational details: Injection volume, 2 μL; injection port temperature, 300 °C; split ratio, 20:1; carrier gas, helium; linear velocity, 35 cm/s; ionization mode, electron ionization; transfer line temperature, 260 °C; ion source, 260 °C. The oven temperature ramp program was 0 →3→4.5→11→13 min; 40→40→70→330→330 °C. Table 1 displays the MS program used for the GC-MS analysis. Based on initial studies of ingredients used in hydraulic fracturing fluid and previous experience, several compounds were thought as likely to be present *a priori*, and the selected ion monitoring mode was used for their detection mode (Table 2). The scan mode was used for the detection of unexpected compounds and the impartation of structural information.

Table 1. Mass spectrometer (MS) program for gas chromatography-mass spectrometry (GC-MS).

Start Time (min)	End Time (min)	Acqu. Mode	Event Time (s)	m/z
0.60	2.25	Scan	0.20	40.00–100.00
0.60	2.25	SIM	0.10	31.10, 55.10, 29.10
2.88	5.78	Scan	0.20	40.00–200.00
2.88	5.78	SIM	0.10	78.10, 56.10, 31.10, 45.10, 91.10, 44.10
5.78	6.35	Scan	0.20	40.00–200.00
5.78	6.35	SIM	0.10	91.10, 57.10, 29.10, 105.10, 44.00
6.35	7.30	Scan	0.20	40.00–250.00
6.35	7.30	SIM	0.10	45.10, 57.10, 59.10, 68.10, 73.00, 91.10, 105.15, 103.00
7.30	8.50	Scan	0.20	40.00–300.00
7.30	8.50	SIM	0.10	128.10, 142.15
8.50	11.00	Scan	0.20	40.00–400.00
8.50	11.00	SIM	0.10	45.10, 144.15, 213.10
11.00	13.00	Scan	0.20	40.00–400.00

Table 2. Gas chromatography-mass spectrometry (GC-MS) targeted compounds with associated CAS number and selected-ion monitoring (SIM) ion.

Compound	CAS Number	SIM Ion	Compound	CAS Number	SIM Ion
Acetaldehyde	75-07-0	29.10	Mesitylene	108-67-8	105.15
Acetophenone	98-86-2	105.10	Methanol	67-56-1	31.10, 29.10
Benzene	71-43-2	78.10	1-Methylnaphthalene	90-12-0	142.15
Benzyl Chloride	100-44-7	91.10	2-Methylnaphthalene	91-57-6	142.15
Bisphenol A	80-05-7	213.10	Naphthalene	91-20-3	128.10
2-Butoxyethanol	111-76-2	57.10	1-Naphthol	90-15-3	144.15
n-Butanol	71-63-3	56.10	2-Naphthol	135-19-3	144.15
Cumene	98-82-8	105.10	1,2-Propanediol	57-55-6	45.10
Dimethylformamide	68-12-2	44.10	n-Propanol	71-23-8	31.10
d-Limonene	5989-27-5	68.10	2-Propyn-1-ol	107-19-7	55.10
Ethanol	64-17-5	31.10, 29.10	Toluene	108-88-3	91.10
Ethylbenzene	100-41-4	91.10	1,2,4-Trimethyl Benzene	95-63-6	105.10
Ethylene Glycol	107-21-1	31.10	*o*-Xylene	95-47-6	91.10
2-Ethylhexanol	104-76-7	57.10	*m*-Xylene	108-38-3	91.10
Glutaraldehyde	111-30-8	44.10	*p*-Xylene	106-42-3	91.10
Isopropanol	67-63-0	45.10, 29.10			

The data were analyzed with GCMSsolutions (ver. 4.20, SSI). Mass spectra were generated by averaging the chromatographic peaks from the inflection points and subtracting an average mass spectrum outside of the peak. Responses at any other *m/z* value where the maximum intensity did not temporally coincide with the chromatographic peak under investigation were removed. A mass spectral similarity index value (0–100) was software generated based on comparison with a library of mass spectra (National Institute of Standards and Technology, ver. 2011, Washington, DC, USA). Except for two bisphenol F isomers (similarity index 85), all other reported compounds had a similarity index of ≥90. In addition, the retention times of toluene and *o*-xylene were known. Compounds for which we could not decipher the chemical formulas or functional groups are not reported.

