HYDRAULIC FRACTURING FLUID ADDITIVES: METHOD FOR DETECTION WITH MASS SPECTROMETRY, NEW IDENTIFICATIONS, AND UTILITY OF BIOLOGICAL TREATMENT

by

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ABSTRACT

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Hydraulic Fracturing Fluid Additives: Method for Detection with Mass Spectrometry, New Identifications, and Utility of Biological Treatment

Dissertation directed by Professor Karl G. Linden

Hydraulic fracturing simultaneously uses and generates billions of gallons of water every year that must be sourced and managed. Fracturing fluid chemicals, including many ethoxylated and propoxylated surfactants, are added to water to make fracturing fluid. Flowback and produced water, the primary contributors to the waste stream, are generated during the drilling operations and throughout the life of the well.

Inherent to developing a management approach is adequate methods of characterization and treatment for dissolved components. This research presents the development of a solid phase extraction method for identifying and detecting common fluid additives with mass spectrometry (MS). With this method, several new fracturing fluid additives were identified by comparing putative identifications to known standards, conducting MS-MS experiments, and applying the Kendrick mass defect. Poly(ethylene glycol) amines (PEG-amines), PEG-amine-carboxylates, and amino-PEG-amines were identified in 20 samples from different basins. Researchers now have an array of compounds that can be easily detected with MS in flowback and produced water and contribute to the "fingerprinting suite" of compounds identified by other researchers.

When flowback and produced water is treated as part of a management strategy, suspended solids, scaling ions, and dissolved organic compounds are typical targets. In this research, biological treatment of a flowback and produced water is examined for reduction of dissolved organic carbon (DOC) and ethoxylated fluid additives (PEGs and PEG-amines). Three flowback

and produced water samples with different water qualities were treated in sequencing batch reactor with an acclimated culture. Observed DOC removal was between ~50-80% and the rate of removal slowed with each cycle. Final DOC concentration was between 6 and 50 mg/L. PEG transformation to PEG-carboxylates and PEG-dicarboxylates was observed in each sample but PEG-dicarboxylates were shown to be recalcitrant to treatment and slowly accumulated in the reactor. This persistence of PEGs could be due to a larger "pool" of ethoxylated compounds feeding the detectable PEGs via biotransformation and PEG shortening. This research highlights the ability of a well-acclimated culture to degrade 50-80% of the DOC in hydraulic fracturing flowback and produced waters and demonstrates the recalcitrance of PEGs and perhaps other ethoxylated compounds to biological treatment.

DEDICATION

I dedicate this dissertation to my loving, caring, beautiful, smart, witty, and hilarious wife Samantha. For being dedicated to me and our relationship through our journeys through graduate school. For supporting me through long hours of work on this research in and out of the lab. For being a practice audience and taking an interest in my research, though you may not have understood all of it. For being an advocate for me and others. I love you, I could not have done it without you, and I look forward to the future!

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CHAPTER 1: INTRODUCTION TO HYDRAULIC FRACTURING

1.1 Motivation

For the foreseeable future, energy derived from fossil fuels, including oil and gas, will be a cornerstone of modern society. Despite intense public opposition and earnest efforts to move towards more sustainable energy sources, hydraulic fracturing will be a mainstay oil and gas extraction in the United States and across the world. While the effects of climate change driven by chronic greenhouse gas pollution are hardly tangible in our day-to-day, the acute contamination and overextension of our water resources devoted to energy extraction are much more palpable. Hydraulic fracturing generates high strength industrial waste streams that must be managed efficiently and, whenever possible, include routes to beneficial reuse. Given the intense levels of treatment necessary, potable reuse is likely not a realistic goal, but other end uses, like agricultural irrigation, livestock watering, and reuse in hydraulic fracturing, are feasible. This can be done through well-tailored treatment schemes and better understanding of this complicated waste stream. Developing adequate methods for analysis of the dissolved components will inform treatment options and future regulations and assist in environmental monitoring of impacted water resources. Biological treatment could serve as an adequate treatment technology to reduce the concentration of dissolved organic carbon in a treatment scheme intended for reuse. The water can be used for hydraulic fracturing if suspended materials and organics are removed to an acceptable level. Providing bench-scale evidence that reduction of dissolved organic compounds is achievable with biological treatment is achievable will hopefully lead others to scale-up the process in the future and develop more sustainable water management practices for this ineluctable energy source.

1.2 Hydraulic Fracturing and Unconventional Oil and Gas

Hydraulic fracturing is the method of injecting fluids and sand at high pressure to fracture oil and gas bearing formations to force oil and gas from the formation to the surface. Fundamentally, this process increases the flow paths from the formation to the well and stimulates production [1]. The process was pioneered in the 1940s but did not become profitable until recent advances in directional drilling and increased demand for oil and gas. Hydraulic fracturing used with horizontal drilling is included in "unconventional" oil and gas extraction methods and contrasted with "conventional" oil and gas extraction, where traditional vertical wells are drilled to access a portion of the formation. Basins accessible by conventional methods have a higher permeability and can flow oil and gas without external stimulation (i.e. hydraulic fracturing). Unconventional plays (including tight gas sands, coal bed methane, tar sands, methane hydrates, and shale formations [2]) are of lower permeability and require external stimulation to flow and a horizontally drilled wellbore to be profitable. Of these different unconventional sources, most hydraulic fracturing occurs in shale formations (called "plays"). Horizontal drilling laterals for a single hydraulically fractured well range from 1,000 to 15,000 feet at depths of several thousand feet below ground. After the well is drilled, it is flushed to remove casing residues before the fracturing treatments (called "stages") are applied. Each stage involves pumping specified volumes of fracturing fluid and proppant into the well to create the fractures and keep them open. After fracturing is complete, the well is opened for production, and a mixture of water, oil, and gas flow to the surface [2].

Though controversial because of potential environmental degradation, horizontal drilling combined with hydraulic fracturing enables oil and gas producers to access more of a formation with fewer wells. It is largely responsible for the low cost of oil and natural gas for the United States becoming a net exporter of natural gas [3]. Unconventional sources of natural gas had been

untapped for years as the supply from conventional sources were meeting demand, but unconventional sources have a much higher estimated proven reserves (>730,000 trillion cubic feet (TCF)) than conventional sources (>6,600 TCF) [2]. In the United States, there are more than 15 plays where it is active (Figure 1.1). The major plays include: the Marcellus (Pennsylvania and West Virginia), Haynesville (Louisiana and Texas), Barnett (Texas), Eagle-Ford (Texas), Bakken (North Dakota), Niobrara (Colorado and Wyoming), and Woodford (Texas) [4]. Though initially dominated in the United States, resource exploration with hydraulic fracturing has since expanded to Canada, South America, north and central Africa, Europe, China [5], and Australia [6].

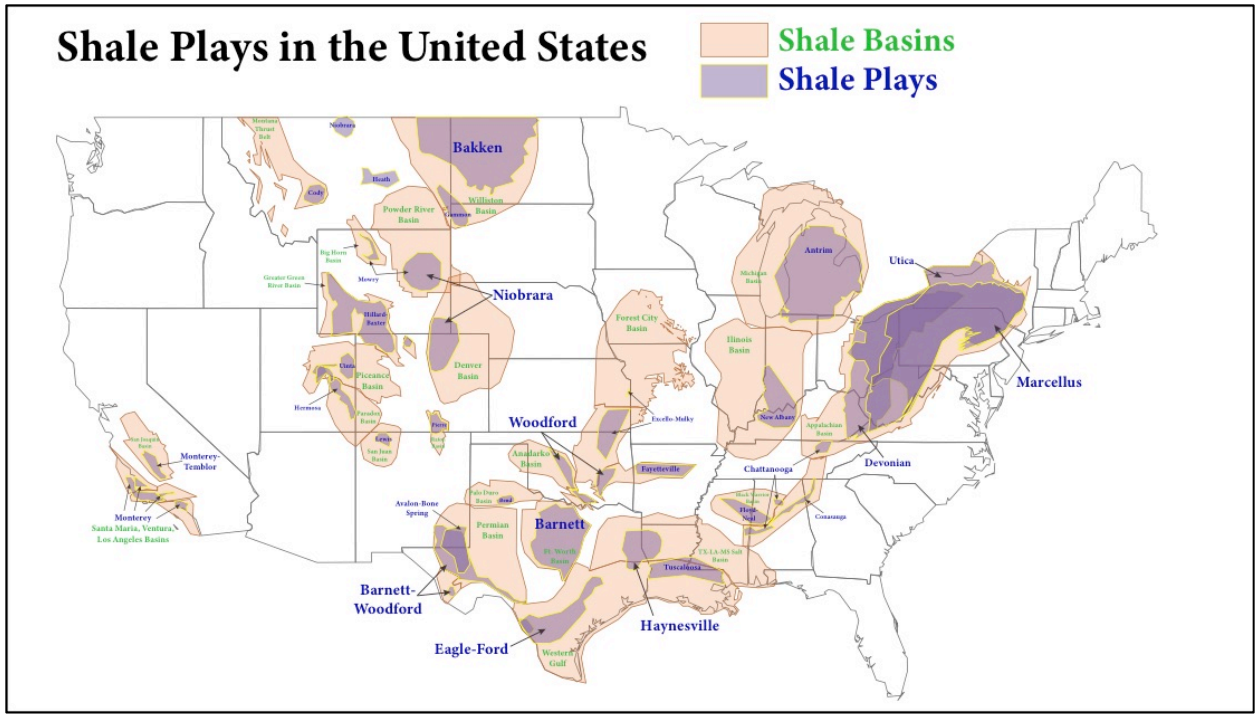

Figure 1.1: Shale basins and shale plays in the United States (adapted from [4]).

Among the advantages that hydraulic fracturing brings to the world energy market is cheap and plentiful natural gas and oil. In the United States, the glut of natural gas has led to suggestions that it will serve as a "bridge fuel" for the transition to more environmentally sustainable methods of energy production because it produces less CO_2 per unit burned than coal [7, 8]. Other benefits

include economic development as a result of job creation and tax collections [9], reduction of criteria air pollutants (e.g. NO_x, SO_2, particulate matter), lower land use, and lower water withdrawal and consumption per unit of energy [10]. Notwithstanding these advantages, hydraulic fracturing involves the use and generation of millions of gallons of water. The following sections summarize the environmental impacts of hydraulic fracturing on air and water resources and water management approaches for flowback and produced water.

1.3 Environmental Impacts

Since hydraulic fracturing has become more widespread in the past decade, impacts to the environment as a direct and indirect result of hydraulic fracturing have been intensely studied. Because it is a technically complex process, there are many points in the production timeline where mechanical or human errors can occur, leading to environmental contamination. Additionally, each play has different geologic characteristics and may be subject to different state regulations, so best practices from one play do not necessarily translate to another. Impacts to air and water are briefly discussed in the following sections.

1.3.1 Impacts to Air

Poor well operation and limited governmental oversight has led to gas leakages of methane from hydraulic fracturing wells, which is a more potent greenhouse as than carbon dioxide [11]. Pétron et al. [12] calculated that between 2.3-7.7% of the total natural gas production was leaking or otherwise being released from well heads in the Denver-Julesburg Basin in Colorado and that 75% of the total methane emissions detected in the region were attributable to oil and gas production [13]. Similar surveys were conducted for the Uinta Basin in Utah, where researchers estimated that 6-12% of the produced natural gas was leaking [9], and Howarth et al. [14] estimate

that 3.6-7.9% of natural gas from shale wells escape to the atmosphere. Leaks are detrimental to the natural and built environment. Explosions related to natural gas leaks have been reported in Pennsylvania, Texas, and Colorado [15, 16].

Volatile hydrocarbons have been detected around wellheads during the development and production phases of the wells [17]. Vinciguerra et al. [18] reported elevated concentrations of ethane in the Baltimore, Maryland and Washington, D.C. area downwind from increased shale extraction operations in Pennsylvania and West Virginia. Concentration of polyaromatic hydrocarbons (PAHs) including phenanthrene, anthracene, pyrene, and fluoranthene, increased by an order of magnitude in ambient air of communities near hydraulic fracturing and maximum residential exposure exceeded the EPA's acceptable risk level [19]. Additionally, wide variety of aromatic and aliphatic hydrocarbons have been detected in the vicinity of hydraulic fracturing wells, leading to increased cancer risk for residents in that radius [20], an association with increase in congenital heart defects [21], and an association with preterm births and high-risk pregnancies [22].

1.3.2 Impacts to Water

Because of the sheer volume of water used and generated in hydraulic fracturing, impacts to water resources have been heavily studied. The impacts to water resources begin with sourcing water to produce hydraulic fracturing fluid, as some of the regions with intense hydraulic fracturing activity are under "severe water stress" (see Figure 1.2) [9, 23]. In 2011, dry drinking water wells in parts of Louisiana overlaying the Haynesville shale were partially attributed to larger than expected withdrawals for hydraulic fracturing [24]. Scanlon et al. [25] documented 100-200 ft drops in the water table in 6% of the Eagle Ford play after increased hydraulic fracturing activity and accounts for 16% of the total water demand in that area. Once this water has been used for

hydraulic fracturing, it can generally not be used for any other purpose besides hydraulic fracturing, so is removed from the water cycle permanently.

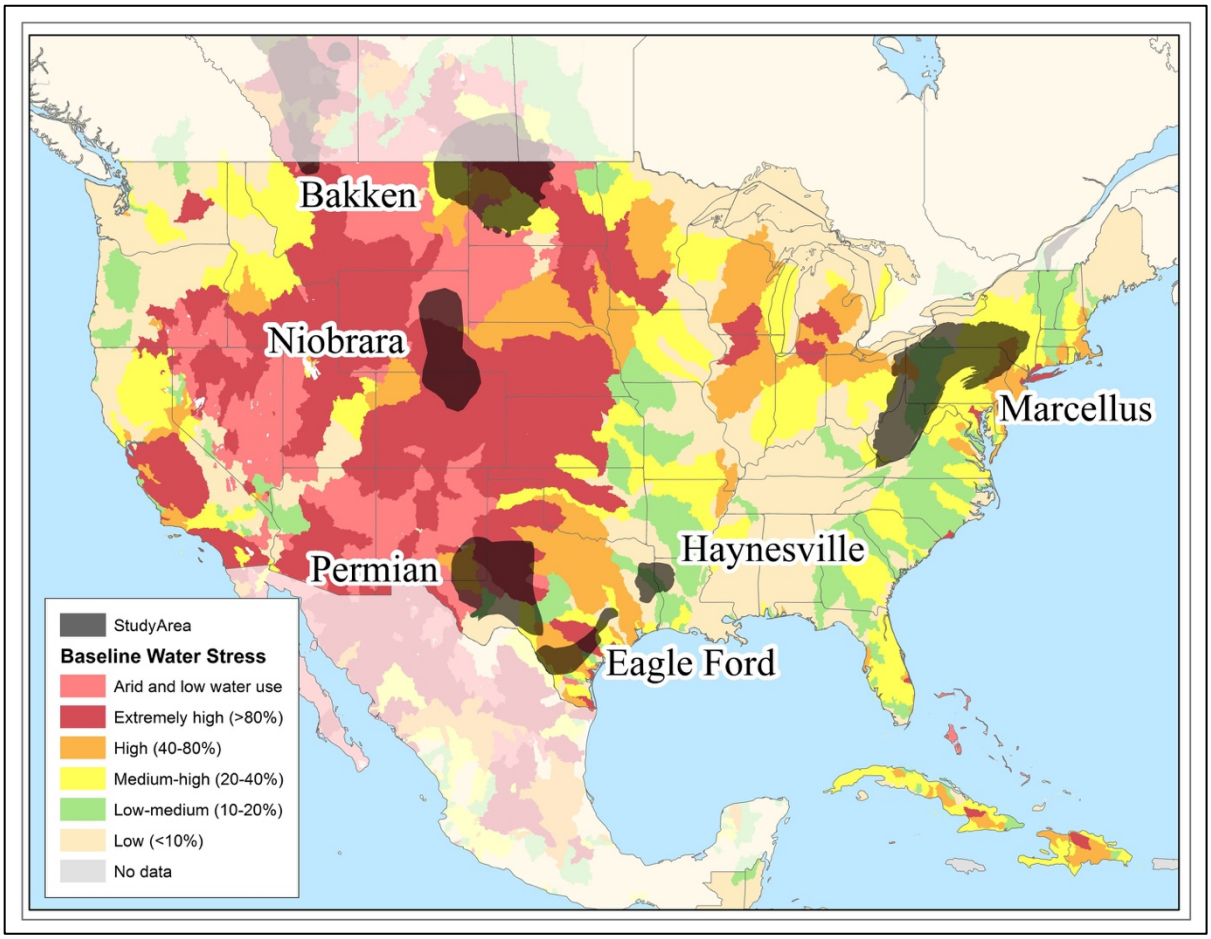

Figure 1.2: Areas of water stress in relation to shale plays in the United States [23].

Groundwater contamination via spills from tank batteries storing flowback and produced water, lined and unlined pits, or trucks transporting water, flooding events, and poor well construction (i.e. cracks in the well) have also caused contamination of water resources [26]. A preliminary EPA study in 2011 attributed groundwater contamination in Pavillion, Wyoming to unlined pits used to store drilling mud, flowback, and produced water for hydraulic fracturing that used gel and slickwater fluids from the 1970s through 2007 [27]. Though the study was never finished, a follow up assessment of publicly available information and data concluded that

groundwater sources were contaminated from hydraulic fracturing fluids [28]. Elevated concentrations of salts and hydrocarbons including methane, ethane, and propane in drinking water wells have been attributed to hydraulic fracturing wells in Pennsylvania [29], New York [30, 31], Colorado [32], and Texas [33], though the link between this contamination and hydraulic fracturing has been disputed [34]. Further, there are ongoing investigations into groundwater contamination via spills in North Dakota [35].

In addition to spills to surface water, flowback and produced water disposal is another route for contamination of surface waters. Management and disposal of flowback and produced waters is more fully discussed the following section, but in some plays it ultimately is partially treated prior to being discharged [24]. In these cases, water contamination and ecological degradation is possible. Inorganic constituents (i.e. chloride, bromide, and other salt ions) and naturally occurring radioactive material (NORM) have been reported in surface waters and river sediment receiving flowback and produced waters in Pennsylvania [36, 37]. These enhanced halide concentrations can increase the incidence of disinfection byproducts such as trihalomethanes (THMs) in the municipal water supplies [38]. Effluents from a facility treating flowback and produced water were shown to contain THMs, benzene, toluene, ethyl benzene, xylenes (BTEX), naphthalene, and aliphatic hydrocarbons at concentrations that exceeded the EPAs maximum contaminant levels (MCLs), as well as ethoxylated surfactants to a stream with flow dominated by this effluent [39].

Contamination of surface water by treated or untreated flowback and produced water can negatively impact stream ecology. Elevated concentrations of heavy metals in streams from spills and treated effluent have been shown to cause more gill lesions and reproductive health in fish [40, 41]. Drinking contaminated water has been associated with increased reproductive effects, seizures, vomiting, rashes, and acute liver, kidney, and respiratory failure in cats, chickens, cows,

dogs, goats, horses, koi, and llamas, though the authors note that more research is needed due to a "lack of highly relevant evidence" of health outcomes caused by hydraulic fracturing [42].

1.4 Water and Hydraulic Fracturing

1.4.1 Water Use

Water is simultaneously a necessary resource for hydraulic fracturing and waste stream of hydraulic fracturing. A general water cycle for a hydraulic fracturing well is shown in Figure 1.3. Water is needed first as a base solvent to mix the hydraulic fracturing fluid.

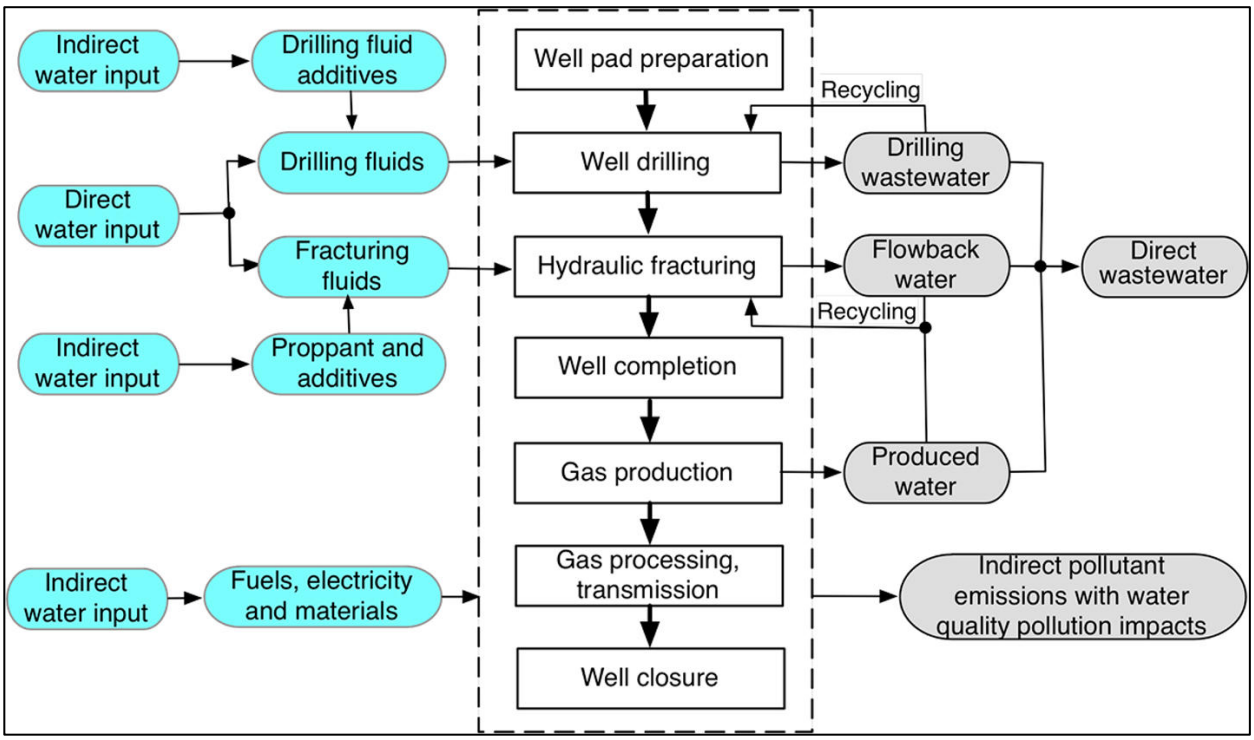

Figure 1.3: Water cycle for hydraulic fracturing [43].

Water is used indirectly to generate fluid additives, drilling mud, and diesel fuel used on pad and in trucks to move water off site [43]. It is often obtained from surface and groundwater

supplies, municipal supplies, treated wastewater, power plant cooling water, and recycled from the fracturing process [44]. The fracturing process itself consists of approximately 85% of the total water use for a well [43], but this amount could be higher in certain plays like the highly saline Bakken, where water is injected throughout the life of the well to maintain well integrity and flush salts [34].

The amount of water use per well varies by region and has been increasing in every major play [23]. As of 2016, hydraulic fracturing in the Bakken play uses the least amount of water (median of 21,600 m^3 per well) and the Permian uses the most (median of 42,500 m^3 per well). From 2011 to 2016, water use per well increased between 20% in the Marcellus and 770% in the Permian [23]. The amount of water used to generate a unit of energy has also increased over this time period, with a low of 11 L/gigajoule (GJ) in the Permian to 28-50 L/GJ in the Bakken, Permian, and Eagle-Ford plays [23]. However, though the gross water withdrawals appear large, they are small relative to other uses of water (e.g. agriculture, municipal). A study that surveyed water acquisition strategies for oil and gas companies in Weld and Garfield Counties in Colorado [45] found that total annual withdrawals in each of these counties attributed to oil and gas was 1.0% and 2.0%, respectively, and was 0.1% of the total withdrawals in the state. This shows that despite technological advances that enable longer lateral drilling and more oil production per well, an adequate water supply will be a factor driving the future of this technology. The consensus among academics and policy makers is that hydraulic fracturing will be a dominant force in energy production in the United States and around the world for the foreseeable future, so there is a need to develop adequate approaches to manage the water supply going to, and coming from, hydraulically fractured wells.