2.4. Inductively Coupled Plasma-Optical Emission Spectroscopy

An ICPE-9000 (SSI) equipped with a CETAC ASX-520 autosampler (Teledyne Technologies, Inc., Omaha, NE, USA), a mini-torch nebulizer, and argon plasma was used to measure concentrations of various metals. Samples were diluted 10× (Sample 2) or 20× (Samples 1 and 3) with 2% by volume ICP-grade aqueous nitric acid solution. Standard addition was performed for quantitation with 0, 100, and 200 ppb spiked concentrations. Blanks consisted of 2% nitric acid in DI water treated in the same manner. The determined blank concentrations, which were all below 10% of the sample concentrations, were subtracted from that of the sample concentrations.

2.5. High Performance Liquid Chromatography-High Resolution Mass Spectrometry

An LCMS-IT-TOF (SSI) liquid chromatograph-mass spectrometer equipped with a 100 mm × 2.1 mm Ultra IBD 3-µm column (Restek Corp., Bellefonte, PA, USA) was used for the analysis of non-volatile

organic compounds. Only Sample 3 was available in sufficient quantity to permit the workup followed by this analysis. Solid phase extraction (SPE) was used to reduce salts as well as to remove insoluble material. Six milliliters of acetonitrile were loaded into a Supelclean LC-18 SPE tube (3 mL, 500 mg) from Supelco Analytical (Bellefonte, PA, USA) for conditioning followed by 6 mL of water-acetonitrile (99:1 v/v). Next, 12 mL of unfiltered sample were loaded into the cartridge followed by 12 mL of water-acetonitrile (99:1 v/v). Finally, the cartridge was eluted by 6 mL of acetonitrile followed by 6 mL of isopropanol; eluent fractions were collected and analyzed separately after filtration with 0.2 μm syringe filters (all syringe filters PTFE, Luer-lock, from VWR International, Radnor, PA, USA) and diluted with acetonitrile 50 times and 20 times for screening and targeted analysis, respectively. The blank in this analysis consisted of LC-MS water treated in the same manner.

Eluents A and B were aqueous 2 mM ammonium acetate and 95:5 v/v acetonitrile-water containing 2 mM ammonium acetate, respectively. Both solvents were LC-MS grade. Two different HPLC-HRMS analyses were conducted on each fraction. The purpose of the first was to screen for ions that would serve as precursor ions for a targeted analysis utilizing MS/MS. The methods differed only with the MS programs. The following conditions were applied to both methods: Injection volume, 50 μL; flow rate, 0.25 mL/min; eluent program: 0→2→10→20 min, % B: 5→5→95→95. MS conditions: ionization mode, electrospray ionization; column oven, 40 °C; positive interface voltage, 4.5 kV; negative interface voltage, −4.0 kV. Additional MS parameters for the screening analysis were: Ion accumulation, 100 ms (repeated 3 times in both positive and negative modes); event time, 432 ms (in both modes); loop time, 1.06 s; both positive and negative ion scan range, 100–1000 *m/z*. Profiling Solutions (ver. 1.0, SSI) software was used to select ions unique to the sample. These *m/z* values were incorporated in the targeted analysis as precursor ions. Within each retention time window, the acquisition m/z scan range was set narrowly bracketing the expected value of the precursor ion. Above an intensity threshold of 500 counts at the precursor ion *m/z*, MS/MS was performed after an acquisition time of 50 ms. The collision induced dissociation energy was optimized for each compound. Fragment ions were scanned from 50 *m/z* to 50 *m/z* units above that of the precursor ion with an accumulation time of 50 ms, repeated 3 times. Accurate Mass Calculator (SSI) was then used to assign elemental formulas to fragment ions as well as the parent ion. Compounds whose molecular formulas could not be identified are not reported.

2.6. High Performance Ion Chromatography

The IC analysis protocol used an IC-25 isocratic pump with an EG40 electrodialytic eluent generator (EG), 2 mm bore AG20/AS20 guard and separation column sets housed in an LC30 temperature controlled oven, ASRS-Ultra II anion suppressor in external water mode, and a CD-25 conductivity detector, (all from Thermo Fisher Dionex).

Samples were passed through a Supelclean LC-18 SPE tube (3 mL, 500 mg) to remove hydrophobic compounds. Three mL of LC-MS acetonitrile were loaded into the tube for conditioning, followed by 3 mL of DI water and 12 mL of sample. 6 mL of sample eluted to waste prior to collecting. The sample was then filtered with a 0.2 μm PTFE syringe filter and diluted 100x in DI water.