1.4.2 Water Generation

Concomitant with oil and gas production is water production for any oil and gas well, hydraulically fractured or not [46]. Conventional oil and gas wells generate what is termed "produced water" during production of oil and gas, but hydraulic fracturing wells also generate "flowback" water during the well development phase [4]. During well development, as stages of the well is drilled and fractured, the injected hydraulic fracturing fluid remains in the formation. At the end of drilling and fracturing, these fluids flow back to the surface (hence the term "flowback") and are collected. There is no concrete definition for when wells transition from generating flowback to produced water, but a general rule is between 30 and 60 days after the well is opened for production [47]. Several attempts have been made to quantify the amount of flowback and produced water generated from hydraulic fracturing using publicly available data and modeling [23, 47-53]. A recent estimate shows that the total amount of flowback and produced water in the major plays in the United States ranged from 1.7 to 14.3 million L per well [47]. The early flowback period of a well is characterized by high flow rates as the injected fluid is flowing out of the well, with an estimated 10-20% of the total flowback and produced water generated during the first three months, and 20-50% generated in the first six months [47]. Adding to the issue of water management, the amount of flowback and produced water has been increasing over time as much as 1440% in some formations (for the Eagle-Ford gas-bearing wells, 1,340 m^3 per well in 2011 to 20,700 m^3 per well in 2015) [23].

Using and managing such large volumes of water has stoked much of the controversy surrounding hydraulic fracturing in recent years [54]. In comparison to other uses for water, like agricultural irrigation, hydraulic fracturing represents a small portion of the total water budget. However, many of the most productive plays in the United States are located in regions that are

severely water stressed (depicted in Figure 1.2), so use of the water supply in these regions has been contentious. Aside from the sheer volume of water used and generated by hydraulic fracturing, the variable quality of flowback and produced water makes management of the waste stream challenging.

1.4.2.1 Regulation of Hydraulic Fracturing Wastewater Streams

Federal regulation of management and disposal of flowback and produced waters is done under rules promulgated under the Clean Water Act (CWA) and the Safe Drinking Water Act (SDWA). Under the CWA (33 U.S.C. § 1251 et seq.), 33 U.S.C. § 1321 (2006) prohibits discharges of oil or hazardous substances to navigable waters, and 33 U.S.C. § 1342 (2008) establishes the National Pollution Discharge Elimination System (NPDES) program that permits discharges to navigable waters, though stormwater runoff from oil and gas exploration are not required to get a permit. The NPDES regulates the quantity and quality of discharges to navigable waters in three categories: conventional, toxic, and non-conventional. Individual permits are specific to an individual facility (like municipal wastewater treatment facilities) and general permits cover multiple facilities generating a similar type of waste. The latter apply to "facilities" that engage in drilling, well completion, and well treatment for oil and gas (i.e. oil and gas wells) [55].

The SDWA established the Underground Injection Control (UIC) program (§ 300h et seq.), which was designed to prevent contamination of underground drinking water resources. However, § 300h (d)(1)(B)(ii) excludes hydraulic fracturing from the term "underground injection", thus, injection of hydraulic fracturing fluids for stimulation and disposal of flowback and produced waters are exempt from this regulation. The SDWA also enables state primacy, so states and Native American tribes can develop their own regulations for oil and gas discharges, provided they are at least as stringent as the EPA's. Rules promulgated under these two federal acts include 40 C.F.R.

pts. 435.30-435.32, which prohibits the discharge of pollutants from any source associated with oil and gas production, and 40 C.F.R. pt. 437 regulates discharges from CWTFs. The EPA recently did a comprehensive study [56] of 40 C.F.R. pt. 437 to determine if it needed to be amended since more facilities are accepting oil and gas waste now than when the rule was promulgated in 2000 [55]. The study found that the current effluent limitation guidelines of 40 C.F.R. pt. 437 are not inclusive of the range of pollutants commonly found in flowback and produced waters and that the permitting process for these facilities is inconsistent.

1.4.3 Flowback and Produced Water Quality

Flowback and produced water is a complicated water matrix, including thousands of organic and inorganic components. There is no standard water quality one can expect from any well, though it is possible to generalize depending on the age of the well and the formation the well is accessing [57]. Flowback and produced waters are most commonly characterized as having high total dissolved solids (TDS), or salts, compared to conventional wastewater. TDS levels will vary depending on the age of the well and the formation the well is accessing from 1,000-400,000 mg/L TDS [47, 58, 59].

The organic characteristics of flowback and produced water are dependent on several factors. As previously discussed, the initial flow of water out of a well is flowback and contains a mixture of anthropogenic and geogenic components. The anthropogenic components are organic compounds that were used as additives in the fracturing fluid. The additives that are in a fracturing fluid vary from play to play, company to company, and even from well to well. Among the most commonly reported fracturing fluid additives in FracFocus are methanol, hydrotreated light petroleum distillates, 2-propanol, ethylene glycol, guar gum, ethanol, and glutaraldehyde [60]. The primary purpose of a fracturing fluid is to deliver a proppant (generally sand) to the fractures

generated by the high-pressure injections. In general, there are two types of fracturing fluids: slickwater and gel-based. Though use of gel-based fluids has declined recently due to increasing prices of gelling agents [61], they are used in some situations because they are more efficient for proppant transport and require less water to mix [62]. Guar is the most commonly used gelling agent in gel-based fluids at concentrations of 0.12-0.96% w/w and distinguishes gel-based fluids from slickwater fluids [62]. Slickwater fluids contain no gelling agents but instead use a friction reducer (hence the name "slick" water) like polyacrylamide to facilitate proppant transport enabled by higher pumping rates of water [62]. Additional additives in formulations of either of these fluids are dependent on the needs of a particular well or formation.

There are hundreds of potential additives that have been used in fracturing fluids for different purposes and in different proportions: breakers, thickeners, lubricants, corrosion inhibitors, scale inhibitors, friction reducers, viscosity control agents, clay stabilizers, shale stabilizers, fluid loss prevention agents, oxygen scavengers, hydrate inhibition agents, and biocides [63]. These can take the form of alcohols, surfactants, polymers, and hydrocarbons [57, 64]. Specifically identified compounds or compound classes in flowback and produced water include ethoxylated surfactants [65], ethoxylated phenols [66], ethoxylated amines [67], alkyl amines, 2-butoxyethanol [68], and phthalates [66, 69-71]. Several biocides have been detected including alkyl dimethyl benzyl ammonium chloride, glutaraldehyde, dibromo-nitrilopropionamide, and hexahydro-1,3,5-trimethyl-1,3,5-triazine-2-thione [72, 73]. The possibility of so many different additives in fracturing fluids is part of the reason flowback and produced water is difficult to characterize and manage. Further complicating the issue is that oil companies are not required to release the fluid formulation for each well, instead being able to only list the purpose of some additives identified as being "proprietary".

Detected geogenic organic components include >30,000 organic oil and gas related compounds like hydrocarbons [66], polyaromatic hydrocarbons (PAHs), and BTEX [57, 58, 66, 74]. There are also indications of halogenated transformation byproducts of some hydrocarbons that are hypothesized to take place down well (e.g. 2-bromohexane, 4-bromoheptane) [69, 75]. Geogenic compounds are some of the most frequently detected and quantified and are well summarized in Luek and Gonsior [57]. Finally, NORMs have been detected in some produced waters across the country [56].

This research is primarily concerned with detection and degradation of the ethoxylated and propoxylated fracturing fluid additives that are commonly detected in flowback and produced water samples. These compounds serve as cross-linkers, scale inhibitors, corrosion inhibitors, friction reducers, and clay swelling inhibitors [60, 67]. Study of these compounds was undertaken for several reasons. First, there are currently no standardized methods for detection and/or quantification of these ethoxylated compounds in hydraulic fracturing flowback and produced water. Second, the physical properties of the compounds are such that they include very hydrophilic and very hydrophobic moieties and are believed to be biodegradable, so may have very different interaction with treatment technologies and the environment. Third, they are commonly found in samples of all ages (i.e. fresh flowback and old produced water) from all around the country and have been suggested as "fingerprinting" compounds [65, 76]; thus, development of enhanced and systemized methods for analysis and detection are warranted. Finally, we hypothesize that due to the high incidence of these compounds in the samples collected to date, there are other previously undetected ethoxylated fluid additives present at lower concentrations that merit identification and would supplement this suite of compounds.

1.4.3.1 Methods for Analysis of Organic Compounds in Flowback and Produced Water

The extreme variability in water quality and complex nature of flowback and produced waters present challenges for conventional analytical methods typically used to detect and quantify dissolved organic compounds. Aside from measurements of the bulk organic content, like dissolved organic carbon (DOC) or chemical oxygen demand (COD), specific non-volatile compounds are separated and detected using reversed phase liquid chromatography (LC) coupled to an ultraviolet (UV) absorbance detector or quadrupole-time-of-flight (QTOF), Orbitrap, or Ion Trap mass spectrometric detector [77]. Direct injection of waters with high salt and high organic content can lead to poor chromatography, column and instrument damage, reduced sensitivity, undesirable adduct formation (e.g. sodium, ammonium, potassium) [78], and increase the minimum detection limit, leading to non-detect of compounds that are actually present [79]. To mitigate some of these detrimental effects, researchers have used dilution, filtration [65, 70, 72, 74, 76], centrifuge direct injection [39, 80], and solid phase extraction (SPE) [38, 67, 68, 77, 81].

Recently, Nell and Helbling [78] have done valuable work quantifying the matrix effects of ionization and adduct formation tendencies of seventeen fluid additives. Quantified methods for non-volatile organic compounds require the researcher to have some *a priori* knowledge of the sample matrix (i.e. a "target" for analysis) and been developed for citric acid, acetate, butyrate, propionate [82], and most recently, for benzalkonium chloride (ADBAC), polyethylene glycols (PEGs), and polypropylene glycols (PPGs) [78]. Non-targeted approaches for mass spectrometric analysis require no prior knowledge of the sample, as the researcher is trying to simply "see what's there" and make identifications rather than quantifications. When making identifications, researchers have used combinations of tandem mass spectrometry (MS-MS), known standards, chromatography intuition, adduct formation, ultrahigh resolution instrumentation, and application of mass defect to identify compound homologues [38, 65, 67, 74, 76]. Non-targeted methods are crucial for making new identifications in flowback and produced waters because many compounds

used in fluid formulations are proprietary and therefore do not have readily available standards or are transformation products of anthropogenic or geogenic compounds that are not listed in fluid additive databases. For example, halogenated transformation byproducts were recently identified in flowback and produced waters using Fourier transform ion cyclotron mass spectrometry (FT-ICR-MS), some of which matched the exact mass of known disinfection byproducts [38]. Understanding the known and unknown compounds in flowback and produced waters is integral to a successful management approach.

Volatile compounds (e.g. BTEX and aliphatic hydrocarbons) are separated with gas chromatography (GC) and detected with flame ionization detector (FID), QTOF, or mass spectrometric detector. Researchers have prepared samples with SPE, solid phase microextraction (SPME), liquid-liquid extraction (LLE), and purge and trap techniques [77]. Quantifiable methods have been developed for volatile and semi-volatile organic compounds [68, 83], PAHs and alkanes [80, 84], organic acids [71], diesel range and gasoline range organics (DRO, GRO) [39], and hydrocarbons, alcohols, carboxylic acids, and halogenated hydrocarbons [69]. There are more quantified methods for volatile and semi-volatile compounds likely because the majority of these compounds are geogenic and so standards are more readily available. These are also some of the most commonly identified, toxic, and well understood compounds in these waters [57], so development of appropriate methods is and will be valuable to assessing management approaches and addressing environmental contamination.

1.5 Flowback and Produced Water Management

The cost of sourcing and treating water is the primary factor in determination of a water management strategy. Water itself costs $0.24-1.75 per barrel and an additional $0.50-8.00 per barrel to truck it to the well, depending on the state and transportation distance [1]. After leaving

the separator, the water flows to onsite tank batteries or pits prior to the next step of the management process. In some cases, evaporation pits are used and the water does not leave the site. However, the majority of this water, estimated to be >93% of the total volume, is transported offsite via trucks to Class II injection wells for disposal [24], which ranges in cost from $0.07-1.60 per barrel of produced water [1]. These wells are regulated by the Environmental Protection Agency (EPA) and are found all over the country, with thousands available in Texas, Kansas, Oklahoma, Louisiana, and Illinois. A notable exception to this practice is in Pennsylvania, where less than ten Class II wells are permitted for flowback and produced water, and often the closest disposal wells are located in Ohio [85]. Due to the cost of transporting the water to Ohio, Pennsylvania has the highest incidence of treatment and reuse of flowback and produced water in the country, with reuse estimates ranging from 56-87% of the total volume produced, and some operators claiming 100% reuse for fracturing fluid [85]. This is contrasted with other plays like the Bakken where <5% of the water is reused. If it is not injected or evaporated, it is trucked offsite to a centralized wastewater treatment facility (CWTF) where it treated to some extent and is either prepared for reuse, discharged to the environment, or discharged to a storm drain where it ends up in a municipal wastewater treatment facility [56].

Due to the increasing prevalence of hydraulic fracturing, decreasing availability of injection wells, changing regulations, and difficulty in sourcing base water for fracturing fluid, treatment and reuse as a management strategy is increasing [86-88]. CWTFs are becoming more common as a way to reuse some of the flowback and produced water to mitigate high water costs. The important contaminants in flowback and produced water and their impacts for reuse in hydraulic fracturing operations are presented in Table 1.1 [89].

Table 1.1: Impacts of important contaminants on reuse for hydraulic fracturing [89].

Contaminant	Impact for Reuse
Particulates	Well Plugging
Suspended Solids	
Oil and Grease	Fracturing Fluid Viscosity & Stability
Dissolved Organics	
Volatile Organics	
Total Dissolved Solids	
Chlorides	
Iron	Scaling/Corrosion of Pumping and Drilling Equipment
Hardness (Ca, Mg, Ba, Sr)	
Silica	
Sulfates	
Bacteria	
NORM	Radioactivity

Treatment cost is extremely variable at $0.20-8.50 per barrel and is dependent on water quality, technology, and end use [1]. In 2000, the EPA identified 223 CWTFs and by 2018, that number had increased to 426 [56]. Several facilities across the country accept hydraulic fracturing wastewater with the intention to reuse in hydraulic fracturing. Treatments are primarily concerned with reduction of suspended solids, oil and grease, and scale causing ions [90]. They typically use physical/chemical treatment technologies like chemical precipitation, flocculation/sedimentation, and filtration. Recently, companies have determined that reduction of TDS is not necessary to mix an adequate hydraulic fracturing fluid and have been developing formulations that use high TDS waters [91] or diluted flowback and produced water [92], though there is evidence that some ions can negatively impact formulations of gel-based fluids [93]. Nevertheless, there are no well-defined water quality parameters that treatment facilities can target when treating for reuse in hydraulic fracturing because fluid formulations vary widely, though some have been published (see Table 1.2) [89, 94].

Table 1.2: Example water quality parameters for fresh, clarified, and blended sources of water intended for reuse in hydraulic fracturing (adapted from [89, 94]). "Fresh" indicates a surface, ground, or municipal water source. "Clarified" indicates a source that has been treated to remove suspended material. "Blended" indicates a flowback or produced water blended with a fresh water source. N.R. = Not Reported.

Parameter	Units	Source		
		Fresh	Clarified	Blended
TDS	mg/L	<500	<35,000 to 50,000	~26,000
TSS	mg/L	<2 to 10	<50	~1,500
Turbidity	NTU	<4	<100	N.R.
Hardness	mg/L as $CaCO_3$	<150	<2,500	<5,000
Alkalinity	mg/L	~50	<600	N.R.
TOC	mg/L	<25	<50	<5
pH	---	6.0 to 8.0	6.5 to 8.5	>8

While the biggest concern is suspended solids and scaling ions, there is a benefit to removing organic matter from produced waters prior to reuse. High levels of organic matter enable microbes to thrive and lead to microbial induced corrosion in transport lines, pumps, and drilling equipment [73, 95]. Further, high levels of organic matter in recycled fracturing fluid yielded gel-based fluids with lower peak viscosities [96], which is a crucial characteristic for an effective fracturing fluid [97]. Recycling produced water reduced water and trucking costs to dispose of flowback and produced waters [94]. Other reuse applications that have been explored, provided the water is of sufficient quality, include irrigation for crops [98, 99], livestock watering [100], and spreading on roads for dust suppression [85].

Other CWTFs treat with the intention of discharging to a surface water or sewer. In a recent EPA profile of 11 such facilities that accept hydraulic fracturing waste, the NPDES permits include effluent limitations or monitoring requirements on bulk constituents like TDS, COD, biochemical oxygen demand (BOD), nutrients, and gross alpha and beta radiation, as well as limits on specific parameters like metals (e.g. copper, arsenic, lead), ions (e.g. chloride, bromide), methanol, bis(2-

ethylhexyl) phthalate, and acrylamide [56]. The treatment technologies used at these facilities include flocculation/sedimentation basins, bag filtration, aeration, evaporation and crystallization, chemical precipitation, oil/water separation, biological treatment, reverse osmosis, and thermal distillation. Like those that treat for reuse, these facilities are primarily concerned with removing and/or reducing the inorganic content of the flowback and produced waters before discharge. In the past, everything from filtration to electrocoagulation to constructed wetlands has been used to treat produced water [1, 90]. Of particular interest here is the use of biological treatment as a pretreatment technology for flowback and produced waters.

1.5.1 Biological Treatment of Hydraulic Fracturing Wastewater

Because of the highly saline nature of many flowback and produced waters, biological treatment was precluded from consideration as a treatment technology in some cases [88]. It is used as a pretreatment step prior to some type of desalination process (membranes, distillation) to reduce biofouling [88]. Fixed film and attached growth biological aerated filters (BAF) have been used to remove oil, suspended solids, and reduce nutrients, COD, BOD and other organics in the effluent, but can be limited by the high salt (>20,000 mg/L chloride) of the influent [1]. Recently, treatment of flowback and produced water with BAF has been examined at the bench- and pilot-scale for DOC reduction. At the bench-scale, Freedman et al. [101] achieved >90% reduction in DOC in 40-72 hrs with combined mechanisms of adsorption, biodegradation, and air stripping from diluted and full strength produced water collected from the Piceance and Denver-Julesburg Basin. In these studies, performance was improved after starting aeration of the columns, indicating that the organic matter in these waters is favorably degraded under aerobic conditions, and performance was not markedly improved by pretreatment with coagulation/flocculation. The initial DOC of the waters evaluated ranged from 240 mg/L for produced water to 2,170 mg/L for

the flowback water. Notably, the TDS for these waters was between 10,460 and 18,170 mg/L, which is on the low range for flowback and produced waters for any basin. This study was followed up by Riley et al. [102], where BAF was combined with ultra- and nanofiltration membranes to treat produced water with 12,600-31,100 mg/L TDS and 36-723 mg/L DOC. Results for Piceance produced water showed 67% DOC removal with BAF and 94% TDS removal with nanofiltration, and 87% DOC removal with BAF and 94% TDS removal from Denver-Julesburg produced water. Further optimization of the GAC media used and nutrient addition in the BAF systems demonstrated 92% reduction in DOC in 24 hours [103]. Finally, this study was followed by a pilot-scale BAF system that operated for 600 days and achieved 85% COD removal in 100 hr batch operations [104]. Analysis of treated and untreated flowback and produced waters presented alongside these studies showed the importance of biological treatment as a pretreatment technology. Results highlighted that biological degradation accounted for the majority of DOC removal and the importance of reduction of low molecular weight aromatic compounds prior to membrane treatment because they can foul the membrane [105].

Other forms of biological treatment have been applied to hydraulic fracturing flowback and produced water and associated additives. Lester et al. [106] achieved 90% reduction in COD as guar gum in 10 hr at 1,500 mg/L TDS, but this degradation slowed to 60% reduction in 31 hr when TDS was increased to 45,000 mg/L, highlighting the detrimental effect that high salinity can have on biological treatment processes. Similarly, removal of COD reached a maximum value of 80% in an aerobic process from a synthetic flowback water that included the common fluid additives polyacrylamide, isopropanol, guar gum, and ethylene glycol and a TDS of up to 50,000 mg/L as NaCl [107].

A less conventional biological treatment method, microbial mats, was considered by Akyon et al. [108] for treatment of synthetic flowback water at TDS concentrations ranging from

50,000 to 200,000 mg/L TDS and 2,500 to 5,000 mg/L COD as guar gum and/or acetate, and real produced water from Pennsylvania with 18,400 and 182,700 mg/L TDS. Degradation rates were shown to be high initially but dropped off after successive loadings, an effect that was more pronounced at higher salinity levels, with no biodegradation taking place at the highest TDS concentrations considered. Aerobic degradation in conjunction with activated carbon of flowback water with 103,000 mg/L TDS and 649 mg/L DOC was shown to be preferential over ozonation for removal of low molecular weight compounds and achieved 83% reduction of DOC in 48 hr [109]. Several other studies have examined biological treatment of oil and gas produced water from conventional wells (i.e. wells that were not hydraulically fractured) that are summarized by Camarillo and Stringfellow [88]. Key findings of their meta-analysis are that COD reduction decreases with >50,000 mg/L TDS, a well-acclimated microbial culture is key, and that biological treatment is well suited as a pretreatment for membrane processes.

Biological treatment has also been used at a full-scale facility to treat flowback and produced water. The Anticline Disposal facility in Pinedale, Wyoming receives flowback and produced water from the Pinedale Anticline field and includes both aerobic and anaerobic biological treatment processes used in series with membrane and other physical/chemical treatment technologies. Though the objective of the treatment process is to produce water of sufficient quality for fracturing fluid, they also discharge to surface water. The plant feed contains 8,000-15,000 mg/L TDS, up to 80 mg/L BTEX, 420 mg/L GRO, and 1,100 mg/L DRO, and is capable of treating these and other constituents to non-detect levels [110].

1.6 Research Needs

In one recent estimate, of the more than 1,600 additives disclosed on FracFocus.org, there are EPA methods for detection and/or quantification <25% of them [100]. Additionally, even if

EPA methods do exist for some compounds, there is concern that they may not be suitable to this complicated matrix. This research seeks to develop straightforward methods for analysis of known and unknown dissolved organic components in hydraulic fracturing flowback and produced water and identify undisclosed additives using these methods. A uniform method for detection of these components in pure and environmentally diluted samples will enable researchers to make one-to-one comparisons across studies and lay the groundwork for future standard methods capable of accurately quantifying these components in raw and treated samples. Sustainable management of this water resource for beneficial reuse will likely involve membranes, so investigations into an adequate, well-understood treatment technology capable of reducing the potential for membrane fouling are needed. One such treatment technology is aerobic biological treatment (activated sludge). Understanding how this technology performs across the wide spectrum of potential produced water qualities, and the characteristics of the effluent, will inform future management practices.