A potassium hydroxide gradient was performed using the EG as follows: 0→3→15→19→27→27.5→30 min: 4→4→10→40→40→4→4 mM. Other parameters: Injection volume, 2 µL; oven temperature, 30 °C; and flow rate, 0.25 mL/min. Eluent generation, (recycle mode) electrodialytic suppression, autoranging conductivity detection, and data acquisition were all conducted using software control from Chromeleon (ver. 8.1); a Finnigan Surveyor Autosampler performed sample delivery and injection (all from Thermo Fisher Scientific, Inc.).

Mixed standards were prepared containing the following ions and ranges: Acetate (10–200 µM), bromide (10–200 µM), chlorate (10–200 µM), chloride (10–1000 µM), chromate (10–200 µM), fluoride (10–500 µM), formate (10–200 µM), nitrate (10–500 µM), perchlorate (10–200 µM), and sulfate (10-1000 µM). All data were interpreted in terms of a 5-point calibration with check standards run daily. Any sample falling outside the calibration range was reanalyzed after appropriate dilution. Sample 1 was not available in sufficient amount to permit IC analysis.

2.7. Total Organic Carbon/Total Nitrogen Analysis

A TOC-L total organic carbon analyzer outfitted with the TNM-L total nitrogen module and an ASI-L autosampler (all from SSI) were used for Total Carbon (TC), Inorganic Carbon (IC), and TN measurements. Samples (100x dilution for Sample 1) were filtered with 0.45 µm PTFE syringe filters as needed and filled a 40 mL volatile organic analysis autosampler vial. TOC was calculated as the difference between TC and IC.

2.8. Conductivity and pH Analysis

An HI2020 Edge multi-parameter meter equipped with an HI11310 pH electrode and an HI763100 conductivity probe (all from HANNA Instruments, Woonsocket, RI, USA) was used to measure the pH and conductivity of filtered and undiluted samples in our laboratory at 20 °C.

3. Results and Discussion

3.1. Analytical Data

Analytical measurements of the wastewater samples as well as shale gas produced water (SGPW), tight gas sand produced water (TGSPW), coal-bed methane produced water (CBMPW), and produced water from conventional natural gas operations (NGPW) from government and industrial records, peer-reviewed literature, and other sources compiled by Alley *et al.*, are displayed in Table 3 [16]. The measurements in all three wastewater samples are within the range of the same parameters for SGPW in Alley *et al.*'s compilation, if reported. It is interesting to note that for Cr, Cu, Ni and Br, the values for our wastewater samples are uniquely higher than those reported by Alley *et al.*, for other types of produced water.

Table 3. Comparison of measurements in wastewater samples with compiled PW data. Shale Gas Produced Water (SGPW), Tight Gas Sand Produced Water (TGSPW), Coalbed Methane Produced Water (CBMPW), and Produced Water from Conventional Natural Gas Operations (NGPW) quality ranges compiled by Alley *et al.* [16]. ND (Not Detected).

Measurement	Sample 1	Sample 2	Sample 3	SGPW	TGSPW	CBMPW	NGPW
pH	7.98	7.06	6.54	1.21–8.36	5–8.6	6.56–9.87	3.1–7
Conductivity (mS/cm)	64.8	151.9	21.27	-	up to 24.40	0.0948–145	4.2–586
TOC (ppm)	200. ± 7	8.6 ± 0.5	151 ± 11	-	-	-	-
TN (ppm)	247 ± 4	397 ± 6	31 ± 2	-	-	-	-
Barium (ppm)	3.48	15.4	8.90	ND–4,370	-	0.01–190	0.091–17
Beryllium (ppm)	0.266	0.151	0.234	-	-	-	-
Cobalt (ppm)	2.46	3.04	4.14	-	-	-	-
Chromium (ppm)	1.35	1.38	2.33	-	up to 0.265	0.001–0.053	0.002–0.231
Copper (ppm)	6.47	7.90	8.56	ND–15	up to 0.539	ND-0.06	0.02–5
Iron (ppm)	2.34	7.52	14.9	ND–2,838	up to 0.015	0.002–220	ND-1,100
Molybdenum (ppm)	2.13	2.20	5.06	-	-	-	-
Nickel (ppm)	3.06	3.19	4.78	-	up to 0.123	0.0003–0.20	0.002–0.303
Strontium (ppm)	78.9	418	16.0	0.03–1,310	-	0.032–565	0.084–917
Titanium (ppm)	1.40	1.44	4.16	-	-	-	-
Vanadium (ppm)	3.44	4.40	4.51	-	-	-	-
Zinc (ppm)	1.00	1.45	2.04	ND–20	up to 0.076	0.00002–0.59	0.02–5
Zirconium (ppm)	7.16	6.64	8.76	-	-	-	-
Acetate (ppm)	-	ND	ND	-	-	-	-
Bromide (ppm)	-	851	15.9	ND–10,600	-	0.002–300	0.038–349
Chlorate (ppm)	-	ND	ND	-	-	-	-
Chloride (ppm)	-	75,100	9000	48.9–212,700	52–216,000	0.7–70,100	1,400–190,000
Dichromate (ppm)	-	ND	ND	-	-	-	-
Fluoride (ppm)	-	ND	ND	ND–33	-	0.05–15.22	-
Formate (ppm)	-	ND	ND	-	-	-	-
Nitrate (ppm)	-	ND	ND	ND–2,670	-	0.002–18.7	-
Perchlorate (ppm)	-	ND	ND	-	-	-	-
Sulfate (ppm)	-	199	2600	ND–3,663	12–48	0.01–5,590	1.0–47