1.7 Hypotheses

Based on the literature and research needs, the following hypotheses were tested:

1. Method development: Sample preparation with solid phase extraction will reduce the impact of salt and enable and enhance detection of ethoxylated hydraulic fracturing fluid additives with mass spectrometry in unadulterated and environmentally diluted flowback and produced waters.
2. Compound Identification: The application of isolation and concentration methods used in conjunction with high-resolution mass spectrometry will enable detection of organic compounds and/or compound classes that were previously below instrument detection limits or masked by background noise and salt interference.

3. Biological Treatment: An adequately acclimated microbial culture will be capable of degrading the ethoxylated fracturing fluid additives in a wide variety of hydraulic fracturing flowback and produced waters.

1.8 Research Overview

The need to facilitate a better understanding of the character and biological degradability of the bulk and specific dissolved organic components of hydraulic fracturing flowback and produced water is the impetus for the hypotheses to be tested here. Adequate detection of fluid additives and their metabolites in raw, treated, and environmentally dilute samples will inform future decisions regarding engineered treatment processes that produce water suitable for a beneficial reuse.

An ideal method should require no *a priori* information of the water sample to be analyzed besides knowledge that it is flowback or produced water from hydraulic fracturing or is potentially impacted by flowback or produced water from hydraulic fracturing. The method would further achieve the necessary objective of removing interferences (e.g. salt) and enhance the signal of the targets of analysis (i.e. non-geogenic ubiquitous fluid additives) to a level that they can be detected by mass spectrometry. Solid phase extraction is a sample preparation technique that is commonly used for a broad spectrum of compounds and is investigated in this research for its ability to desalt and concentrate ubiquitous fracturing fluid additives with a spectrum of characteristics.

An ideal treatment technology should be one that is well understood, reliable, and flexible: well understood in the sense that changes in process performance can be troubleshot with a long history of research and operators can be easily trained. Reliable in the sense that the process can achieve the treatment goals consistently, does not require constant oversight under steady state conditions, and is not prone to failure. Flexible in the sense that it can achieve the treatment goals

with a wide range of feed water qualities. Aerobic biological treatment meets all of these requirements, and bench-scale application of this technology to several flowback and produced water samples is examined in this dissertation.

1.8.1 Hypothesis 1: Method Development

1.8.1.1 Approach

Chapter 3 describes the process of developing a solid phase extraction method applicable to hydraulic fracturing flowback and produced waters. Seven commercially available solid phase extraction cartridges were considered: HLB (Waters), C-18 (Agilent), PAX (Agilent), MCX (Waters), Evolute (Biotage), Carbon (Supelco), and PPL (Agilent). These cartridges were evaluated for their ability to desalt and concentrate the analytes of interest (common fracturing fluid additives). First, a DOC breakthrough curve was generated for each cartridge for up to 50 mL of filtered sample. Based on the results from this breakthrough curve, a loading volume was determined and evaluated for four different samples with different organic and salt contents. Then, to limit the amount of salt in the extract as much as possible, the conductivity of the rinse step was measured to determine an adequate rinse volume. After the mechanics of the method were determined, recoveries of ubiquitous hydraulic fracturing fluid additives were measured using liquid chromatography mass spectrometry (LC-MS) from extracts from four samples for cartridges that yielded low DOC breakthroughs at the determined loading volume. A cartridge recommendation was made based on these results. Then, using the developed method, one of the samples was spiked into a groundwater source at 1:200 and 1:1,000 dilutions. Each of these dilutions was processed using the developed method and recoveries were again calculated for the fracturing fluid additives.

1.8.1.2 Results

The results of the DOC breakthrough curve showed MCX, PAX, and Evolute with >95% DOC breakthrough after loading 10 mL of sample, and HLB, C-18, PPL, and Carbon with 57.0%, 87.7%, 65.4%, and 43.5%, respectively. Based on these results, a loading volume of 10 mL was deemed appropriate and four cartridges (HLB, C-18, PPL, Carbon) warranted further study for recovery of fluid additives. The conductivity of the rinse showed that >99% of the salt content was removed after 10 mL of rinse. With the loading volume and rinse volume determined, extracts were prepared using the developed method for four cartridges and four different samples. The steps of the method were: (1) Condition cartridge with 5 mL methanol, (2) equilibrate with 5 mL water, (3) load 10 mL of filtered sample, (4) rinse with 10 mL water, (5) elute with 5 mL methanol, and (6) concentrate with N_2 to 0.5 mL. Concentration from 10 mL to 0.5 mL represents a 20x volumetric concentration. The samples included two produced water samples from Oklahoma, one flowback water from Oklahoma, and one flowback water from Colorado. The samples ranged from 38 – 610 mg/L DOC and 24,700 – 157,100 mg/L TDS, encompassing the broad spectrum of water qualities encountered with flowback and produced water.

Each sample contained at least two of the following common hydraulic fracturing fluid additives/metabolites: PEGs, PEG-carboxylates, PEG-amines, PEG-amine-carboxylates, LAEs (various lengths), and PPGs. Recoveries were determined by dividing the peak area in the extract by the peak area in the pure sample. PEGs were present in all samples and recoveries were <20× for the smaller PEGs but increased for larger PEGs to >20× in some cases. The concentration factors were higher for samples with a higher TDS and the extraction enabled detection of the largest PEG and PPG homologues for the saltiest samples. Recoveries for cartridges varied: HLB showed the highest recoveries across all samples, followed by C-18, PPL, and Carbon. PEG-carboxylates were detected in three samples. They were not recovered at all in Carbon extracts for

any samples. Recoveries were highest for HLB and PPL extracts of the saltiest samples and the effect was increased for the longest PEG-carboxylates. PEG-amines were detected in two samples. Contrasting with the PEG-carboxylates, Carbon gave the best recoveries of these compounds, and increased with larger PEG-amines, followed by HLB. Extracts with C-18 and PPL showed poor recoveries of PEG-amines. LAEs were detected in only one sample and HLB gave the best recoveries of these compounds, in all cases >20×, followed by C-18. PPL and Carbon yielded almost no recovery or recoveries <3.0×. PPGs were detected in one sample and HLB, C-18, PPL, and Carbon all gave very comparable recoveries <20×, but Carbon recoveries dropped for larger PPG homologues. These results were used as a basis to recommend HLB as the preferred cartridge because it recovered all compounds considered, from the most hydrophilic (PEG-amines) to the most hydrophobic (LAEs).

Using HLB, extractions of a 1:200 (Dilution A) and 1:1,000 (Dilution B) dilution of the Colorado flowback sample were performed using the method with a loading volume of 100 mL. Based on a mass balance, recoveries were expected to be 1.0 for Dilution A and 0.20 for Dilution B if all the mass of the compound were recovered. PEGs, PEG-carboxylates, PEG-amines, PEG-amine-carboxylates, and PPGs were recovered from both dilutions: Dilution A showed an average recovery of 0.85 ± 0.09, 0.96 ± 0.40, 0.97 ± 0.30, 0.84 ± 0.24, and 1.37 ± 1.01, respectively; Dilution B showed an average recovery of 0.32 ± 0.14, 0.37 ± 0.33, 0.25 ± 0.14, 0.22 ± 0.11, and 0.39 ± 0.35, respectively. These results show almost complete recovery of the compounds of interest for both dilutions and show that, in some cases, dilution/extraction increased the mass spectrometric signal over the pure sample.

These results confirm Hypothesis 1, that sample preparation with solid phase extraction reduces the impact of salt on detection and enhances mass spectrometric signal of these compounds. It also provides a developed method that can be used across hydraulic fracturing

flowback and produced samples with a wide spectrum of DOC and TDS concentrations and can be used in diluted environmental samples. Next, the method was used to explore parts of the total ion chromatogram for produced water samples to identify previously undisclosed proprietary fluid additives.

1.8.2 Hypothesis 2: Compound Identification

1.8.2.1 Approach

Chapter 4 describes the techniques used to identify three new ethoxylated surfactant classes used as proprietary additives in hydraulic fracturing fluid and the utility of the method developed in Chapter 3 when used with a more sensitive mass spectrometer (QTOF). The method developed in Chapter 3 was used to enhance the mass spectrometric signal of the sample. Attention was focused on the early eluting compounds (retention time of <10 minutes, the "hydrophilic" portion) because this was the part of the chromatogram that would be most susceptible to obfuscation by high salts. The largest series of peaks in this section revealed molecular ions separated by 44.0262 mass units – the exact mass of ethylene oxide. Further investigation revealed two other series of early eluting ions separated by the same mass. The identity of these compounds was determined using a combination of accurate mass, MS-MS, comparison of accurate mass and chromatography to standards, and application of the Kendrick mass defect. Their purpose in fracturing fluids was investigated using literature research, and their presence in twenty samples from five basins was tested.

1.8.2.2 Results

The method again gave excellent recovery of the common fluid additives studied. The trends were the same in that there were higher recoveries for longer ethoxylated and propoxylated additives and higher recoveries in saltier samples. The recoveries were higher due to the increased sensitivity of the instrument. Non-targeted analysis began with the most prominent peaks. The most prominent peaks were identified as PEG-amines with nominal masses from *m/z* 150-986. Less prominent peaks were identified as PEG-amine-carboxylates with nominal masses from *m/z* 252-912, and amino-PEG-amines with nominal masses from *m/z* 193-677. The average mass accuracy for all of these compounds was 0.55 ± 0.51 ppm, illustrating the advantage of using accurate mass as a tool for identification. Almost all of these compounds were shown to have at least one isomer, with many having several, up to seventeen for PEG10-carboylate-amine, for a grand total of 245 compound identifications. Other insights were revealed throughout the study related to the fragmentation of each of these compounds and further confirmed a diagnostic ion that can be used to identify carboxylated ethoxylate compounds in future research.

The FracFocus report (obtained from well identifying information provided by industry partner) did not specifically mention these compounds by name or CAS number but included several additives as “proprietary” or a “trade secret” for compounds with the purpose of “friction reducer”, “acid corrosion inhibitor”, and “permanent clay stabilizer”. Investigation into the purpose these additives could serve in a fracturing fluid revealed several patents and peer-reviewed literature that showed they have been used as shale hydration inhibition agents, friction reducers, thickeners, and clay stabilizations agents. However, without standards from producers, their definitive purpose is unknown. We checked for their presence in twenty fracturing flowback and produced water samples from eight basins and five states. PEG-amines were detected in all of the

samples, PEG-amine-carboxylates were detected in thirteen, and amino-PEG-amines were detected in two.

These results confirm Hypothesis 2, that sample preparation would enable the detection of new fracturing fluid additives. Identification of these additives adds more compounds to the "fingerprinting suite" of additives that are commonly found in flowback and produced waters so they could be used as an indicator of water resource contamination or indications of treatment through a treatment system. Because of the hydrophilic nature of these compounds, they are likely to be more mobile in the environment and could be a good indication of surface or groundwater contamination. The next step in the research was to research to what extent these ubiquitous fluid additives moved through an aerobic biological treatment system.

1.8.3 Hypothesis 3: Biological Treatment

1.8.3.1 Approach

Chapter 5 shows the aerobic biodegradability of organic matter and ethoxylated surfactants from three hydraulic fracturing wastewaters in a sequencing batch reactor (SBR). The samples were sampled from wells accessing the Anadarko Basin in Oklahoma and included one flowback water (designated "PR": 420 mg/L DOC; 26,400 mg/L TDS), one early stage produced water (designated "VL": 180 mg/L DOC; 96,200 mg/L TDS), and one late stage produced water (designated "CR": 29 mg/L DOC; 157,100 mg/L TDS). These samples were chosen because they are representative of the spectrum of DOC and TDS concentration expected in flowback and produced waters. SBRs were seeded with activated sludge collected from the 75th Street Wastewater Treatment Facility in Boulder, Colorado. The microbial community was slowly acclimated the salt content of the waters by feeding an additional 4,000 mg/L TDS every other day

until reaching the full concentration of the water. After acclimation, DOC and LC-MS samples were collected at regular intervals and analyzed to determine degradation rates and pathways. Each water sample went through three treatment cycles with cycle times determined by their DOC and salt content.

1.8.3.2 Results

The tests showed that 50-80% of the DOC in these flowback and produced waters was readily biodegraded under aerobic conditions. In the first treatment cycle, DOC degradation for PR showed a maximum of 83% removal in the first 12 hrs of treatment, 73% in 120 hrs for VL, and 67% in 12 hrs for CR. The following two cycles showed equivalent DOC reduction for PR and CR, but it took longer in PR, likely due to the long treatment cycle. VL only achieved a maximum of 52% DOC degradation in the next two cycles. First order rate coefficients (k) were fitted to the data and were 0.260 ± 0.037/hr, 0.056 ± 0.011/hr, and 0.019 ± 0.004/hr for PR cycle 1, 2, and 3, respectively; 0.083 ± 0.053/hr, 0.072 ± 0.016/hr, and 0.047 ± 0.013/hr for VL; and 0.281 ± 0.092/hr, 0.317 ± 0.070/hr, and 0.262 ± 0.100/hr for CR. PEGs and PEG-amines were also degraded to some extent in the SBRs. The microbial degradation pathway for PEGs involves oxidizing the terminal alcohol groups to carboxylic acid groups via alcohol and aldehyde dehydrogenase and then cleavage of the terminal ether bond to produce a shorter PEG (termed "PEG shortening"). PEGs were shown to degrade in all reactors, but degradation did not move past the PEG-dicarboxylate, which persisted for all treatment cycles. PEG-amines were shown to quickly degrade in PR, and were transformed to PEG-amine-carboxylates, suggesting that they were a biological degradation product rather than a fluid additive. Overall this shows that a culture well acclimated to highly saline environments can degrade DOC in flowback and produced waters.

However, it is unsure if the remaining 20-50% of DOC remaining after degradation would be a problem for downstream processes like membranes.

CHAPTER 2: CHARACTERIZATION OF SAMPLES COLLECTED

This chapter describes the methods and results of the characterization of the flowback and produced waters collected and used in these studies, including the organic and inorganic composition, region they were collected from, and the age of the well at the time of collection.

2.1 Introduction

The research contained herein is part of a larger collection of research that sought to take a holistic approach to understanding the environmental, economic, and social tradeoffs of oil and gas development. The overall objective was to incorporate research findings and outcomes into policies and regulations related to this industry. Twelve topic-focused research teams were assembled from ten universities and national labs across the country, with each performing research relating to their research specialty. In particular, the work here is part of the water quality and water treatment efforts of this National Science Foundation Sustainability Research Network known as AirWaterGas.

Integral to the success of this research was obtaining sufficient quantities of hydraulic fracturing flowback and produced water samples. At the beginning of this research project, experimentation was limited by a lack of access to any flowback and produced water samples. The first sample ever received was <1L in volume collected from an unknown well in Colorado. Over time, the networking efforts of team members and research partners enabled access to and collection of large volumes (estimated at >500 L total) of water that enabled a better understanding of the variability in flowback and produced water composition and treatment studies that required large volumes of water.

When this research began (2012), oil and gas companies were hesitant to provide samples of flowback and produced waters to academic researchers for characterization and treatment studies. Thanks largely to networking efforts of Dr. James Rosenblum, a postdoctoral researcher on the project at the time, we were eventually able to obtain samples at volumes that would enable thorough study. Initially the samples came from an operator in the Denver-Julesburg Basin in Colorado with little information on its origin besides the well age. Eventually, the network grew and the project gained access to several wells in the Denver-Julesburg Basin, as well as samples

from the Bakken (North Dakota), Anadarko (Oklahoma), and Marcellus (Pennsylvania) shale formations. Over the course of the project, we obtained dozens of samples. The samples described in this chapter are only those that were used to perform the research in these studies. But, with the experience of studying several flowback and produced waters, we believe they represent the types of water generated by hydraulic fracturing. In all cases, the producers required that their identity remain confidential.

2.2 Collection

During the project, samples were both collected by others and shipped, or collected directly by someone on the project. Collecting samples of flowback and produced water require the cooperation and presence of a company representative to grant access to the well and well pad. This is both a requirement by law (well pads are private property) and helpful for collection because wells and well pads can be a very confusing assortment of pipes, tubing, and valves that would make it impossible to know where to collect water from without guidance. Regulations require everyone on a well pad wear personal protective equipment including fire retardant clothing, appropriate footwear, safety glasses, and head protection (i.e. a hard hat). After meeting the company representative and preparing the sampling equipment, the sample was collected and transported back to the lab.

All samples were collected from either the separator or tank battery on the well pad with the exception of one sample that was collected from a centralized disposal facility. For lower volume samples (<5 L), samples were collected in new or furnaced amber glass bottles, capped, and preserved on ice until they reached the lab, where they were stored at 4°C for further analysis. For larger volume samples (>5 L), samples were collected in 5-, 15-, or 55-gal PTFE drums and sealed; these were the samples that were used for treatment studies, including the biological

treatment studied described in Chapter 5. Due to the logistics in chilling these large containers, they were not chilled during transportation, but all efforts were made to get them to a refrigerator as quickly as possible (<4 hr). Alongside these large volumes, smaller aliquots were collected in new or furnaced amber glass bottles for the purpose of limiting storage vessel contamination of the sample for mass spectrometric analysis.

In many cases, an advantage to collecting the sample in person enabled collection of valuable identifiers about the well (e.g. API number) due to the signage around the wellhead. This made retrieving a FracFocus report for the well straightforward and gave insight into the age and other information about the well. It also allowed researchers to meet and talk with individuals who are involved in the day-to-day operations of hydraulic fracturing. Over the years, these conversations provided insight and perspective into the state of the industry, the types of fluids that are being used, and their general disposition about the hydraulic fracturing as viewed by the public. This added depth and value to the overall experience as someone researching hydraulic fracturing wastewater streams.

2.3 Methods of Analysis

After receiving the samples back in the lab, a plan was formed to begin characterization of the samples. Samples were analyzed for bulk characteristics and individual analytes. A summary of the type of analysis performed and the method/instrumentation used is presented in Table 2.1. The following sections describe methods used for mass spectrometric analysis that can not be adequately described in a table. Parts of these sections were taken from publications that used these samples.

Table 2.1: Summary of methods used to characterize flowback and produced water samples obtained for this research.

Analyte	Method/Instrument
pH	ThermoSci Orion Meter
Turbidity	Standard Method 2130/Hach Turbidimeter 2100N
TOC/DOC	Shimadzu TOC-V CSH/NDIR-combustion
Volatile Organic Compounds (VOCs)	EPA Method 8260C/Agilent 6890 & 7890 GC-MS
Chemical Oxygen Demand (COD)	Hach Method 8000/Hach DR5000
Total Suspended Solids (TSS)	Standard Method 2540D
Volatile Suspended Solids (VSS)	Standard Method 2540E
Total Dissolved Solids (TDS)	Standard Method 2540C
Major Cations	LEGS Lab ICP-AES/ThermoSci ARL 3410+
Anions	Ion Chromatography/Dionex Series 4500I
Metals	LEGS Lab ICP-MS/Perkin Elmer SCIEX Elan DRC-e

2.3.1 High-Resolution Mass Spectrometry

Significant portions of the research performed on these samples required the use of high-resolution mass spectrometry to make determinations and inferences about the dissolved organic compounds present in these samples. The Center for Environmental Mass Spectrometry located on the University of Colorado Boulder campus provided instrument time and uses liquid chromatography in tandem with quadrupole time-of-flight mass spectrometry (LC-QTOF-MS). The use of this analytical technology was fundamental to the results and analysis presented in Thurman et al. [65, 76, 111], Rosenblum et al. [74, 112], Rogers et al. [113], and Sitterley et al. [67], all of which used samples collected for this project in some way. The LC-QTOF-MS method used in each of these studies was similar (though the instrument used has been updated over time), and the most recent version is summarized in the following paragraph, taken from Sitterley et al. [67].

The separation of the analytes was carried out using an ultrahigh performance liquid chromatography (UHPLC) system consisting of thermostated autosampler, column department,

and a binary pump (Agilent Series 1290; Agilent Technologies; Santa Clara, CA) equipped with a reverse phase C8 analytical column of 150 mm × 4.6 mm and a 3.5 μm particle size (Zorbax Eclipse XDB-C8). Column temperature was maintained at 25°C. The injected sample volume was 20 μL. Mobile phases A and B were water with 0.1% formic acid and acetonitrile, respectively. The optimized chromatographic method held the initial mobile phase composition (10% B) constant for 5 min, followed by a linear gradient to 100% B after 30 min. The flow rate used was 0.6 mL/min. A 10 min postrun was used after each analysis. This UHPLC column was connected to an ultrahigh definition quadrupole time-of-flight mass spectrometer model 6545 Agilent (Agilent Technologies; Santa Clara, CA) equipped with electrospray Jet Stream Technology, operating in positive ion mode, using the following operation parameters: capillary voltage, 4,000 V; nebulizer pressure, 45 psig; drying gas, 10 L/min; gas temperature, 250°C; sheath gas flow, 11 L/min; sheath gas temperature, 350°C; nozzle voltage, 0 V; fragmentor voltage, 175 V; skimmer voltage, 65 V; octopole RF, 750 V. LC/MS accurate mass spectra were recorded across the range 50-1,000 *m/z* at 2 GHz. The data recorded were processed with MassHunter software (version 6.1). Accurate mass measurements of each peak from the total ion chromatograms were obtained by means of an automated calibrant delivery system using a low flow of a calibrating solution (calibrant solution A, Agilent Technologies, Inc.), which contains the internal reference masses (purine at *m/z* 121.0509 and HP-921 at *m/z* 922.0098). The instrument provided a typical mass resolving power of 30,000 at *m/z* 922.

2.3.2 Elemental & Inorganic Ion Analysis

A defining characteristic of flowback and produced water samples is the presence of high concentrations of salt. Though most of the studies that came from this research project concerned the organic portion of these waters (with the exception of Rosenblum et al. [58]), it was important

to have inorganic information to know if there were substances that would interfere with other analysis. For example, chloride data was needed to know the proper dilution factor when preparing samples for COD determination using the colorimetric method. On account of a lack of proper instrumentation in-lab, samples for elemental and inorganic ions were sent to the Laboratory for Environmental and Geological Studies (LEGS lab), located in the Department of Geological Sciences at the University of Colorado Boulder. This lab is local and has been used in several studies characterizing flowback and produced water [58, 70, 102, 114, 115], and a brief description of their methods and instrumentation was adapted from Rosenblum et al. [58].

Prior to analysis, samples were filtered using 0.45 μm PTFE filter and diluted 1:10 and/or 1:100. Trace elements and metals were measured by inductively coupled plasma-mass spectrometry (ICP-MS; Perkin Elmer SCIEX Elan DRC-e), anions were measured by ion chromatography (IC; Dionex Series 4500I), and major cations were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES; ARL 3410+, Thermo Scientific).

2.3.3 Dissolved Organic Carbon Measurement

The measurement of dissolved organic carbon (DOC) was essential and used extensively in the research presented here. Samples prepared for DOC analysis were filtered through 0.45 μm nylon filter and diluted from between 1:3-1:20, depending on the salt and DOC content of the sample. DOC was measured as non-purgeable organic carbon (NPOC) using a Shimadzu TOC-V CSH with the non-dispersive infrared (NDIR)/combustion method. This method requires pre-acidification of the sample to pH < 3 with 6N hydrochloric acid to oxidize inorganic carbon (IC), purging the IC with zero air, and then sending the sample to a combustion tube at 680 °C where the remaining organic carbon is combusted, and the CO_2 generated is measured with an NDIR

detector. Sample runs for DOC included several standards prepared using potassium hydrogen phthalate (KHP) and the majority of the samples were analyzed in duplicate.