3.2. Organic Compounds Identified in Wastewater Samples

Organic compounds present in the wastewater samples identified by GC-MS and HPLC-HRMS are displayed in Tables 4 and 5, respectively. The following compounds (and their intended roles) identified in the wastewater samples are known to be used in fracturing fluids according to FracFocus, a publicly accessible registry [14]: 2-butoxyethanol (acid dispersant/solvent/non-emulsifier for acids/water recovery surfactant); alkyl amines (acid dispersants/surfactants) cocamide diethanolamine and salts (non-emulsifier for acids); toluene/xylene (solvent/ scale inhibitor), and methyl chloride (purpose unknown).

Many N-alkyl-N,N-dimethylamines (NNDA), $(CH_3)_2NC_xH_{2x+1}$, were detected in Sample 1 (Figure 1), and one was detected in Sample 3. The molecular weights of only 2 associated chromatographic peaks have been identified due to the very low abundance of the molecular ion characteristic of NNDAs. The base peak of an aliphatic amine is typically the fragment ion resulting from alpha cleavage of the largest alkyl group of the amine [17], which is m/z 58 in NNDAs.

Table 4. Compounds identified by gas chromatography-mass spectrometry (GC-MS).

Retention Time (min)	m/z	Compound	CAS	Samples Contained
1.58	50	Methyl Chloride	74-87-3	1
1.97	76	Carbon Disulfide	75-15-0	1,3
4.54	91	Toluene	108-88-3	3
6.02	91	o-Xylene	95-47-6	3
6.10	57	2-Butoxyethanol	111-76-2	3
8.94	58	N-dodecyl-N,N-dimethylamine	-	1
9.56	58	N-tetradecyl-N,N-dimethylamine	-	1
10.50	107	Bisphenol F Isomer	-	1
10.68	107	Bisphenol F Isomer	-	1

Table 5. Compounds identified by high performance liquid chromatography-high resolution mass spectrometry (HPLC-HRMS). These represent a homologous series of cocamide diethanolamines.

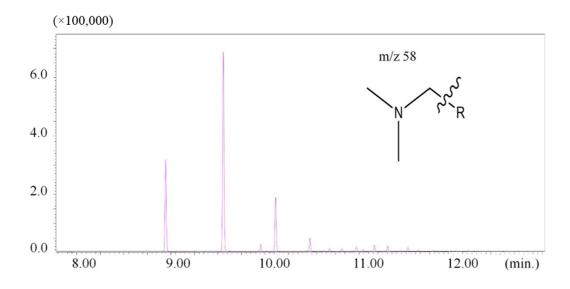| R.T. (min)	Measured (M + H)$^+$ m/z	Chemical Formula (M)	Error (ppm)
7.20	204.1655	$C_{10}H_{21}NO_3$	26.6
8.70	232.1932	$C_{12}H_{25}NO_3$	7.8
9.78	260.2239	$C_{14}H_{29}NO_3$	4.6
10.87	288.2557	$C_{16}H_{33}NO_3$	5.9

Figure 1. Gas chromatography-mass spectrometry (GC-MS) extracted ion chromatogram of Sample 1 at m/z 58, the characteristic base peak of an N-alkyl-N,N-dimethylamine.