The complex nature of flowback and produced waters made measurement of DOC a tricky endeavor throughout the project. Since flowback and produced waters can contain high concentrations of volatile organic compounds (VOCs), these were lost during measurement of DOC as NPOC. However, this was considered less of an issue for the purposes of the research presented here for three reasons: (1) the concentration of VOCs was measured by other methods, both in third-party labs and in house, (2) the methods development described in Chapter 3 was targeting dissolved compounds amenable to LC-MS, which does not apply to VOCs, and (3) the biological treatment studies involved constant aeration, so VOCs were purged as a result. It was also a challenge at times to strike a balance between the levels of dilution necessary to avoid interference from salts and ensuring that the range of measured values would be in the detection limit for the method. This was most of an issue for the highest salt sample used in this research because it also contained low DOC. Additionally, throughout the course of the research presented here, hundreds of samples (most in duplicate) were analyzed with the Shimadzu TOC-V CSH analyzer. The high salts lead to more rapid degradation of the platinum catalyst that required regeneration and replacement more often, quick oxidation of the combustion tube leading to cracks, rusting and corrosion of fittings, precipitation of salts in tubing, and standard drift over the course of a run that necessitated re-analysis and regular recalibrations with standard curves.

2.4 Characterization Results

2.4.1 Well Location and Age

The designation, location collected, formation accessed, age, and classification of each of the samples used in this research are presented in Table 2.2. Two samples were collected from wells accessing the Meramec and Osage formations in the STACK play in Oklahoma, and one was collected from the Denver-Julesburg Basin. Well age (as defined as the time since flowback began) ranged from <30 days to 240 days, so includes both flowback and produced waters. The exception in the table is the SWD sample, which was collected from a central facility in Oklahoma that collected, stored, and then disposed of flowback and produced waters from the Meramec and Osage formations. The first three samples listed – PR, CR, and VL – are the primary samples used for method development and biological treatment studies in this research.

Table 2.2: Sample designations, location and formation of origin, age, and classification for the flowback and produced water samples used in this research.

Sample	Location	Formation	Age	Classification
PR	Oklahoma	Meramec	30 days	Flowback
CR	Oklahoma	Osage	240 days	Produced
VL	Oklahoma	Osage	92 days	Produced
MAR	Oklahoma	Meramec	98 days	Produced
SWD	Oklahoma	Mix	Mix	Mix
JR5	Colorado	Niobrara	30 days	Flowback

2.4.2 Bulk Characterization

The pH, turbidity, DOC, COD, and solids analysis for each of these samples is summarized in Table 2.3. The measurements for each of these analytes falls within the range of flowback and produced waters previously published, so are thought to be good representations of this water matrix [24, 70, 116]. They also follow the general trend published in Rosenblum et al. [58] showing decreasing DOC and increasing TDS over time.

Table 2.3: Bulk characterization results for the flowback and produced water samples used in this research.

Sample	pH	Turbidity (NTU)	DOC (mg/L)	COD (mg/L)	TSS (mg/L)	TDS (mg/L)	VSS (mg/L)
PR	7.4	265	350	1,650	425	26,400	265
CR	6.4	460	30	5,050	1,940	157,100	580
VL	6.5	440	180	5,050	1,330	96,200	670
MAR	7.5	190	220	1,460	550	25,640	380
SWD	7.6	65	135	920	357	13,680	93
JR5	6.8	320	680	2,150	850	24,700	780

2.4.3 Volatile Organic Compounds

Several VOCs were detected in the Oklahoma samples, presented in Table 2.4. This analysis was not performed for JR5 because proper samples were not collected when the well was sampled (i.e. headspace free 40 mL VOA vials). BTEX compounds and toluene specifically were detected in the highest concentrations for all the Oklahoma samples. VL and CR, the two produced water samples had the highest cumulative concentrations of VOCs. Since they are produced waters, there is a higher concentration of formation water along with oil and gas.

2.4.4 Inorganic Ions

Table 2.5 presents the inorganic ions detected in these samples. Chloride is the most dominant ion and represents between 57.7% (MAR) and 70.9% (JR5) of the total TDS content independent of well age, which is in agreement with previous research [58, 80]. Sulfate was a dominant ion for the two waters accessing the Osage formation (PR and MAR) but not for those accessing the Meramec or Niobrara formation (CR, VL, and JR5), so this may be related to subsurface geology or fracturing fluid formulation, or the age of the well [58]. Notably, phosphate was not present in any of the Oklahoma waters except SWD, which was taken from a centralized facility.

Table 2.4: Concentrations of common volatile organic compounds in flowback and produced water samples used in this research. All values in µg/L. N.D. = non-detect. VOC analysis was not performed on JR5 at the time of collection.

Sample	Benzene	Toluene	Ethyl-benzene	m,p-Xylene	o-Xylene	1,2,4-Trimethyl-benzene	1,3,5-Trimethyl-benzene	4-Isopropyl-toluene	Acetone	Isopropyl-benzene	Naph-thalene	n-Butyl-benzene	n-Propyl-benzene	sec-Butyl-benzene
PR	1750	1950	167	816	375	290	94	11.0	N.D.	30.3	21.3	12.6	44.2	10.1
CR	3110	17400	116	1510	571	129	74	2.0	103	8.7	9.5	3.0	15.6	2.0
VL	5860	16800	1340	12400	4200	3760	1960	7.0	821	163	N.D.	10.8	669	13
MAR	1730	3270	155	1510	644	386	119	4.4	N.D.	13.9	10.1	3.5	25.5	4.5
SWD	2850	5900	136	2840	784	370	196	4.0	713	11	9.5	6.0	15.5	2.8

Table 2.5: Concentration of dominant and common inorganic anions in flowback and produced water samples used in this research. D.L. = below detection limit for method/instrumentation.

Sample	Chloride (mg/L)	Bromide (mg/L)	Phosphate (mg/L)	Sulfate (mg/L)	Nitrite (mg/L)	Nitrate (mg/L)
PR	15,300	200	D.L.	1,590	D.L.	1.0
CR	98,500	D.L.	D.L.	385	D.L.	D.L.
VL	60,400	250	D.L.	730	D.L.	145
MAR	14,800	260	D.L.	1,700	D.L.	1.2
SWD	8,800	150	6.3	460	D.L.	3.2
JR5	17,500	190	7.2	8.5	D.L.	D.L.

Table 2.6: Concentration of dominant metals in flowback and produced water samples used in this research.

Sample	Barium (mg/L)	Calcium (mg/L)	Magnesium (mg/L)	Strontium (mg/L)	Manganese (mg/L)	Iron (mg/L)	Potassium (mg/L)	Silicon (mg/L)	Sodium (mg/L)
PR	0.2	81	80	41	0.2	2	98	28	9,200
CR	9.6	10,200	1,150	635	1.8	24	1,200	14	43,300
VL	3.9	4,300	610	310	0.7	7.8	730	27	28,800
MAR	0.3	560	63	37	0.2	4.4	135	35	9,000
SWD	2.4	83	18	19	0.2	D.L.	120	39	5,300
JR5	41	550	71	78	1	3	52	32	10,400

2.4.5 Metals

The ICP-MS and ICP-AES analysis included a full scan of every element, but the elements with highest concentration and/or of interest for their scaling potential are presented in Table 2.6. Sodium is the metal detected at highest concentrations and represents between 27.5% (CR) and 42.1% (JR5) of the TDS content, and sodium chloride was calculated to be >92% of the total TDS content for all samples. Magnesium, strontium, barium, and calcium are all scale causing ions that are targets for removal when flowback and produced water are treated for reuse [92, 93, 117]. These ions are detected as higher proportions of the TDS in older samples (CR and VL) than younger samples (PR, MAR, and JR5), which could prevent challenges for reuse. These challenges would be related to the impact of scale on equipment rather than an impact on fracturing fluid formulation because high TDS waters have been shown to be adequate for successful fracturing fluids [97, 118-121].

2.4.6 Fracturing Fluid Additives

The presence or absence of common hydraulic fracturing fluid additives and their metabolites was done using high-resolution mass spectrometry and is presented in Table 2.7. PEGs, PEG-amines, PPGs, LAEs, and their carboxylated metabolites are detected in most samples and are the most commonly detected known additives in flowback and produced waters [57, 65, 67]. The ubiquitousness of these compounds in samples of all ages and origin warrants methods that enable their detection in pure and environmentally diluted samples, and determination of their biological degradability.

Table 2.7: Presence or absence of common fluid additives considered in this work in each of the flowback and produced water samples used in this research.

Sample	PEGs	PEG-carboxylates	PEG-amines	PEG-amine-carboxylates	Amino-PEG-amines	PPGs	LAEs
PR	Yes	Yes	Yes	Yes	No	Yes	Yes
CR	Yes	Yes	Yes	No	No	Yes	No
VL	Yes	Yes	Yes	Yes	No	Yes	Yes
MAR	Yes	Yes	Yes	Yes	No	Yes	Yes
SWD	Yes	Yes	Yes	Yes	Yes	Yes	Yes
JR5	Yes	Yes	Yes	Yes	Yes	Yes	No

2.5 Summary and Sample Use

The data presented in this chapter is meant to provide a brief summary into the methods and results of characterization efforts of the samples collected over the course of this project. The samples used for the method development, compound identification, and biological studies presented in the following chapters are: JR5, PR, VL, SWD, and CR. These samples were chosen because of their variable characteristics and because they contain several of the fluid additives that are present in flowback and produced waters.

CHAPTER 3: DESALTING AND CONCENTRATION OF COMMON HYDRAULIC FRACTURING FLUID ADDITIVES AND THEIR METABOLITES WITH SOLID PHASE EXTRACTION

This chapter describes the development and application of a solid phase extraction method for enhancement and detection of common hydraulic fracturing fluid additives.

This work will be published following manuscript review by co-authors:

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3.1 Introduction

Exploitation of unconventional sources of oil and natural gas, such as coalbed methane, shale, and tight gas formations, has surged in recent years [122]. Hydraulic fracturing is commonly used to access these formations. This technology involves drilling a well and injecting a fracturing fluid at sufficiently high pressures to perforate the formation and allow oil and gas to flow to the surface [123]. Additives in this fluid mix with the native groundwater from the geologic formation and return to the surface as produced water in two phases: first during well development and then during oil and gas production [58]. From a water management perspective, characterizing waste streams is important in the event of an environmental release or if the water is to be treated before reuse or discharge to the environment.

The extreme variability in water quality and complex nature of flowback and produced waters present challenges for conventional analytical methods typically used to detect and quantify dissolved organic compounds. Aside from measurements of the bulk organic content, like dissolved organic carbon (DOC) or chemical oxygen demand (COD), specific non-volatile compounds are separated and detected using reversed phase liquid chromatography (LC) coupled to an ultraviolet (UV) absorbance detector or quadrupole-time-of-flight (QTOF), Orbitrap, or Ion Trap mass spectrometric detector [77]. Direct injection of waters with high salt and high organic content can lead to poor chromatography, column and instrument damage, reduced sensitivity, undesirable adduct formation (e.g. sodium, ammonium, potassium) [78], and increase the minimum detection limit, leading to non-detect of compounds that are actually present [79]. To mitigate some of these detrimental effects, researchers have used dilution, filtration [65, 70, 72, 74, 76, 112], centrifuge direct injection [39, 80], and solid phase extraction (SPE) [38, 67, 68, 77, 81]. These methods have the advantage of being easy and straightforward and have been successful for identifying major additives in hydraulic fracturing wastewaters. Recently, Nell and Helbling

[78] did valuable work quantifying the matrix effects of ionization and adduct formation tendencies of seventeen fluid additives. Quantified methods for non-volatile organic compounds have been developed for citric acid, acetate, butyrate, propionate [82], and most recently, for benzalkonium chloride (ADBAC), polyethylene glycols (PEGs), and polypropylene glycols (PPGs) [78].

However, there is yet no consensus on a standard method that will achieve detection of non-volatile dissolved fluid additives commonly detected in flowback and produced water samples. Thacker et al. [68] used Supelclean LC-18 SPE cartridges with unfiltered samples to perform liquid, gas, and ion chromatography, but did not detect any of these common additives. Cluff et al. [81] used SEP C-18 cartridges for detection of ethoxylated surfactants but did not mention which ethoxylated surfactants or make attempt at quantifying recovery. Further, no attempts have been made at detection of these additives in environmentally diluted samples (e.g. surface and groundwater) using solid phase extraction. McLaughlin et al. [124] used microcosm experiments with synthetic surface water spiked with PEGs to determine the fate in the environment but diluted the samples prior to direct injection. Rogers et al. [125] measured degradation kinetics of PEGs and PPGs in groundwater, but also used diluted direct injection for analysis. Indeed, there is a need for a consistent method that can desalt, concentrate, and detect common and unidentified hydraulic fracturing additives in pure and environmentally diluted samples, as mentioned in Ferrer and Thurman [123].

The distinct objectives of this work were (1) to test different solid phase extraction sorbents for their ability to desalt and retain the DOC in hydraulic fracturing fluids, (2) develop and outline a solid phase extraction method that enables detection of common hydraulic fracturing fluid additives and their metabolites, (3) to examine the recovery of these fluid additives from diluted groundwater samples.

3.2 Materials and Methods

3.2.1 Sample Collection

Four produced water samples were used for method development. Samples were collected in amber glass containers and stored at 4°C until time of analysis. Samples were filtered through surfactant-free 0.45 μm Acrodisc PTFE filters (PALL Corp.; Port Washington, NY) prior to preparation and analysis. All of the sampled wells were hydraulically fractured and come from Oklahoma, accessing the Osage or Meramec formation, or from Colorado, accessing the Niobrara formation. These samples were selected for this work because they collectively contain identified and commonly detected hydraulic fracturing fluid additives, thus enabling recovery estimates for all of the compounds of interest. They also span the spectrum of DOC and TDS content that can be expected from flowback and produced waters from hydraulically fractured wells.

3.2.2 Solid Phase Extraction Cartridges Tested

The SPE cartridges tested contained 500 mg of their respective sorbents. They included Supelco Carbon (Sigma Aldrich; St. Louis, MO), PPL, C-18, the ion exchange sorbents PAX (Agilent Technologies, Inc.; Santa Clara, CA) and MCX (Waters Corporation; Milford, MA), and the polymeric sorbents Evolute (Biotage USA; Charlotte, NC), and HLB (Waters Corporation; Milford, MA). These cartridges were selected because they are both readily available and contain sorbents capable of capturing dissolved organic carbon (DOC) with an assortment of characteristics, as the nature of the majority of the DOC in hydraulic fracturing samples is unknown and complicated.

3.2.3 DOC Breakthrough

Determining the loading volume for a solid phase extraction method is a crucial and defining step in the method's utility [126]. A full breakthrough curve was done with the JR5 sample to determine DOC breakthrough for all cartridges. After determination of a loading volume, DOC breakthrough was analyzed for the other three samples. The DOC breakthrough was generated as such: cartridges were conditioned by passing through 5 mL HPLC grade methanol, rinsing with 20 mL HPLC grade water (Fisher Scientific International Inc.; Hampton, New Hampshire), then loading sample in 2 mL increments and capturing the filtrate in 10 mL glass vials (VWR International; Radnor, Pennsylvania). Prior to DOC analysis, samples were diluted so the salts would be below the limit of the instrument. DOC measurement was done with a Shimadzu TOC-V_{CSH} (Shimadzu Corp.; Kyoto, Japan) with the combustion/NDIR method and regular rinses and calibration with potassium hydrogen phthalate standards. In preparing the breakthrough curve, a 20 mL rinse was found to be necessary to eliminate the potential for methanol to be present in the first few DOC measurements of sample filtrate. The last 5 mL of the water rinse was retained to be the first point on the breakthrough curve (i.e. the "0 mL" data point). Flow through the cartridge was kept at 5 mL/min.

3.2.4 Conductivity Breakthrough

After the sample is passed through the cartridge, a rinse step is necessary to remove salts entrained in the interstitial space formed by media granules. The volume of rinse is important to optimize because excess rinse can remove some of the bonded organic compounds, but insufficient rinse can leave salts that are then eluted with the organic compounds of interest and can interfere with MS analysis. Adequate rinse volume was determined after determining the loading volume from the DOC breakthrough curve. It was determined by first conditioning the cartridge as before,

loading the sample, and then rinsing with HPLC grade water in 2 mL increments, capturing the rinse in test vials, and measuring the conductivity with a conductivity probe. The cartridge was considered adequately rinsed when the conductivity of the rinse water was within an order of magnitude of the ultrapure water. After determination of the rinse volume with JR5, the conductivity of the rinse for other samples was determined.

3.2.5 Elution and Concentration

Following determination of loading volume and rinse volume, the sample can be prepared for mass spectrometric analysis. In this step, the appropriate SPE cartridge is rinsed and conditioned identically as before. The proper sample loading volume (as determined from breakthrough curve) is then passed through the cartridge and the sample filtrate is discarded. Flow rate through the cartridge is identical as before at 5 mL/min. Elution of analytes off cartridge is done with 5 mL of HPLC grade methanol at a flow rate of 1 mL/min. This elution is captured in a glass test vial and then concentrated by N_2 evaporation with a Turbovap LV evaporator (Zymark Corp.; Hopkinton, MA) to a final volume of 0.5 mL, measured gravimetrically. This represents a volumetric concentration of 20× of the DOC over the raw water. The resulting extract was pipetted into a new HPLC vial for analysis.

3.2.6 Mass Spectrometry Analysis and Compound Identification

Fluid additives in pure and extracted samples were separated using an Agilent 1100 series high performance liquid chromatography unit with a reverse phase 150 mm × 4.6 mm C8 analytical column with a 3.5 μm particle size (Zorbax Eclipse XDB-C8) and detected by an Agilent LC/MSD Ion Trap XCT Plus (Agilent Technologies Inc., Santa Clara, CA) with positive ion electrospray ionization. Mobile phase A was HPLC grade water with 0.1% formic acid (Fluka; St. Louis,

Missouri) and mobile phase B was HPLC grade acetonitrile (Honeywell Burdick & Jackson; Morristown, New Jersey). The gradient elution began with 90% A and 10% B for 5 minutes and then was increased to 100% B until 25 minutes, where it was held for 5 minutes at 100% B.

Fluid additives were identified using a combination of chromatography, nominal mass, and adduct formation as presented in previous publications [65, 67, 76]. Concentration factors were evaluated as the peak area in the extract divided by the peak area in the pure sample and is presented as a whole number rather than a percentage. Select recovery extracts and extracts from environmentally diluted samples were analyzed with a quadrupole time-of-flight mass spectrometer to confirm compound identification with accurate mass using the method outlined in Sitterley et al. [67].

3.3 Results & Discussion

3.3.1 Dissolved Organic Carbon Breakthrough

Figure 3.1A (top frame) shows the full breakthrough curve generated with JR5. DOC was used as a total measurement of the retentive capacity of each cartridge. Each point corresponds to a discrete DOC measurement of the water that passed through the SPE cartridge, taken in 2 mL increments. As the measured DOC increases, the percent DOC retained on the sorbent, which is the target for analysis, is decreasing. The DOC of the raw JR5 sample is 610 mg/L, so as the DOC measurements in Figure 3.1A approach 610 mg/L, they are nearing complete breakthrough, indicating that the retentive capacity of that sorbent has been exhausted. Four sorbents (C-18, Evolute, MCX, PAX) approach this limit within the first 10 mL of loaded sample and have completely broken through at 50 mL, showing low retention of the total DOC in this sample. For example, at 6 mL of loaded sample, Evolute, MCX, and PAX show 96.4%, 94.7%, and 92.4%

breakthrough, respectively, whereas Carbon, PPL, and HLB show only 39.1%, 58.3%, and 48.2% breakthrough, respectively. HLB, PPL, and Carbon showed an average of 77.8% breakthrough at 50 mL of loaded sample, suggesting that there is still some capacity for DOC remaining on each of these cartridges.

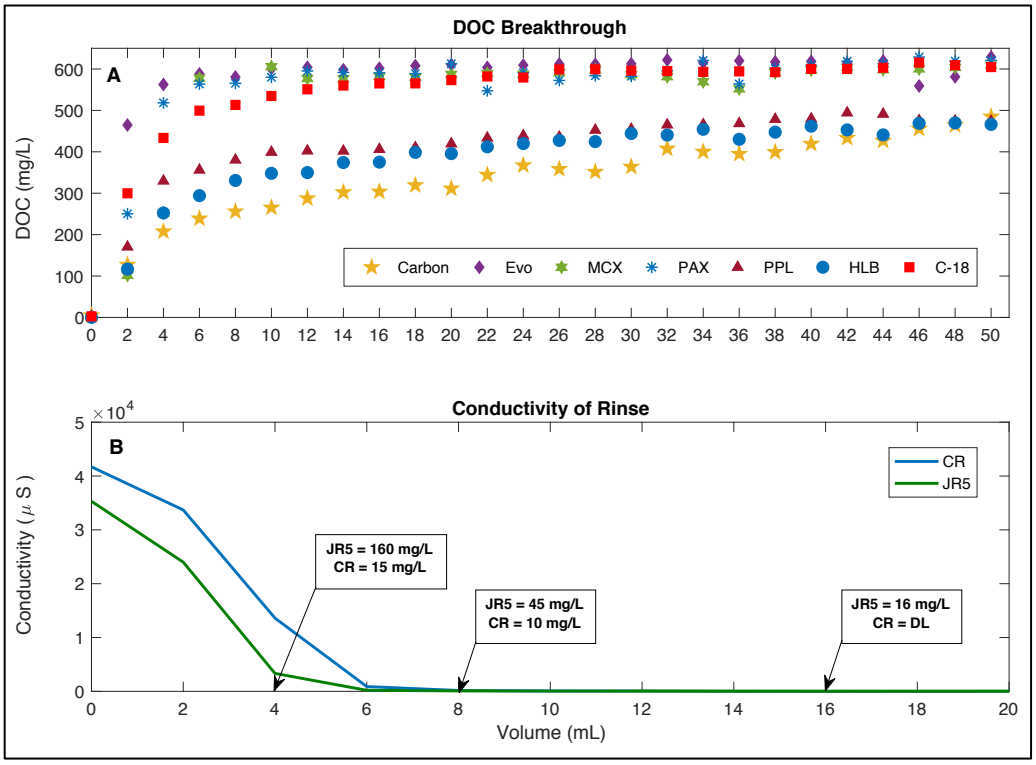

Figure 3.1: (A) DOC breakthrough: Polymeric sorbents HLB (blue circle) and PPL (red triangle), Carbon (yellow star), and C-18 (red square) evaluated for additive recovery. (B) Conductivity of rinse after loading 10 mL of CR (blue line) and JR5 (green line) used to determine loading volume and rinsing volume for solid phase extraction.

Because the sample does not completely break through at the 50 mL point for HLB, Carbon and PPL, 50 mL (or more, due to remaining capacity) might be a logical loading volume for this method. However, because of the high DOC concentration of this sample and hydraulic fracturing fluids in general, concentrating a sample from 50 mL down to 0.5 mL (100× volumetric concentration) would result in an elution with very high DOC, which runs the risk of saturating the MS detector and reducing sensitivity of the instrument. Similarly, overloading the cartridge

can cause some of the more lightly bound, hydrophilic compounds to be washed away, which is an important target of this method because these compounds are likely to be more mobile in the environment. For JR5, HLB, PPL, and Carbon have retained 43.0%, 34.6%, and 56.5%, respectively, of the DOC at this loading volume. C-18 retained only 12.3% at 10 mL loading but was also considered due to its popularity as a sorbent and as an example with different sorbent characteristics (i.e. polymeric vs. silica bonded sorbents). These four cartridges were selected for further experimentation of their potential to enhance hydraulic fracturing fluid additives with JR5 and the other samples.