Overlaid extracted ion chromatograms from HPLC-HRMS are shown in Figure 2. These compounds were determined to be a homologous series of cocamide diethanolamines, having a characteristic fragment of approximately 106.09 m/z, representing $C_4H_{12}NO_2^+$. Acyl chain lengths were determined to be C6, C8, C10, and C12. Although the discrepancy between the known and observed exact mass for the C6 compound is relatively high (26.6 ppm), the errors associated with the assignments of the longer chain compounds were quite low (≤7.8 ppm) and suggests that the C6 assignment is likely correct. Higher chain cocamide diethanolamines, if present, may not have been detected due to their retention in the SPE tube.
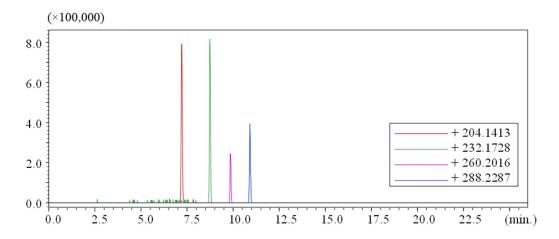
Figure 2. High performance liquid chromatography-high resolution mass spectrometry (HPLC-HRMS) overlaid extracted ion chromatograms of screening analysis with acetonitrile eluent. These masses represent a homologous series of cocamide diethanolamines.

3.3. Comparison of Results to Other Studies

It should be noted that the use of these data reported in this study in direct comparisons to produced water and flowback water quality across other regions is of limited value due to the lack of detailed information regarding the origin of these samples. For example, although it may be tempting to describe Samples 1 and 3 as flowback water based on the presence of compounds known to compose HF fluid and the high TOC content and low conductivity relative to Sample 2, it is not known if the gas well Sample 1 was collected from was producing or if the waste pit from which Sample 3 was collected from contained flowback water, exclusively. For similar reasons, it may not be appropriate to label Sample 2 as produced water, because the DW it was taken from likely consisted of wastewater from various stages of HF.

Several other studies on the chemical composition of wastewater samples from UDO have reported far more organic compounds in their samples by GC-MS than our own [3,10]. This is undoubtedly due to their use of multiple extractions to a larger volume of sample followed by the removal of most of the extractant solvent by rotary evaporation under a gentle stream of nitrogen gas at a low temperature. The adoption of this or another preconcentration technique, such as SPE, would greatly improve the sensitivity of our GC-MS method.

4. Conclusions

Information gained from detailed chemical analyses of wastewater can be used to manage it more appropriately, develop targeted treatment methods, source it, and assess the relative health risk associated with exposure to it. The methods described in this paper may also be of value for the assessment of remediation strategies, potentially contaminated groundwater, and other industrial wastewaters.

This report is not an exhaustive characterization of wastewater. Organic speciation through GC-MS and HPLC-HRMS data from methods intended for surveying generally unknown samples has also been presented here. In all cases, it is important to incorporate best practices from standard methods available for various targeted analyses; it is also, however, important to maintain the ability to discover

unexpected analytes that were not targeted. More information of wastewater constituents can be gained through additional advanced analytical chemistry, primarily for specific classes or functional groups of organic compounds, trace metal detection, and complementary separation and detection techniques.

For future studies, we have a number of recommendations based on our experience. Though not always easily obtained, it would be most desirable to only analyze samples whose history is known in sufficient detail to permit a deeper discussion of the context of measured parameters and a more direct comparison to wastewater from other studies. We also recommend taking into consideration the volumes of sample required for method development and sample preparation when sampling to ensure that all desired chemical analyses can be performed. The volumes necessary for method development and analysis are related to the concentration of the analyte targets, the sensitivity of the analytical methods, and the selected sample preparation techniques. Many EPA methods for the analysis of volatile and semi-volatile organic compounds in water-based samples require up to 1 liter of sample to concentrate analytes prior to GC-MS analysis. Metal and ion analysis methods typically do not require preconcentration steps, therefore less initial volume required. Storage space for these samples is also a practical consideration in the volume collected.

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Author Contributions

Jonathan B. Thacker, Doug D. Carlton, Jr., Zacariah L. Hildenbrand and Kevin A. Schug conceived and designed experiments; Jonathan B. Thacker and Akinde F. Kadjo performed the research; Jonathan B. Thacker analyzed the data; Jonathan B. Thacker, Doug D. Carlton, Jr., Zacariah L. Hildenbrand and Kevin A. Schug wrote the paper.

Conflicts of Interest

The authors declare no conflict of interest.

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