The breakthrough at 5 and 10 mL was then determined for these cartridges for the other samples. The location, age, DOC, salt content, and DOC breakthrough at 5 and 10 mL of loaded sample for the four samples used in this study are summarized in Table 3.1. Overall, the trend was the same: Carbon, HLB, and PPL retained the most DOC, and C-18 retained the least. The next step in the method development was to determine a proper rinse volume. Then, the recovery of fracturing fluid additives is evaluated.

Table 3.1: DOC, TDS, and conductivity for each of the four samples; DOC breakthrough for each sample and each sorbent at 5 and 10 mL of loaded sample; conductivity reduction at 5 and 10 mL of rinse for each sample and each sorbent after loading 10 mL of sample.

Sample	DOC (mg/L)	TDS (g/L)	Conductivity (mS/cm)	*%DOC Breakthrough 5 mL Loaded Sample*				*%DOC Breakthrough 10 mL Loaded Sample*				*%Conductivity Reduction 5 mL Rinse*				*%Conductivity Reduction 10 mL Rinse*			
				HLB (%)	C-18 (%)	PPL (%)	Carb. (%)	HLB (%)	C-18 (%)	PPL (%)	Carb. (%)	HLB (%)	C-18 (%)	PPL (%)	Carb. (%)	HLB (%)	C-18 (%)	PPL (%)	Carb. (%)
JR5	610	24.7	35.4	44.8	76.4	56.2	36.6	57.0	87.7	65.4	43.4	76.9	90.3	82.1	79.8	99.0	99.8	99.6	99.9
PR	465	26.4	25.4	67.1	88.4	69.7	59.1	88.2	95.5	68.0	75.7	73.1	87.9	79.4	74.3	99.7	99.9	99.8	99.8
VL	185	96.2	44.2	69.7	58.9	41.6	38.9	87.6	68.1	55.1	44.9	32.6	73.3	54.8	49.3	99.4	99.6	99.4	99.6
CR	38	157.1	65.9	68.4	86.8	81.6	78.9	76.3	94.7	81.6	78.9	82.0	90.6	84.0	81.3%	99.8	99.9	99.8	100.0

3.3.2 Determination of Rinse Volume

Figure 3.1B (bottom frame) shows the conductivity of the rinse water passing through each cartridge in 2 mL increments up to 20 mL after loading 10 mL of JR5 (initial conductivity 35,000 µS/cm) and CR (initial conductivity 41,700 µS/cm). Because high salt concentrations are known to suppress electrospray signal in mass spectrometry [78], it is important to not only concentrate the sample but to desalt before mass spectrometric analysis. The conductivity starts near the raw conductance of each water sample and decreases to the conductance of deionized water after approximately 10 mL of rinse. For both samples, the conductance decreases by about an order of magnitude for every 4 mL of rinse and the conductance is near baseline for all points past 10 mL.

Additionally, inset boxes in Figure 3.1B show the DOC of the rinse water at certain intervals. This was measured to account for the possibility that some of the sorbed DOC is being rinsed away. At 4 mL, the rinse of the JR5 cartridge still had 160 mg/L DOC and the CR rinse had 15 mg/L of DOC. This rinsed DOC is a combination of DOC in the water entrained in the pore spaces of the sorbent prior to rinse and some of sorbed DOC. By 8 mL, the JR5 rinse DOC had decreased 3.5× to 45 mg/L, but the CR rinse still contained 10 mg/L DOC – a third of the total DOC. For the method, we used a rinse of 10 mL because the results indicate that most of the salts had been rinsed away by this point, which was a primary objective of the method. Thus, the final method that was developed for the flowback and produced waters in this study involved loading 10 mL of sample followed by a 10 mL rinse and an elution with 5 mL of methanol, which is then concentrated to 0.5 mL for mass spectrometric analysis. The utility of this method for recovery and detection of fracturing fluid additives is discussed in following sections.

3.3.3 Recovery of Hydraulic Fracturing Fluid Additives

Figure 3.2 shows the total ion chromatograms (TIC) for JR5 via direct analysis (i.e. no SPE) and the TIC after preparation with HLB and Carbon SPE cartridges. Despite the differences in DOC breakthrough between these four cartridges, the TIC results suggest that they have been concentrated to some extent for all the compounds in the TIC. Concentration factors for different fluid additives are presented in the following sections.

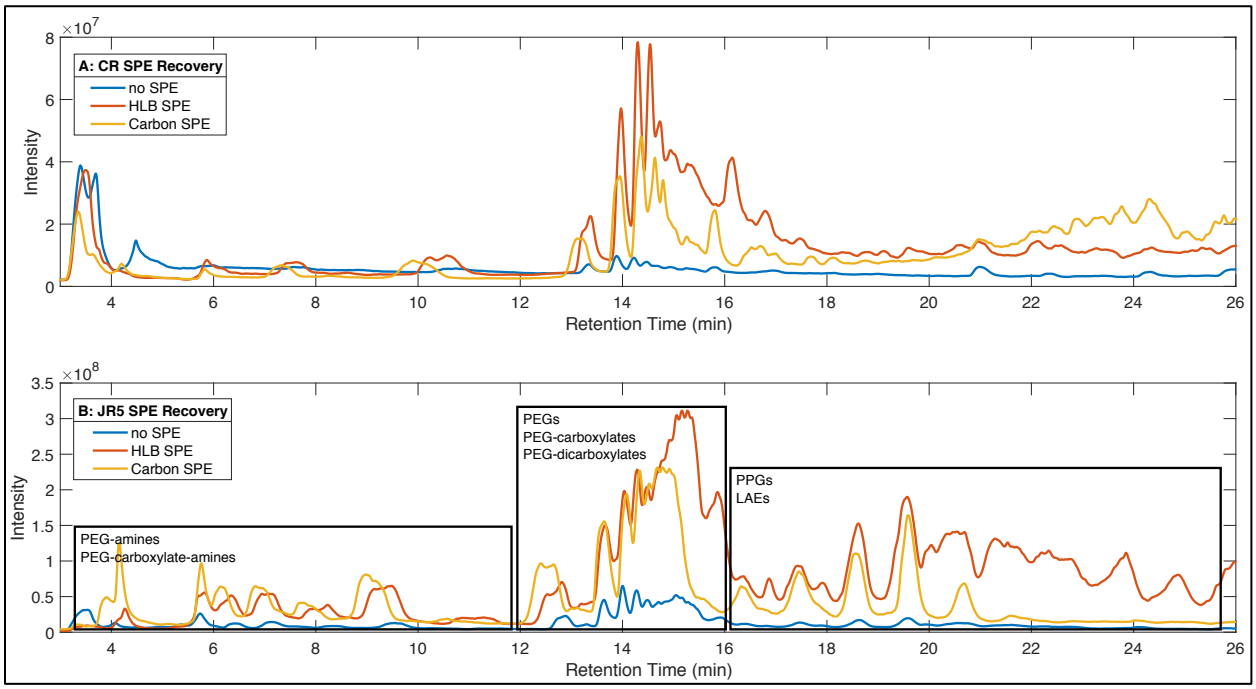

Figure 3.2: (A) Total ion chromatogram (TIC) for CR with no SPE (blue), HLB (red), and carbon (yellow); (B) TIC for JR5 with no SPE, HLB, and carbon. Both samples show enhancement after solid phase extraction. Inset boxes indicate approximate regions of elution for common hydraulic fracturing fluid additives.

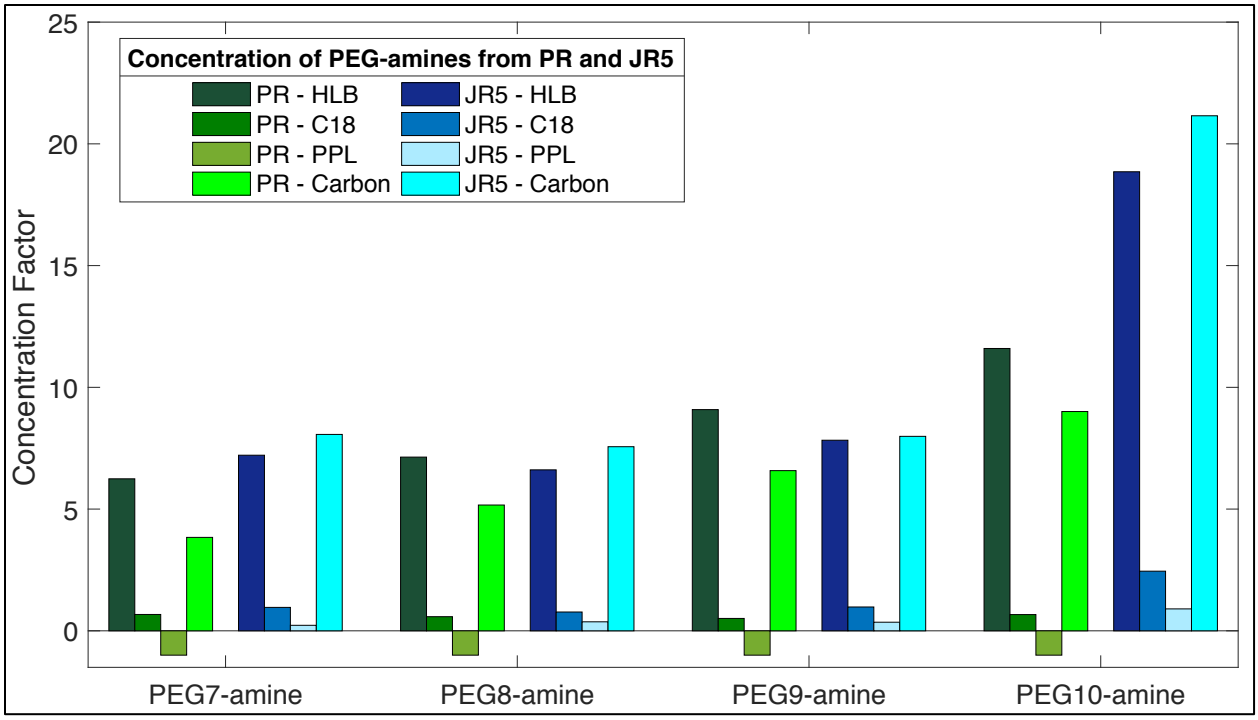

Figure 3.3: Concentration factors for PEG-amines with each sorbent from PR (green bars, left to right: HLB, C-18, PPL, Carbon) and JR5 (blue bars). Bars with negative values indicate the compound was not recovered from that sorbent. HLB and Carbon provided the highest concentration factors for PEG-amines in both samples. PPL did not recover any PEG-amines from PR.

The earliest eluting fracturing fluid additives are the PEG-amines and PEG-amine-carboxylates, which were identified by Sitterley et al. [67]. Figure 3.3 presents the recoveries of select PEG-amines from the JR5 and PR samples, and Figure 3.4 presents recoveries of select PEG-amine-carboxylates recovered from JR5. Concentration of these compounds via SPE is important because they have been detected in many hydraulic fracturing produced waters collected across a spectrum of time points during production from across the United States. This means they may be quite mobile in the environment if released to groundwater or a surface water body, so a method that can detect them at low levels is important.

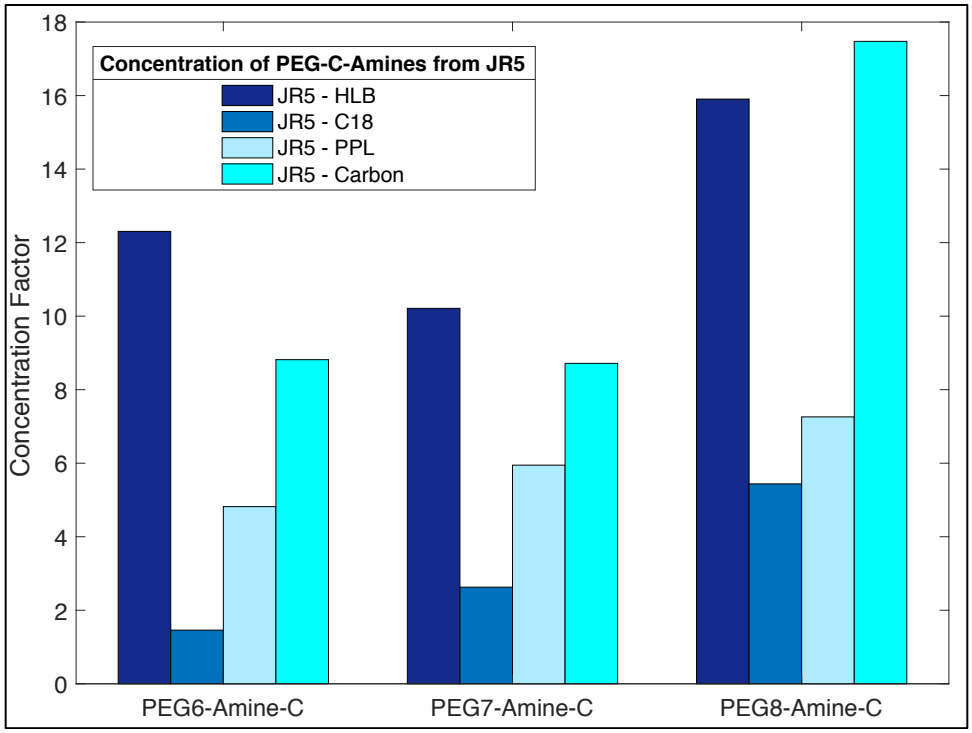

Figure 3.4: Concentration factors for PEG-amine-carboxylates with each sorbent from JR5 (blue bars, left to right: HLB, C-18, PPL, Carbon). HLB and Carbon yielded the highest concentration factors for PEG-amine-carboxylates.

The HLB cartridge yielded recoveries of between 6.2× and 18.9× (average 9.3×) and the Carbon cartridge gave concentration factors between 3.8× and 21.2× (average 8.7×). PPL did not detect the PEG-amines in PR and gave <1.0× concentration factor (average 0.5×) in JR5. C-18 gave <1.0× concentration factor (average 0.9×) for all PEG-amines except PEG10-amine in JR5 at 2.4×. Therefore, both PPL and C-18 were a detriment to analysis of these compounds. The concentration factors for HLB and Carbon increased with increased chain length. Shorter chain ethylene oxides have weaker interaction with the sorbent due to fewer pi-electrons in the ethers, so are less likely to be sorbed and eluted.

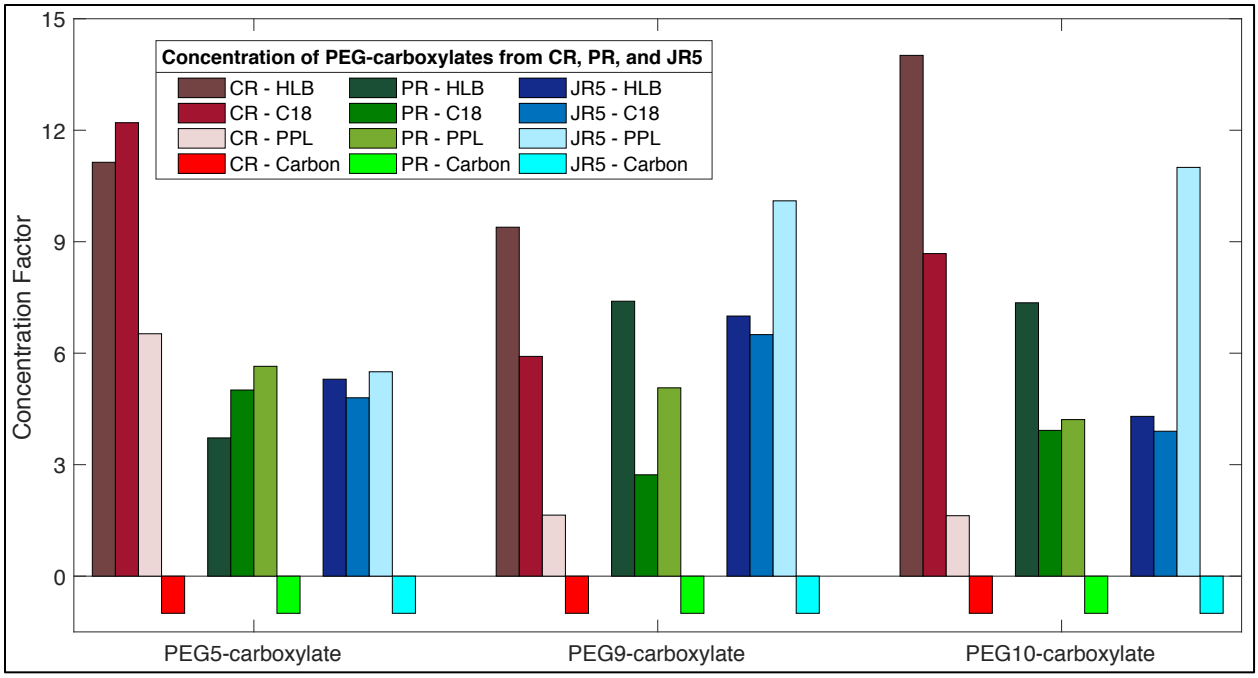

Figure 3.5: Concentration factors for PEG-carboxylates from CR (red bars, left to right: HLB, C-18, PPL, Carbon), PR (green bars), and JR5 (blue bars). Bars with negative values indicate the compound was not recovered from that sorbent. Carbon did not recover any PEG-carboxylates.

PEG-carboxylates, byproducts of the microbial degradation of PEGs [76, 127], were detected in every sample, and the concentration factors for select PEG-carboxylates are presented in Figure 3.5. HLB gave the highest concentration factors with an average of 7.7× and ranging between 3.7-14.0×. C-18 and PPL gave lower average concentration factors at 6.0× and 5.7×, respectively. The Carbon cartridge gave no recovery of any of the PEG-carboxylates (indicated by the bar below the origin in Figure 3.5). Notably, concentration factors for all PEG-carboxylates were higher for CR, the saltiest sample evaluated (157,100 mg/L TDS), which illustrates the importance of desalting for detection of these compounds at low concentrations. PEG-carboxylates are a good test compound to evaluate because they present the first step in microbial degradation of PEGs [125, 127]. Microbial communities have been discovered in hydraulic fracturing produced waters [128], so PEG-carboxylates are also frequently present, but at lower abundance than PEGs.

They are also important to evaluate because, due to the carboxyl group on one end of the molecule, they can be difficult to capture on a solid phase and are sensitive to pH [126], so good recovery from a sorbent would be a strong indicator that it is well suited for this application.

PPGs are the second most hydrophobic of the compounds evaluated and elute toward the end of the chromatogram. Recoveries of select PPGs from the JR5 sample are presented in Figure 3.6. HLB, C-18, and PPL all yielded about the same concentration factors for these compounds at 11.4×, 11.6×, and 12.6×, respectively. Carbon concentration (average 6.6×) were very similar for PPG5 and PPG6 but dropped off at longer PPGs due to Carbon's affinity for more hydrophobic compounds. Like the other compounds evaluated, these compounds are present in samples from across the country and throughout the life of the well, but their concentration will diminish as the well ages [74], so detection of these compounds in older samples is necessary.

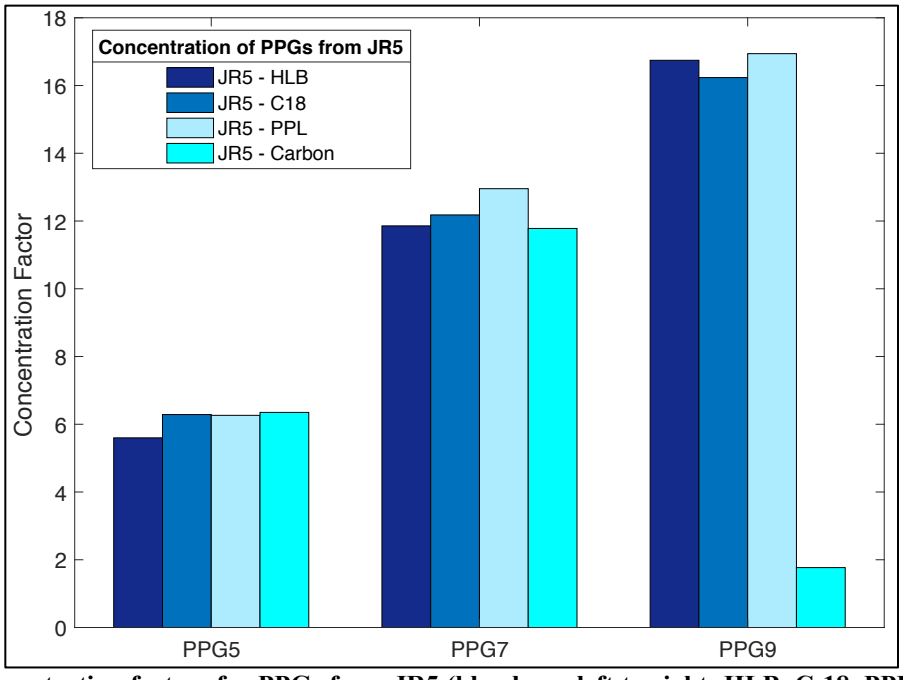

Figure 3.6: Concentration factors for PPGs from JR5 (blue bars, left to right: HLB, C-18, PPL, Carbon). All sorbbents recovered PPGs to approximately the same extent. Recoveries drop off for Carbon as propoxylate chain gets larger.

The most hydrophobic fluid additives evaluated with this method is the linear alkyl ethoxylates (LAEs). LAEs were detected only in the VL sample and included LAE-C_9s, -C_{10}s, and -C_{11}s. Figure 3.7 presents the concentration factors for select LAEs from this sample. Again, HLB gave the highest average concentration at 25.9× and ranged from 22.8-32.5×. C-18 also gave good concentration factors, averaging 18.7× and ranging from 12.5-39.3×. PPL and Carbon again gave poor recoveries, with a maximum concentration factor of 1.8× and 2.6×, respectively, and did not detect LAE5- and LAE10-C_{11}, the most hydrophobic compounds considered. For these more hydrophobic compounds, it is possible that they did sorb to the solid phase, but the eluant (methanol) was not strong enough to bring them off, or more eluant was needed.

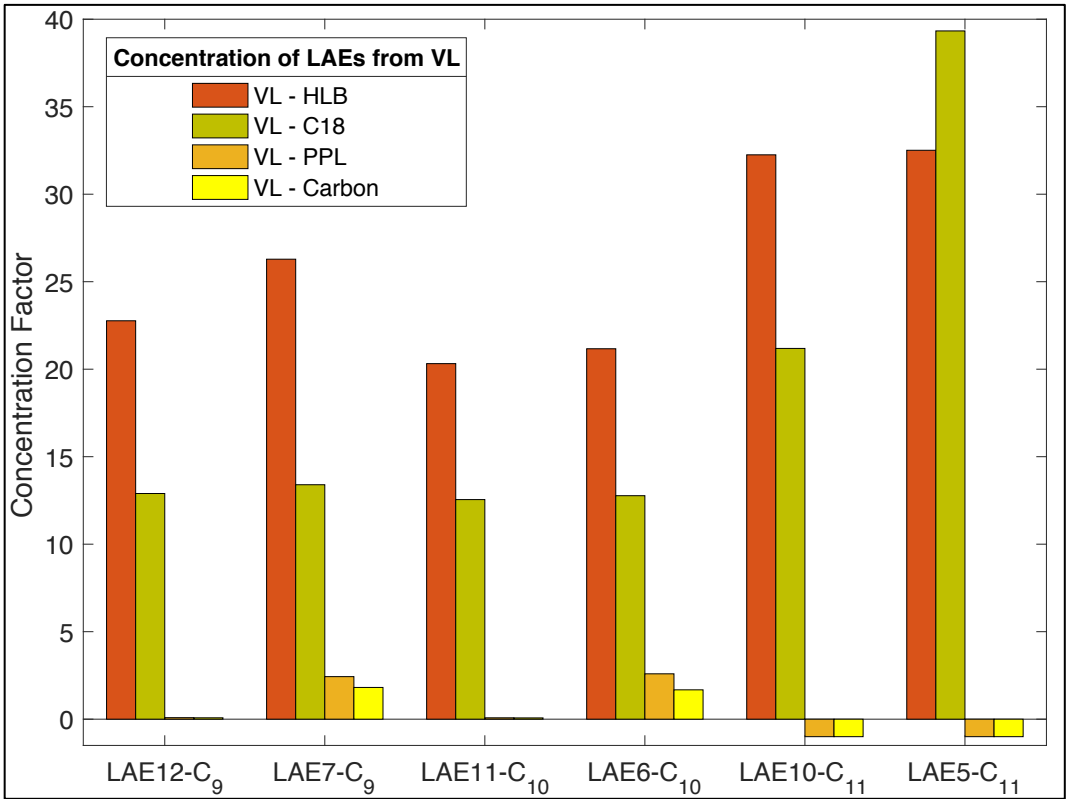

Figure 3.7: Concentration factors for LAEs from VL with HLB (dark orange bars), C-18 (gold bars), PPL (orange bars), Carbon (yellow bars). HLB and C-18 yielded the highest concentration factors for LAEs. Bars with negative values indicate the compound was not recovered from that sorbent.

Finally, PEG recoveries for VL and CR are presented in Figure 3.8 for PEG4 through PEG17. We chose to show this data last because it encapsulates the general results of the

experiments. All four cartridges gave similar concentrations of smaller PEGs (PEG4 through PEG10), but as the PEG gets longer, HLB recoveries increase with increasing ethoxylation more than the other cartridges, and PPL and Carbon begin to decrease to the point that concentration factors are <1.0× and thus, a detriment to analysis. Another result of this research that is well described by this figure is the different effect SPE has on samples with different salt contents. The VL sample (96,200 mg/L TDS) shows a maximum PEG concentration of 12.3× for PEG14 with HLB; for the CR sample (157,100 mg/L TDS) concentration factor of PEG14 with HLB was 70.7×, illustrating the different degrees that desalting and concentrating with SPE has on samples with different salt contents. A more in-depth analysis of the desalting impact is discussed in a following section.

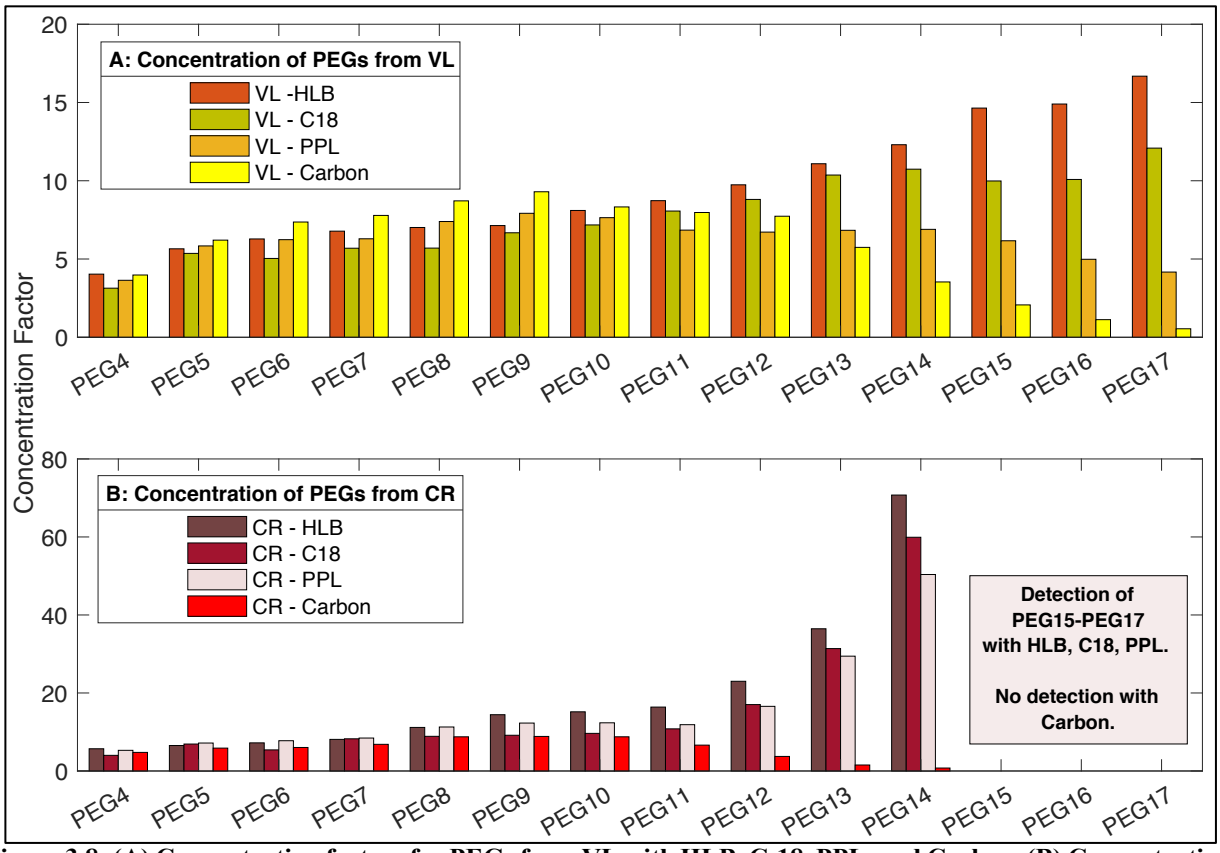

Figure 3.8: (A) Concentration factors for PEGs from VL with HLB, C-18, PPL, and Carbon. (B) Concentration factors for PEGs from CR with HLB, C-18, PPL, and Carbon. The four bars for each compound represent (from left to right): HLB, C-18, PPL, Carbon. PEG15, PEG16, and PEG17 were not present in the raw CR sample, so concentration factors could not be calculated. Concentration factors were higher for longer ethoxylate chains and in CR, the saltier sample.

Each of the four sorbents was able to recover some of the fluid additives evaluated. HLB concentrated (i.e. average >1.0×) all six to some extent, C-18 recovered four, and PPL and Carbon recovered three. Based on the DOC breakthrough curve, it was expected that HLB, PPL, and Carbon would yield better concentrations than C-18 because they retained more mass, but that was not observed. The superior concentration of ethoxylated surfactants with HLB over C-18 and Carbon has been reported before from marine sediments [129, 130]. This result highlights the importance of evaluating recoveries of specific analytes rather than relying on bulk indicators like DOC when developing a method for SPE and suggests a few points of discussion: first, that the

increased capacity of HLB, PPL, and Carbon for the DOC in this sample was of no consequence to the concentration of these common fracturing fluid additives. This may indicate that the additional DOC that sorbed to these cartridges was so strongly bound to the solid phase that it was not eluted with methanol and requires a stronger solvent. Ethoxylated and propoxylated surfactants sorbed just as well to HLB as they did to C-18. We assume that the hydrophobic compounds remain sorbed to Carbon and that they could be eluted with a different method, which could be an advantage if hydrophobic compounds were the target for analysis. However, because this was not evaluated in this work, we do not recommend using Carbon for analysis of hydraulic fracturing wastewaters, but due to its high concentration for PEG-amines, it might be useful for dilute groundwater samples. PPL was eliminated from further consideration as a sorbent for environmentally diluted samples because it gave no concentration of PEG-amines. C-18 gave some concentration of PEG-amines to warrant further investigation with a more sensitive instrument. HLB is the sorbent of choice for analysis of pure flowback and produced water because it recovered all compounds to some extent. In a following section, HLB, C-18, and Carbon are evaluated for their efficiency in recovering the most hydrophilic additives from a dilute sample before evaluating which is best for recovery from a spiked groundwater sample at 1:200 and 1:1000 dilutions.

3.3.4 Impact of Desalting

To demonstrate the impact of desalting on compound detection, recoveries of hydrogen adduct for several PEGs with HLB are presented in Figure 3.9. Hydrogen is the dominant adduct formed for PEGs using the ion trap, which is in contrast to the hydrogen-ammonium-sodium pattern that was observed when using a QTOF [65]. This data shows that the enhancement of the hydrogen adduct was most pronounced for CR (157,100 mg/L TDS) and lowest for PR (26,400

mg/L TDS). For the purposes of this study, concentration factors >20.0× are considered to be attributable to desalting. Every PEG in CR achieved this concentration, but only PEGs with more than 13 ethylene oxide units achieved this for PR. Hydrogen adducts for PEGs in VL (96,200 mg/L TDS) showed >20.0× starting with 9 ethylene oxide units. Higher concentrations for saltier samples were observed for PEG-carboxylates as well.

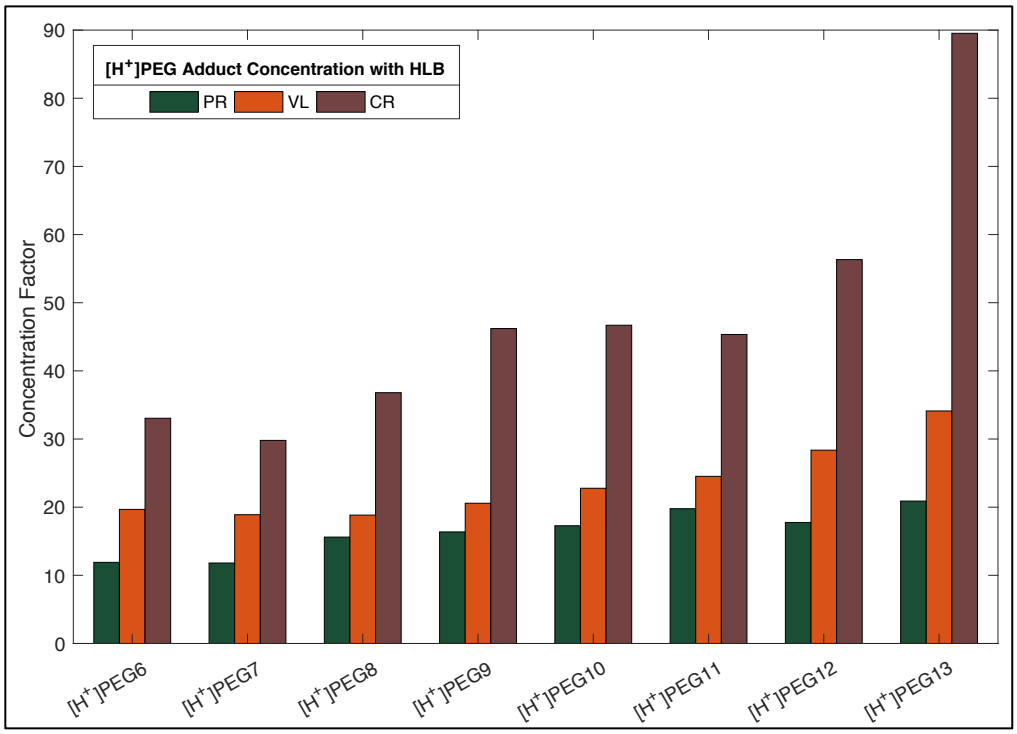

Figure 3.9: Concentration of [H$^+$]PEG adducts from PR (green bars), VL (orange bars), and CR (red bars) using HLB cartridge. Concentration factors increased with increasing salt in the sample.

An important aspect of this research that is not captured in figures is that the combination of desalting and concentration with SPE enabled the detection of some compounds in the saltier samples. This is arguably more relevant than the recoveries if the objective is to track these fluid additives in the environment or through a treatment system. This was most relevant for the saltiest samples and included detection of LAEs in VL and PEGs, PEG-carboxylates, and PEG-amines in CR. Additionally, the method applied here was used in Sitterley et al. [67], which resulted in

successful identification of previously undisclosed proprietary fluid additives (PEG-amines, PEG-amine-carboxylates, amino-PEG-amines) that were part of the research done here.

3.3.5 Proposed Method Summary

Results from the previous suggestion show that SPE with HLB gives good concentration factors for the suite of fracturing fluid compounds present in many hydraulic fracturing flowback and produced waters. The high salt of these samples can limit adduct formation via ion suppression and hinder detection of these compounds, but the straightforward method developed and described here is sufficient to desalt and concentrate the mass spectrometric signal to enable analysis. The method, recommended for use with Waters' HLB cartridges in analysis of hydraulic fracturing flowback and produced waters, is described step-wise as follows:

1. Condition cartridge with 5 mL HPLC grade methanol at 5 mL/min.
2. Condition cartridge with 5 mL HPLC grade water at 5 mL/min.
3. Load 10 mL of hydraulic fracturing sample filtered through 0.45 μm PTFE filter at 5 mL/min. Discard filtrate.
4. Rinse cartridge with 10 mL of HPLC grade water at 5 mL/min.
5. Elute cartridge with 5 mL HPLC grade methanol at 1 mL/min into a cleaned 10 mL glass vial.
6. Concentrate the extract via blowdown with N_2 gas to 0.5 mL, measured gravimetrically.
7. Pipette concentrated extract into new HPLC vial for mass spectrometric analysis.

Furnaced beakers were used to store the water and methanol during the extraction and new pipette tips were used for each solvent and sample.

3.4 Method Utility in Environmental Samples

This section examines how a corollary method could be used to detect hydraulic fracturing fluid compounds present at very low levels in an environmental groundwater sample using the HLB cartridge. Two recovery experiments were performed: (1) standards for hydrophilic (i.e. early eluting) compounds identified in hydraulic fracturing wastewater (PEG-amines, PEG-amine-carboxylates, and amino-PEG-amines) were spiked into 100 mL of groundwater and recovered, and (2) a 500 µL and 100 µL spike of JR5 into a 100 mL groundwater sample representing a 1:200 (Dilution A) and 1:1000 dilution (Dilution B), respectively. These samples were then processed through an SPE cartridge, eluted with 5 mL methanol, and evaporated to a final volume of 0.5 mL. The first recovery experiment was performed to inform cartridge selection for recovery of diluted hydrophilic compounds. It was thought that the cartridge with the best recoveries of these compounds would also yield acceptable recoveries of the other compounds considered in this study. The second recovery experiment was performed to determine the efficiency of recovery of these compounds from a contaminated environmental sample. A spiked volume of 500 µL was chosen because, when a 1:200 dilution is concentrated 200×, it is the equivalent of analyzing the pure sample. If 100% recovery were achieved, the TIC for Dilution A would match up well with the TIC of the pure sample and the peak areas for these compounds would be nearly identical. Similarly, we would expect the recoveries of Dilution B spike to be 20% of the pure sample if recovery were 100%. These samples were analyzed with the QTOF due to lower concentration of compounds and the need for higher sensitivity.

3.4.1 Recovery of Spiked Standards

Figure 3.10 shows the chromatogram for recovery experiments for each of the hydrophilic nitrogen-containing PEGs with HLB (blue trace), C-18 (green), and Carbon (black); recoveries are

quantified in Table 3.2. Each compound was spiked into a groundwater source to a known concentration and the peak areas of the hydrogen adduct in the eluted sample was compared to prepared standards. Once again, HLB showed the highest recovery for all three compounds with almost complete recovery (>99%) of PEG6-amine and PEG6-amine-carboxylate, and 84% recovery of amino-PEG5-amine, thus further confirming the previous results. The C-18 cartridge showed no recovery of either the amino-PEG5-amine or the PEG6-amine, but partial recovery (66%) of the PEG6-amine-carboxylate, reflecting results from the Ion Trap. Carbon showed approximately the same recovery as C-18 for PEG6-amine-carboxylate (64%), higher recovery of the PEG6-amine (69%), and no recovery of the amino-PEG5-amine. This result shows the importance in proper selection of the solid phase when performing extraction experiments because both polar and nonpolar interactions are needed for highest recovery. HLB was again selected as the best sorbent for recovery from diluted samples.

Table 3.2: Recovery of PEG-amine standards from select sorbents using solid phase extraction and analyzed with the QTOF.

Compound	Nominal *m/z* $[H^+]$	HLB Recovery (%)	C-18 Recovery (%)	Carbon Recovery (%)
Amino-PEG5-Amine	281	84.3%	0.0%	0.0%
PEG6-Amine	282	100.0%	0.1%	69.3%
PEG6-C-Amine	296	99.2%	66.3%	64.9%

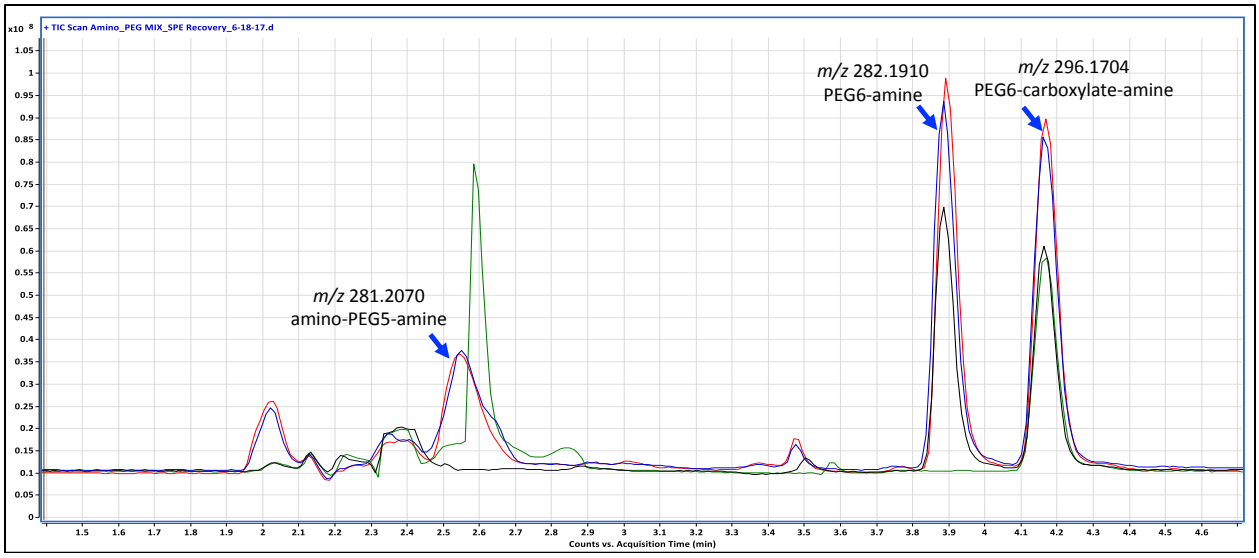

Figure 3.10: Total ion chromatogram for recovery of nitrogen-containing PEG standards (red trace) with HLB (blue), C-18 (green), and Carbon (black). HLB provided the best recovery for all three standards.

3.4.2 Recovery of Spiked Produced Water

Table 3.3 shows the results of the recovery experiments performed with Dilution A and Dilution B extracted with HLB for selected fracturing fluid compounds that have been previously detected in hydraulic fracturing wastewaters: PEGs, PEG-carboxylates, PPGs, triisopropanolamine (TIPA), PEG-amines, and PEG-amine-carboxylates. All compounds were detected as a proton, ammonium, or sodium adduct. PEG3 through PEG20 were in Dilution A and Dilution B with average recoveries of 85.1 ± 9.1%, and 32.4 ± 14.0%, respectively, and show that recoveries did not change with increasing PEG size. Average recovery from Dilution B was higher than the expected 20% recovery. PEG-carboxylates were detected from PEG6-carboxylate through PEG18-carboxylate in Dilution A and Dilution B and showed 95.8 ± 40.9% recovery for Dilution A and 36.8 ± 32.6% recovery for Dilution B. PPG2 through PPG15 were detected in both dilutions and had higher recoveries overall. Average recovery for Dilution A was 137.2 ± 101.1% and average recovery for Dilution B was 39.2 ± 34.6%. The reason for the large standard deviation on PPG recoveries is due to the larger PPGs (PPG11 through PPG15) yielded recoveries >100% in

Dilution A (102.9-372.8%) and >30% in Dilution B (46.6-122.9%). PEG-amines were detected as proton adducts with between 4 and 20 ethylene oxide units, with some detected as mixed isomers. Dilution A recovered an average of 96.7 ± 29.6% and Dilution B recovered an average of 25.2 ± 13.9%. PEG-amine-carboxylates were also detected as proton adducts and recovered an average of 84.0 ± 23.7% in Dilution A and an average of 22.3 ± 10.8% for Dilution B. Finally, TIPA had an average recovery of 392.7% from Dilution A and 99.2% for Dilution B.

These results show that the HLB cartridge is able to achieve excellent recoveries of ethoxylated and propoxylated compounds, even at 0.1% dilutions. Higher recovery of PPGs than PEGs in the recovery experiments correlates well to previous results that showed PPGs with a higher recovery. Compounds that are more hydrophobic will preferentially sorb to the HLB media and more readily elute in methanol than more hydrophilic compounds, such as the PEGs, PEG-amines, and their metabolites. Because average recoveries were higher than expected, it once again suggests the important role desalting plays in achieving detections and increasing instrument sensitivity of these compounds at low concentrations. The enhanced recoveries of PPGs over the raw sample provide evidence that high salts suppress these compounds and that this may affect longer and more hydrophobic compounds more than hydrophilics.

Table 3.3: Recoveries from diluted samples for select fluid additives and descriptive statistics for all recoveries for Dilution A and Dilution B.

Compound	RT (min)	Dilution A	Dilution B	Recovery Statistics Dilution A	Recovery Statistics Dilution B
PEG4	4.3	80.9%	52.0%	Average: 85.1±9.1% Min: 64.9% Max: 107.7 Median: 84.3%	Average: 32.4±14.0% Min: 15.9% Max: 52.0% Median: 33.4%
PEG5	5.5	85.2%	45.7%		
PEG6	7.5	88.9%	37.0%		
PEG18	12.6	82.0%	19.2%		
PEG19	12.7	80.6%	18.1%		
PEG20	12.8	64.9%	15.9%		
PEG5-carboxylate	6.0	0.0%	0.4%	Average: 95.8±40.9% Min: 0.0% Max: 162.4% Median: 103.2%	Average: 36.8±32.6% Min: 0.4% Max: 132.8% Median: 27.4%
PEG6-carboxylate	8.4	21.3%	7.2%		
PEG7-carboxylate	9.9	95.2%	24.0%		
PEG16-carboxylate	12.5	114.0%	132.8%		
PEG17-carboxylate	12.7	162.4%	61.4%		
PEG18-carboxylate	12.8	134.9%	63.5%		
PPG5	14.2	50.7%	14.2%	Average: 137.2±101.1% Min: 50.7% Max: 372.8% Median: 101.4%	Average: 39.2±34.6% Min: 14.0% Max: 122.9% Median: 23.7%
PPG6	15.4	58.5%	14.8%		
PPG7	16.7	64.5%	16.2%		
PPG11	21.4	159.2%	46.6%		
PPG12	22.5	260.9%	83.4%		
PPG13	23.6	294.8%	122.9%		
PEG4-amine	3.1	32.3%	10.1%	Average: 96.7±29.6% Min: 32.3% Max: 243.8% Median: 95.4%	Average: 25.2±13.9% Min: 10.1% Max: 90.8% Median: 22.3%
PEG5-amine	3.5	68.8%	22.7%		
PEG6-amine	3.8	71.3%	17.6%		
PEG17-amine	10.9	106.7%	25.7%		
PEG18-amine	11.0	115.6%	60.3%		
PEG19-amine	11.2	123.5%	38.6%		
PEG20-amine	11.4	243.8%	90.8%		
PEG5-amine-carboxylate	4.1	68.2%	0.0%	Average: 84.0±23.7% Min: 22.4% Max: 126.8% Median: 90.8%	Average: 22.3±10.8% Min: 0.0% Max: 45.4% Median: 19.5%
PEG6-amine-carboxylate	4.1	90.4%	22.4%		
PEG7-amine-carboxylate	5.2	100.4%	21.1%		
PEG13-amine-carboxylate	10.5	103.6%	35.0%		
PEG14-amine-carboxylate	10.4	95.8%	40.3%		
PEG15-amine-carboxylate	10.6	126.8%	40.3%		
PEG16-amine-carboxylate	10.8	107.1%	33.4%		
Triisopopanolamine	2.6	392.7%	99.2%	---	---

Produced water can be released to the environment via a centralized treatment facility or an accidental spill. As of June 2017, the Environmental Protection Agency identified 426 centralized treatment facilities that operate in the United States accepting all types of waste including hydraulic fracturing flowback and produced water, some that discharge directly to a surface water body and some that discharge to a stormwater drain or treat for reuse [56]. Discharge permits for these facilities are largely concerned with monitoring and removal of suspended solids, dissolved salts, volatile organic compounds, and bulk water quality indicators like chemical and biochemical oxygen demand, nitrogen, and phosphorous. Dissolved non-volatile compounds like the ethoxylated and propoxylated compounds discussed in this work are not mentioned as being monitored, though it is possible that they may be removed as a result of treatment for other target constituents. In the event that they are monitored in the future, the method described here would be useful. Ethoxylated surfactants were detected in the effluent of one centralized facility in Pennsylvania that used oil/water separation, aeration, and chemical precipitation as treatment with a discharge volume of >5% the receiving water body's minimum average flow, while other facilities showed discharge volumes that were >50% of the receiving water body's minimum average flow [39]. The method used in that study involved no SPE, so it is likely that some ethoxylated compounds were not detected based on the results of extractions with this method (i.e. non-detect of some longer compounds). Other data from 11 facilities reviewed by the EPA show that the proportion of discharge to stream flow is estimated between 0.002-0.2%, with the lower proportions being for facilities that discharge to large rivers like the Monongahela and Allegheny in Pennsylvania. This method was only shown to be effective for dilutions >0.1%, but due to the high recovery demonstrated, may be useful at lower dilutions and further study is warranted. The compounds considered here have been previously suggested to be tracers for contamination via hydraulic fracturing produced water spill [74] and have been shown to be mobile and

biodegradable in groundwater based on their hydrophilic nature [125], highlighting the need to detect the singly- and doubly-carboxylated PEGs.

3.5 Conclusions

This work shows the development and deployment of a solid phase extraction method capable of detecting all the most commonly identified hydraulic fracturing fluid additives present in flowback and produced water. The results show that a straightforward extraction with HLB is adequate for the detection of these additives with loading volumes of 10 mL (pure samples) and 100 mL (dilute environmental samples) for flowback and produced water samples. Additionally, it highlights the importance of not just concentration but also desalting of these samples for enhanced mass spectrometric analysis. Future research should build on this work to develop a method that can accurately quantify these compounds in different flowback and produced water matrices.

CHAPTER 4: IDENTIFICATION OF PROPRIETARY AMINO ETHOXYLATES IN HYDRAULIC FRACTURING WASTEWATER USING LIQUID CHROMATOGRAPHY/TIME-OF-FLIGHT MASS SPECTROMETRY WITH SOLID PHASE EXTRACTION

This chapter describes the identification of several new ethoxylated surfactants in flowback and produced waters and their utility in fracturing fluid.

This work was condensed into a publication:

Sitterley, K.A., Linden, K.G., Ferrer, I., Thurman, E.M., Identification of Proprietary Amino Ethoxylates in Hydraulic Fracturing Wastewater Using Liquid Chromatography/Time-of-Flight Mass Spectrometry with Solid-Phase Extraction. *Anal. Chem.*, 2018. 90(18): p. 10927-10934.

4.1 Introduction

Exploitation of unconventional sources of oil and natural gas, such as coalbed methane, shale-gas, and tight gas formations, has surged in recent years [122]. Hydraulic fracturing is commonly used to access these formations. This technology involves drilling a well, either vertically or horizontally, and then injecting a fracturing fluid at sufficiently high pressures to perforate the formation and allow oil and gas to flow to the surface [123]. The escape of methane gas has been one of the main dangers for contamination near the drilling sites with deaths and explosions possible [16]. A second concern is additives in this fluid that can mix with the native groundwater from the geologic formation and subsequently contaminate surface and groundwater [28].

The laws regarding disclosure of chemicals used in fracturing fluid vary from state to state [131]. Even in states that require disclosure, operators use vague terms and claim some additives as proprietary, listing only a general description or purpose. To date, the identity of these proprietary chemicals is largely unknown. Therefore, having appropriate analytical methods available that are capable of detecting and identifying proprietary compounds from hydraulic fracturing fluid is a critical tool in environmental monitoring, and is one of the challenges for the analytical chemistry of hydraulic fracturing fluids.

Liquid chromatography/mass spectrometry (LC/MS) has been the most effective instrumentation for analysis of wastewater associated with hydraulic fracturing, while gas chromatography/mass spectrometry (GC/MS) is the most effective for the oil fraction [65, 72, 76, 123]. However, sample preparation methods are not fully developed for hydraulic fracturing wastewater analysis and standard EPA methods are insufficient to identify hydraulic fracturing compounds in exposure pathways (e.g. surface water and groundwater). Regnery et al. [84] used a solid phase extraction (SPE) method with C-18 for quantitative analysis of semi-volatile linear

aliphatic hydrocarbons with GC/MS in hydraulic fracturing wastewaters. Thus, sample preparation methods have been focused on GC/MS analysis, including purge and trap, liquid/liquid extraction, and SPE [39, 68, 71, 84]. Furthermore, Leuk et al. [38] used a polymer resin, PPL, while Thacker et al. [68] used C-18 SPE for sample preparation. However, no systemized studies have been carried out with SPE for best application to wastewater from hydraulic fracturing.

Thus, the work described herein emphasizes the application of sample preparation with SPE to accomplish several goals. First, because hydraulic fracturing fluids contain salt levels sometimes 10 times greater than seawater, it is important to desalt the samples prior to mass spectral analysis in order to remove the suppression and allow detection and identification of the more polar proprietary surfactants. Some of these surfactants elute in the early part of the chromatogram where salts co-elute and suppress signal. Secondly, SPE will also concentrate the polar surfactants to enable a good signal for MS-MS identification. Previous work by our group includes the identification of the more prominent surfactants that are used as hydraulic fracturing fluid additives, such as the polyethylene and polypropylene glycols [65, 76]. Thus, the objectives of this work were (1) to present a SPE method that enriches and desalts hydraulic fracturing wastewater for organic analysis, (2) to identify undisclosed organic compounds, such as ethoxylated amines, that are listed as proprietary additives in fracturing fluids using UHPLC/Q-TOF/MS, and (3) to show with samples of flowback and produced waters from multiple shale deposits that organic amines appear commonly in hydraulic fracturing wastewater, and are an important ingredient in the chemistry of hydraulic fracturing fluids.

4.2 Materials and Methods

4.2.1 Sample Collection

A unique set of twenty samples was collected from various shale deposits in the United States as part of a study on the chemistry of hydraulic fracturing wastewaters. These samples required the cooperation and assistance of oil companies and their partners in order to get a representative set of both produced and flowback samples. This was accomplished with the help of the Environmental Defense Fund and their partners in industry. The samples were collected on-site from oil/water/gas separators of hydraulic fractured wells in Colorado, Oklahoma, Texas, Wyoming, and North Dakota and included both produced and flowback waters. Samples were collected by the authors in muffled amber glass bottles and stored at 4°C for up to 1 month prior to analysis.

4.2.2 Amino Ethoxylate Standards

The commercially available standards used for compound identification were synthesized by PurePEG (San Diego, CA) and all are >95% purity. Each compound was analyzed individually using the following UHPLC method with liquid LC/Q-TOF/MS for further verification of retention times, accurate mass, and structure from the samples analyzed in this study.

4.2.3 SPE Extraction Method

The SPE cartridge used was Oasis HLB (Waters Corporation; Milford, MA). All reagents used were HPLC grade. The SPE cartridge was first conditioned with 5 mL of methanol and rinsed with 10 mL of water. Then, 10 mL of sample was filtered through an Acrodisc 0.45 μm PTFE syringe filter (PALL Corp.; Port Washington, NY) and was loaded on the cartridge at 5 mL/min

followed by a 10 mL rinse with water to desalt. All filtrate was discarded. Following the rinse step, the cartridge was eluted with 5 mL of methanol at 1 mL/min and collected in a cleaned 10 mL test tube. Finally, the collected blank and sample eluant was evaporated to a volume of 0.5 mL, measured gravimetrically, with N_2 in a Turbovap LV Evaporator (Zymark Corp.; Hopkinton, MA). This represents a 20× volumetric concentration over the raw water with a 99% removal of salt. The concentrated eluant was then pipetted into a HPLC vial prior to LC/Q-TOF/MS analysis. For blank analysis, HPLC grade water was filtered through the Acrodisc 0.45 μm PTFE syringe filter and then extracted using an identical method.

4.2.4 LC/Q-TOF/MS Analysis

The separation of the analytes was carried out using an UHPLC system consisting of thermostated autosampler, column department, and a binary pump (Agilent Series 1290; Agilent Technologies; Santa Clara, CA) equipped with a reverse phase C8 analytical column of 150 mm × 4.6 mm and a 3.5 μm particle size (Zorbax Eclipse XDB-C8). Column temperature was maintained at 25°C. The injected sample volume was 20 μL. Mobile phases A and B were water with 0.1% formic acid and acetonitrile, respectively. The optimized chromatographic method held the initial mobile phase composition (10% B) constant for 5 min, followed by a linear gradient to 100% B after 30 min. The flow rate used was 0.6 mL/min. A 10 min postrun was used after each analysis. This UHPLC column was connected to an ultrahigh definition quadrupole time-of-flight mass spectrometer model 6545 Agilent (Agilent Technologies; Santa Clara, CA) equipped with electrospray Jet Stream Technology, operating in positive ion mode, using the following operation parameters: capillary voltage, 4,000 V; nebulizer pressure, 45 psig; drying gas, 10 L/min; gas temperature, 250°C; sheath gas flow, 11 L/min; sheath gas temperature, 350°C; nozzle voltage, 1,000 V; fragmentor voltage, 175 V; skimmer voltage, 65 V; octopole RF, 750 V. LC/MS accurate

mass spectra were recorded across the range 50-1,000 *m/z* at 2 GHz. The data recorded were processed with MassHunter software (version 6.1). Accurate mass measurements of each peak from the total ion chromatograms were obtained by means of an automated calibrant delivery system using a low flow of a calibrating solution (calibrant solution A, Agilent Technologies, Inc.), which contains the internal reference masses (purine at *m/z* 121.0509 and HP-921 at *m/z* 922.0098). The instrument provided a typical mass resolving power of 30,000 at *m/z* 922. Unknown analysis was carried out using our protocol previously published [65, 76].

4.3 Results and Discussion

4.3.1 Desalting and Compound Detection Using SPE

Previous studies have used direct analysis of water samples of hydraulic fracturing fluids because the organic compounds were present at high concentrations, from 500-1,000 mg/L measured as dissolved organic carbon (DOC) [65, 76]. Furthermore, these earlier studies dealt with water samples of relatively low salt content for hydraulic fracturing fluids, i.e. ~20,000 mg/L measured as total dissolved solids (TDS). The more comprehensive study here that included 20 samples from five major oil and gas basins shows that hydraulic fracturing fluids may have much lower organic concentrations (<30 mg/L as DOC) and much higher concentrations of dissolved salts (>150,000 mg/L as TDS). Thus, solid phase extraction is necessary to both concentrate the unknown organic compounds and to lessen the negative effects of salt suppression on mass spectrometric detection.

Figure 4.1 shows the total ion chromatograms for four samples with varying DOC and TDS compositions, summarized in Table 4.1. All samples show that desalting by solid phase extraction enhanced the total signal obtained by mass spectrometry (shown here as the total ion

chromatogram as a black trace without solid phase extraction and a colored trace with solid phase extraction). In all four samples, there is a large signal enhancement throughout the chromatogram and the appearance of a new set of unknown compounds in the 3-9 minute region. The combination of salt removal and concentration of dissolved organic compounds visibly enhances mass spectrometric signal. The following sections detail the impact of desalting on the most commonly identified fluid additives in flowback and produced waters.

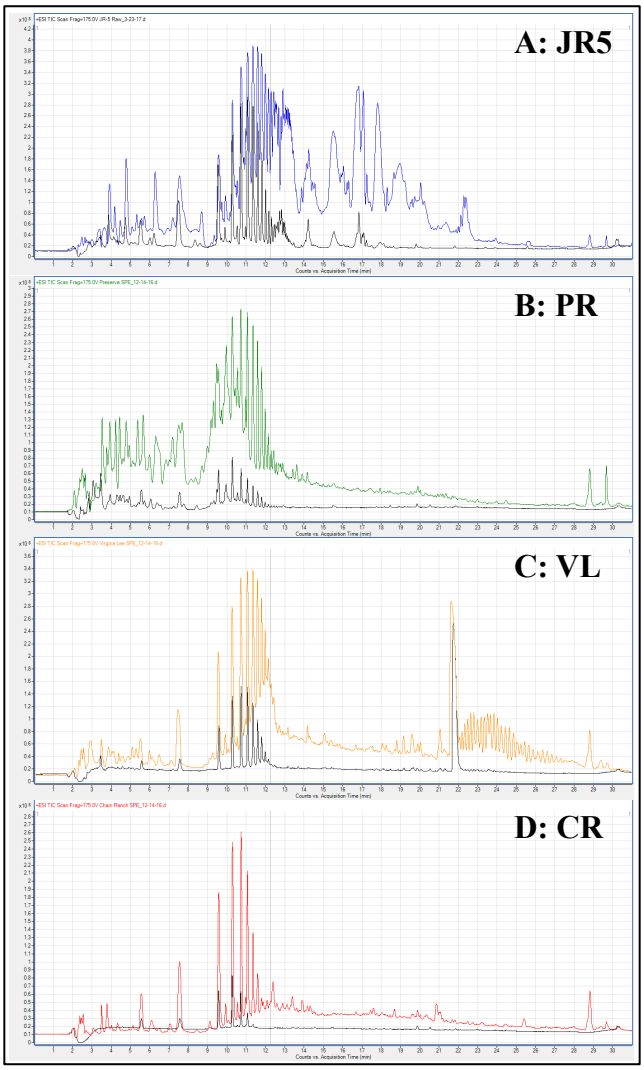

Figure 4.1: Total ion chromatograms for four different flowback and produced water samples: (A) JR5 – 30 day flowback water from CO; 610 mg/L DOC, 21,400 mg/L TDS, (B) PR – 30 day flowback water from OK; 350 mg/L DOC, 26,400 mg/L TDS, (C) VL – 92 day produced water from OK; 180 mg/L DOC, 96,200 mg/L TDS, (D) CR – 240 day produced water from OK; 30 mg/L DOC, 157,100 mg/L TDS.

Table 4.1: Total dissolved solids (TDS) and dissolved organic carbon (DOC) for flowback and produced water samples.

Sample	DOC (mg/L)	TDS (mg/L)
PR	350	26,400
CR	30	157,100
VL	180	96,200
JR5	680	24,700

4.3.1.1 Desalting of PEGs, PEG-carboxylates, PPGs, and LAEs

PEGs are commonly detected in flowback and produced water samples [57] and were detected with direct analysis of both JR5 and CR. Recoveries for these PEGs in JR5 ranged from 0.6× to 4.2× and averaged 2.2×, while in CR they ranged from 4.3× to 331.6× and averaged 66.1× (see Figure 4.2). For all PEGs, the ratio of concentration for the two samples (JR5/CR) for these compounds was <1, showing that enhancements for CR were always higher than JR5 and illustrating the impact of desalting on detection of ethoxylated compounds. The highest concentration for individual PEG adducts in both samples is 113.8× for $[NH_4^+]$PEG21 in JR5 and 274.5× for $[NH_4^+]$PEG14.

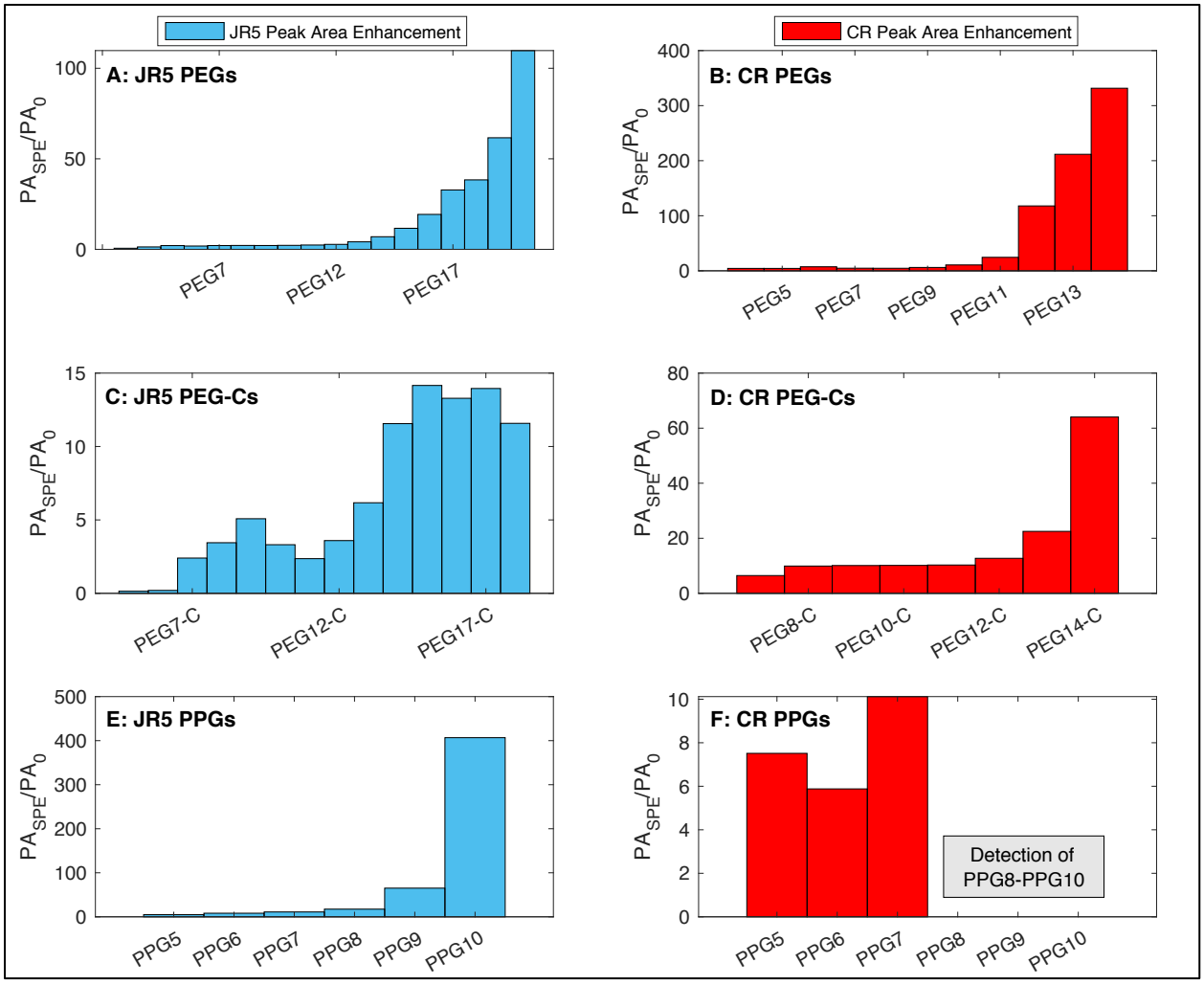

Figure 4.2: Peak Area (PA) enhancement for different hydraulic fracturing compounds in flowback (JR5) and produced (CR) water sample determined by dividing peak area after SPE (PA_{SPE}) by peak area of raw sample (PA_0).

The concentration of PEG-carboxylates in both samples gave a similar result. PEG6-carboxylate through PEG12-carboxylate was detected via direct analysis of both samples. Again, concentration increased with larger PEG-carboxylates and JR5 showed an average enhancement of 2.9× while CR showed an average of 18.3×; ammonium adducts again showed the highest enhancement of the adducts detected (see Figure 4.3). CR also showed an increase of >20× (the volumetric concentration) for PEG11-carboxylate (22.5×) and PEG12-carboxylate (64.0×), highlighting the importance of desalting and ammonium adduct formation in detection of these

longer ethoxylated surfactants in saltier samples (Figure 4.2). A possible explanation for this phenomenon is that the shorter chain surfactants have a weaker interaction with the sorbent and are rinsed away and less abundant in the analyzed aliquot. PEG-carboxylates also showed the ratio of concentration factors of JR5/CR to be <1 showing that recoveries for CR are higher in all cases and thus a result of desalting.

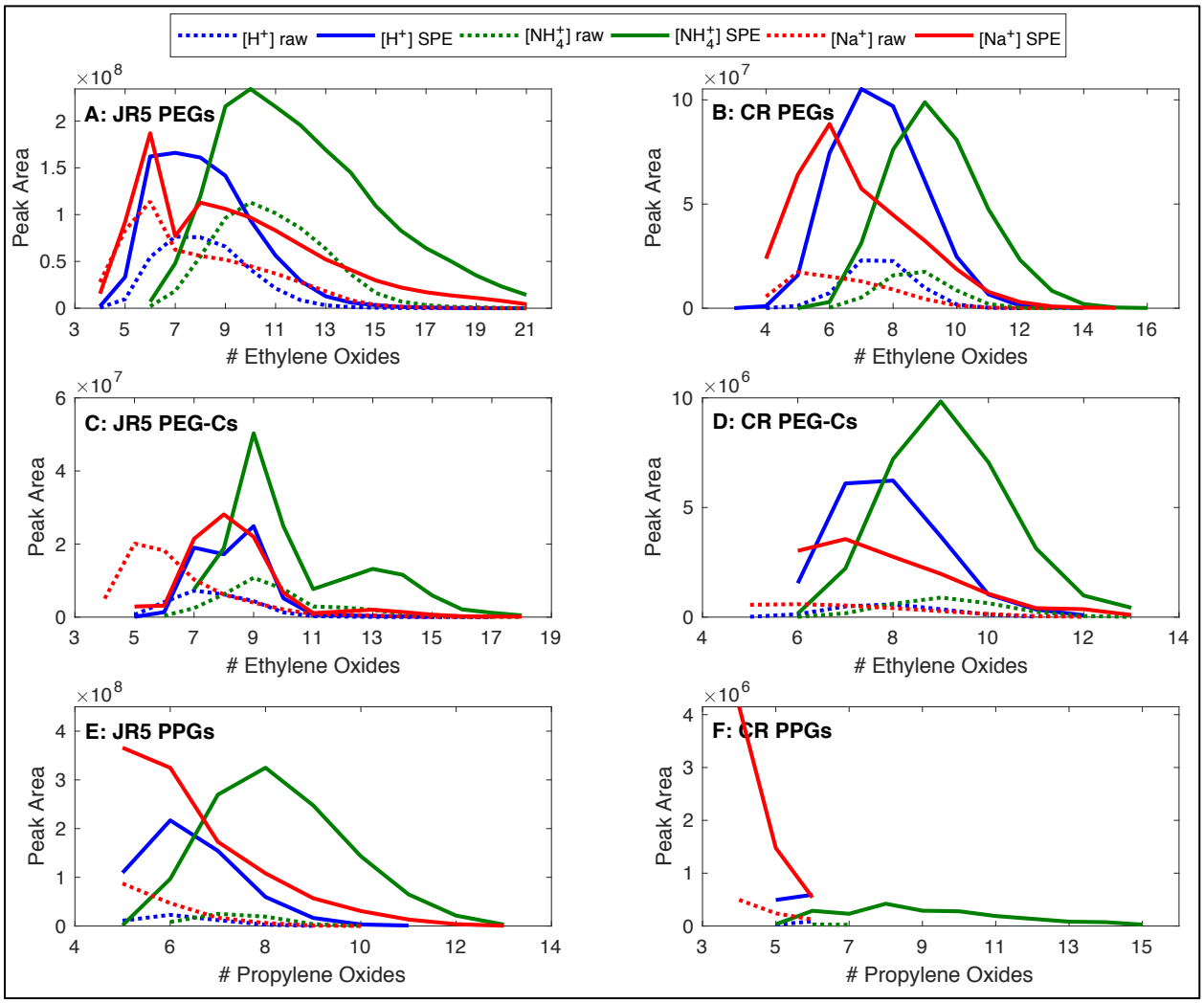

Figure 4.3: Peak area of hydrogen [H^+], ammonium [NH_4^+], and sodium [Na^+] adducts for PEGs, PEG-carboxylates, and PPGs in JR5 (panel A, C, E) and CR (panel B, D, F), highlighting the importance of the ammonium adduct for detection of longer propoxylated and ethoxylated fracturing fluid additives.

PPGs from PPG5 to PPG7 were also detected in both JR5 and CR raw samples, and SPE enabled detection of PPG11 in JR5 and PPG8 through PPG11 in CR. Average recoveries for PPG5 through PPG7 in JR5 was 8.0× and was 7.8× for CR. The effect of desalting is again illustrated by higher recoveries for ammonium adducts of PPGs (see Figure 4.3). As the primary adduct formed for PPGs with PO>8 [76], sufficient formation of the ammonium adduct of PPGs is crucial to its detection in hydraulic fracturing samples and suppression of this adduct by salts would limit its formation. Furthermore, Figure 4.4 shows the difference in PPGs peak areas in SWD. The average signal was 26.8× with a variation dependent on chain length. The shortest chains (PPG5 and PPG6) showed only a 10-13× signal increase; the longer chains (PPG7 through PPG9) showed 20.1×, 51.4× and 38.5×, respectively, with ammonium and sodium adducts showing about the same level of enhancement between 9.5-53.5×. These results indicate that mass spectral enhancement occurs to a different extent as a function of chain length, most probably caused by salt removal. That the ammonium adducts gave the highest enhancement for these compounds is important as ammonium adducts can give better results than proton or sodium adducts for MS-MS experiments, which are crucial for identification of unknown ethoxylated surfactants [111]. In general, it is clear that desalting greatly increases mass spectral detection overall, which is important for identification by accurate mass as will be shown in the next sections.

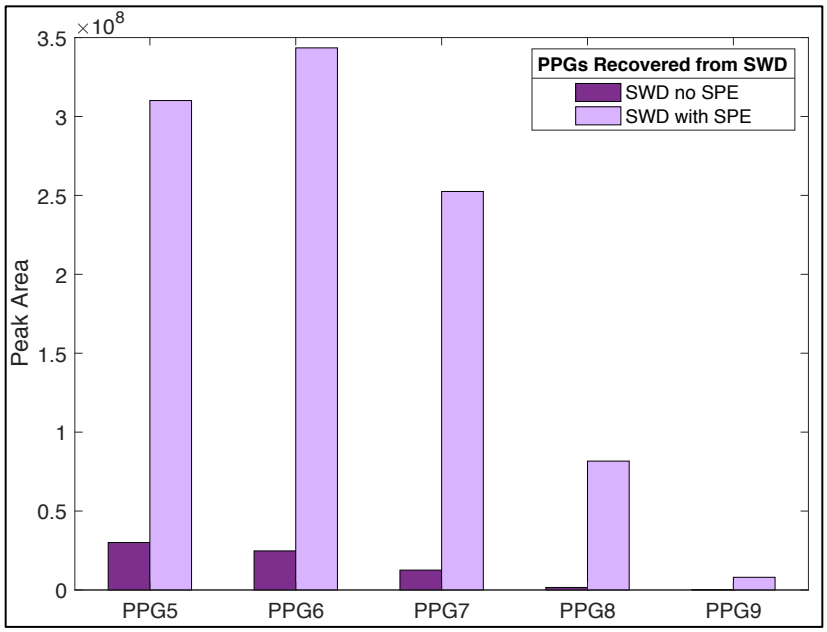

Figure 4.4: Peak area of PPGs with and without SPE in SWD.

Enhancement of mass spectral data for C_{11} and C_{10}-LAEs in VL are shown in Figure 4.5. Results show enhancement of C_{11}-LAEs with ethylene oxide chains of 3 to 18 ranged from 75.3-331.4× and had a median signal 75× when using solid phase extraction. Enhancements for C_{10}-LAEs were lower, ranging from 22.0-43.5× and a median signal 30.3× with solid phase extraction. The effect of desalting on chain length for LAEs was the opposite that it was for PEGs and PPGs – shorter chain lengths saw greater enhancement because they are more hydrophobic. Because the volumetric concentration factor by solid phase extraction was 20×, the additional signal enhancement is attributed to desalting. This result is not surprising given the high salt content of hydraulic fracturing fluids.

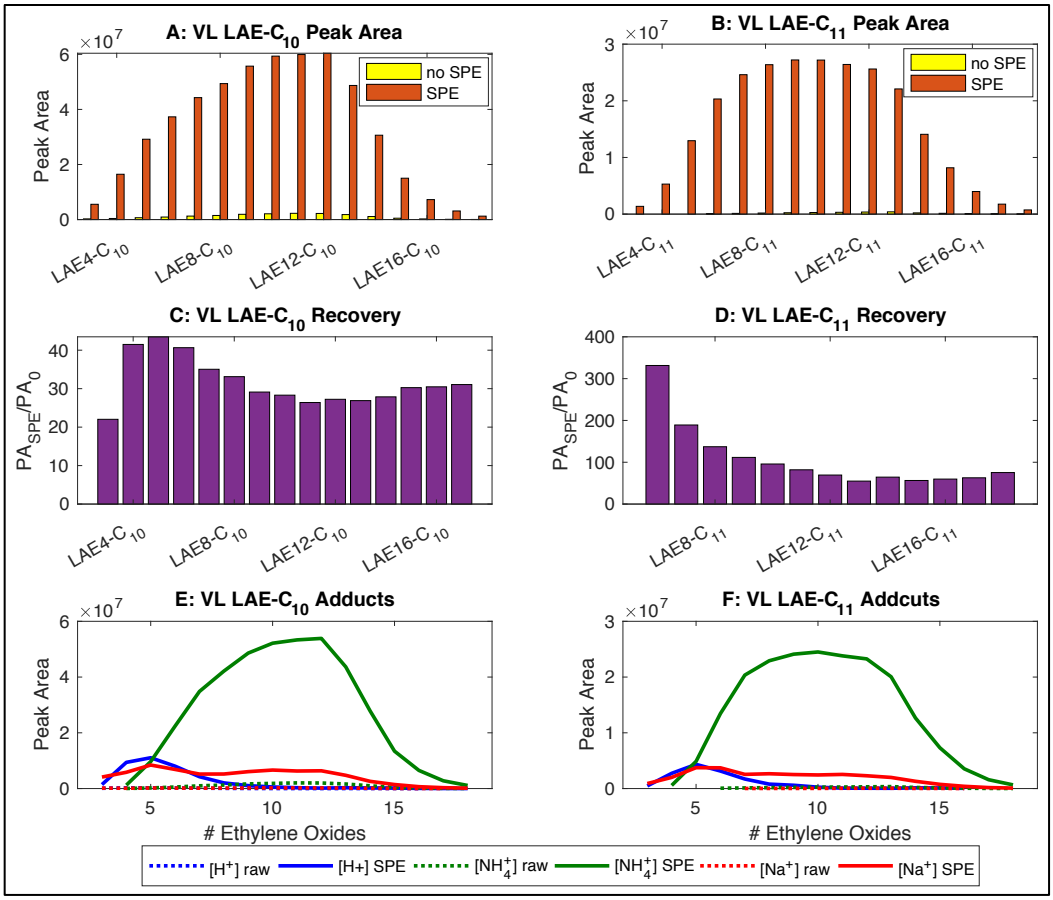

Figure 4.5: Mass spectral data for LAE-C10 (panel A, C, E) and LAE-C11 (panel B, D, F) detected in VL with and without SPE: (A) and (B) peak areas, (C) and (D) recoveries, (E) and (F) peak areas of hydrogen [H^+], ammonium [NH_4^+], and sodium [Na^+] adducts.

Lastly, not only has SPE increased the signal of known surfactants (PEGs, PPGs, and LAEs) in the samples of hydraulic fracturing fluids, but also it has shown the appearance of a set of unknown compounds in the early region of the chromatogram, from 3-9 minutes. The identity of these compounds is the main theme of this paper and discussed in the following sections.

4.3.2 Identification of polyethylene glycol amines (PEG-amines)

In Figure 4.1 there are four large peaks in the first 9 minutes of the chromatogram with masses at measured masses of *m/z* 282.1910, *m/z* 326.2176, *m/z* 370.2438 and *m/z* 414.2697. The

extracted peaks and mass spectra are presented in Figure 4.6. These four peaks are separated by an average of 44.0262 ± 0.0003 mass units, which is the calculated exact mass of an ethylene oxide unit (O-CH_2-CH_2, calculated exact mass 44.0262). This result led to the hypothesis that these peaks represent a yet undiscovered series of ethoxylated compounds in the hydrophilic region of the chromatogram, similar to our previous work on the identification of PEGs, PPGs, PEG-carboxylates, and LAEs [76]. Because the measured masses of the protonated molecules were even, these compounds must contain an odd number of nitrogen atoms (1, 3, 5, etc. per the nitrogen rule) [132].

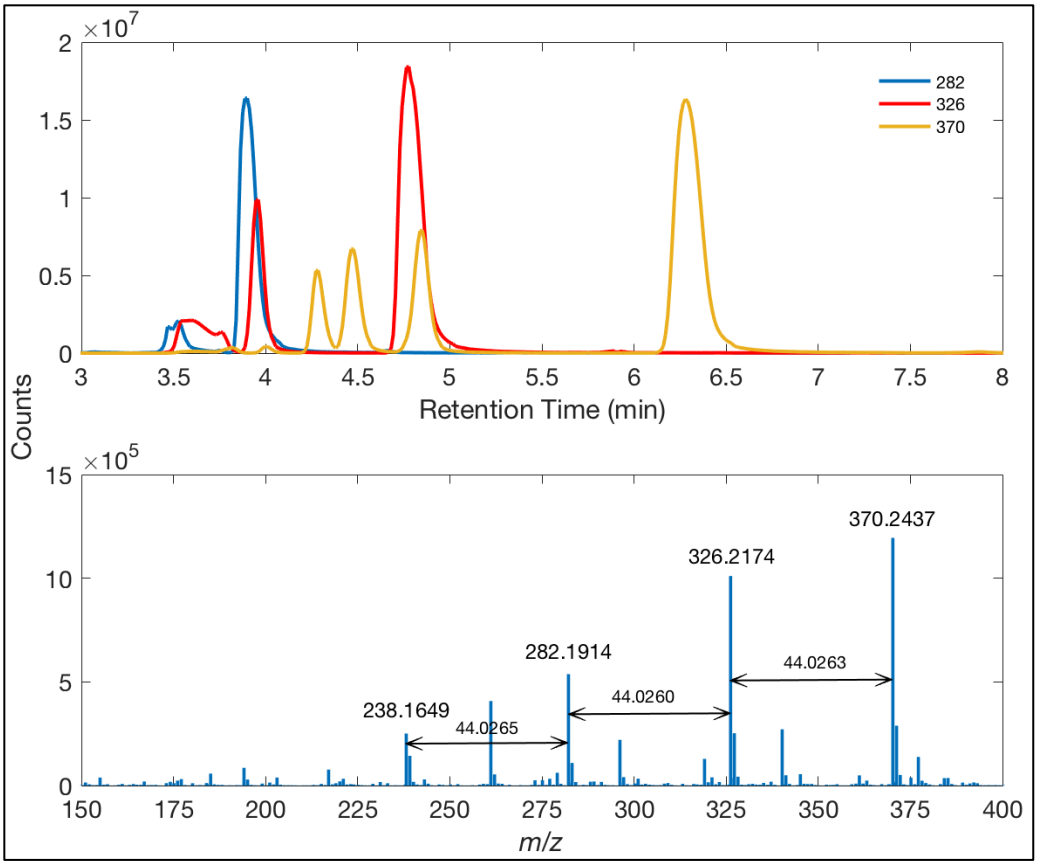

Figure 4.6: JR5 total ion chromatogram from 3-7 minutes showing unknown peaks and extracted nominal masses *m/z* 282, 326, and 370 (top panel). Extracted mass spectra of unknown peaks showing 44.0262 ± 0.0003 mass unit separation of unknown compounds (bottom panel).

The neutral formula obtained for *m/z* 282.1910 was a single formula of $C_{12}H_{27}NO_6$ for a 4-ppm mass window with the MassHunter formula generator set to default elements and limits (30 C, 120 H, 30 O, 30 N, 5 S, 3 Cl). Searching the ChemSpider database for this formula gave a compound with a PEG structure containing a primary amine on one end and a hydroxyl group on the other end (CAS no. 39160-70-8; IUPAC name: 17-amino-3,6,9,12,15-pentaoxaheptadecan-1-ol; common name: PEG6-amine). Thus, these four peaks were suspected to be PEG-amines with ethoxylated chains in the range of n=5-8, pending a comparison to a known standard, MS-MS analysis, and application of Kendrick mass defect.

The putative PEG6-amine in sample JR5 was chosen for MS-MS analysis because it was available as a standard and had sufficient abundance in this sample for a good MS-MS spectrum. Figure 4.7 shows both the MS-MS spectra for the standard and the sample. The chromatograms for each one has the same retention time of 3.8 ± 0.05 minutes and a nearly identical MS-MS mass spectrum. The standard MS-MS spectrum in Figure 4.7 (top frame) shows the major proposed fragmentation pathway for PEG6-amine, beginning at the hydroxyl end of the protonated ion with a water loss (*m/z* 264.1801) followed by a series of five losses of 44.0262 mass units as the ion "unzips" [76] until its terminus as ethaniminium (*m/z* 44.0495), the even mass indicating the presence of a single nitrogen atom in the final structure.

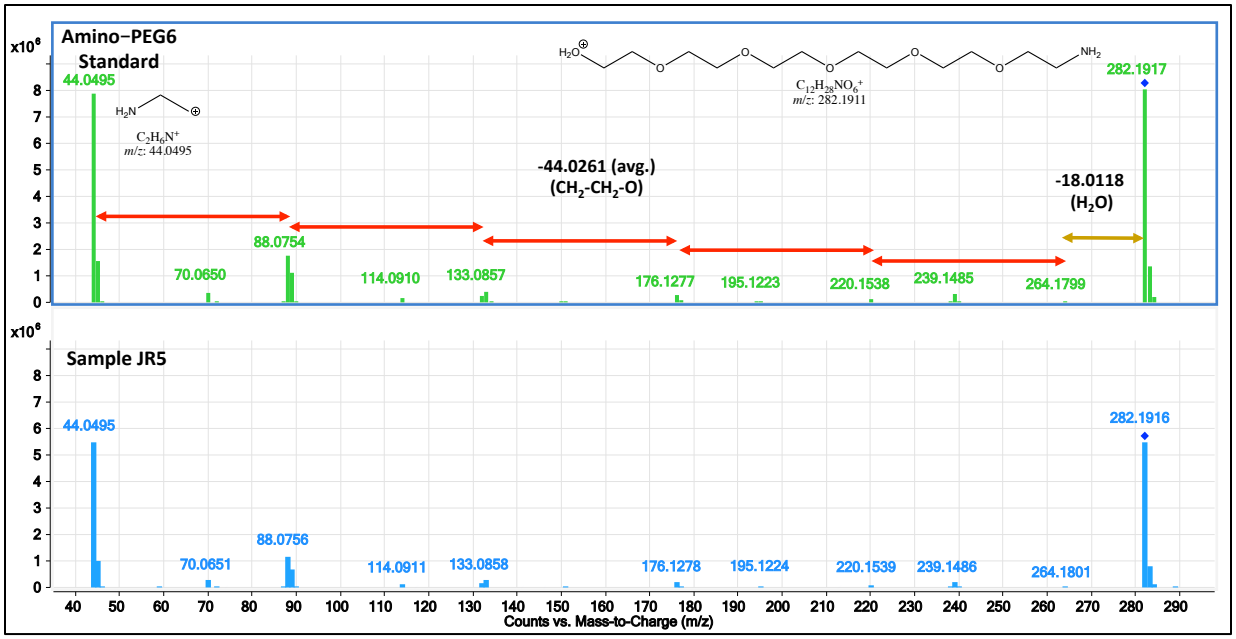

Figure 4.7: MS-MS fragmentation mass spectrum of PEG6-amine in standard (top panel) and JR5 (bottom panel).

There is also a secondary fragmentation pathway (Figure 4.8) that begins at the amine end with a neutral loss of acetaldimine (CH_3-CH=NH, calculated exact mass 43.0432) to *m/z* 239.1486, which continues to lose two EO units followed by a water loss, and then two more EO units before the terminus as protonated EO ($C_2H_5O^+$, *m/z* 45.0332). Because of the matching of the standard and putative PEG6-amine with accurate masses, MS-MS, and retention time, this PEG6-amine was confirmed in the JR5 sample.

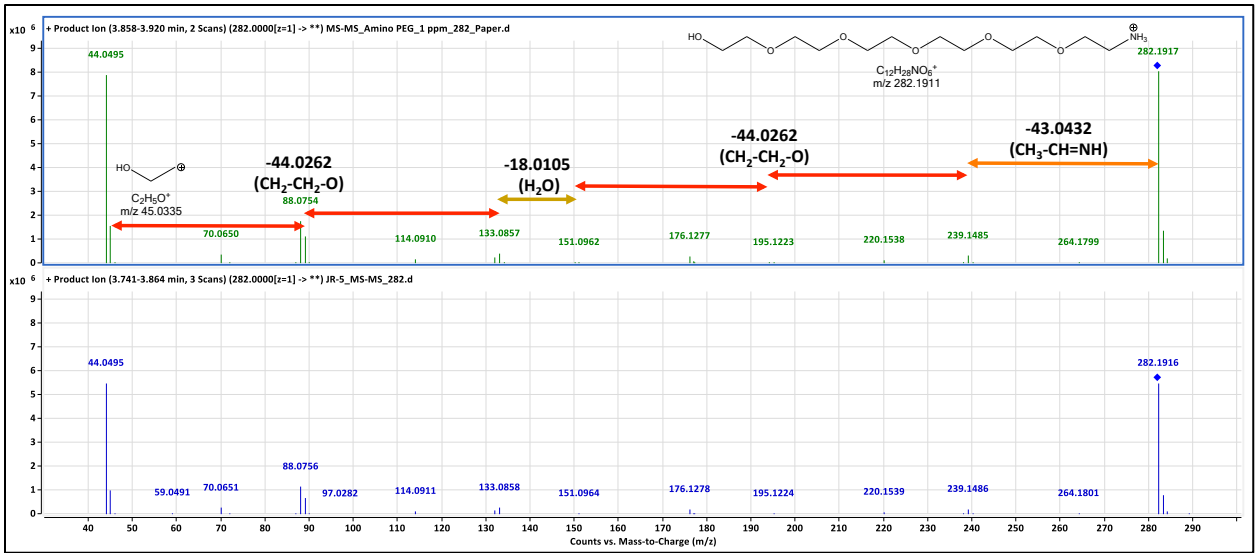

Figure 4.8: Alternative MS-MS fragmentation mass spectrum of PEG6-amine in standard (top panel) and JR5 (bottom panel).

Next, the Kendrick mass scaling factor was applied similarly as in Thurman et al. [76] in order to find the series of related PEG-amines that were present in the JR5 sample. The Kendrick mass is determined by dividing the nominal mass of ethylene oxide (nominal mass of 44), by the calculated exact mass of 44.0262, for a scaling factor of 0.99404559. The scaling factor is then multiplied by the measured accurate mass to determine the Kendrick mass, and finally the nominal measured mass is subtracted from the Kendrick mass to yield the Kendrick mass defect. Compounds that only differ by the addition or subtraction of one or more ethylene oxide units are related by having the same Kendrick mass defect.

For this reason, it is only necessary to verify the identity of one structure with a standard (i.e. PEG6-amine) because the remaining structures would be verified by comparison of the Kendrick mass defect. Kendrick mass data for these compounds in sample JR5 is presented in Table 4.2 and shows the Kendrick mass defect was calculated to be -0.023 and is consistent for all compounds in this group from nominal *m/z* 150 to 986. Twenty different PEG-amines were found

with the same Kendrick mass defect (n=2-21) in total in this series with a total of 108 observed isomers (Table 4.2).

Table 4.2: Formula, calculated exact mass (proton adduct), retention time, measured mass, mass accuracy, Kendrick mass, Kendrick mass defect, and number of isomers for PEG3-Amine through PEG22-Amine discovered in JR5. Measured mass and Kendrick mass is for the largest isomer present.

Name	Formula	Calculated Exact Mass ($M+[H^+]$)	Retention Time (min)	Measured Mass ($M+[H^+]$)	Mass Accuracy (ppm)	Kendrick Mass ($M+[H^+]$)	Kendrick Mass Defect	# Isomers
PEG3-Amine	$C_6H_{15}NO_3$	150.1125	2.6	150.1128	2.2	150.0234	-0.023	4
PEG4-Amine	$C_8H_{19}NO_4$	194.1387	2.6	194.1388	0.6	194.0232	-0.023	7
PEG5-Amine	$C_{10}H_{23}NO_5$	238.1649	2.7	238.1651	0.8	238.0233	-0.023	11
PEG6-Amine	$C_{12}H_{27}NO_6$	282.1912	3.9	282.1910	-0.7	282.0230	-0.023	5
PEG7-Amine	$C_{14}H_{31}NO_7$	326.2173	4.8	326.2176	0.8	326.0234	-0.023	4
PEG8-Amine	$C_{16}H_{35}NO_8$	370.2435	6.3	370.2438	0.7	370.0233	-0.023	6
PEG9-Amine	$C_{18}H_{39}NO_9$	414.2698	8.7	414.2697	-0.1	414.0230	-0.023	9
PEG10-Amine	$C_{20}H_{43}NO_{10}$	458.2960	9.8	458.2955	-1.0	458.0226	-0.023	9
PEG11-Amine	$C_{22}H_{47}NO_{11}$	502.3222	9.5	502.3226	0.8	502.0235	-0.023	9
PEG12-Amine	$C_{24}H_{51}NO_{12}$	546.3484	10.0	546.3493	1.6	546.0240	-0.024	8
PEG13-Amine	$C_{26}H_{55}NO_{13}$	590.3746	9.9	590.3746	0.0	590.0231	-0.023	8
PEG14-Amine	$C_{28}H_{59}NO_{14}$	634.4008	10.2	634.4009	0.1	634.0232	-0.023	6
PEG15-Amine	$C_{30}H_{63}NO_{15}$	678.4270	10.5	678.4272	0.2	678.0232	-0.023	5
PEG16-Amine	$C_{32}H_{67}NO_{16}$	722.4533	10.7	722.4530	-0.4	722.0228	-0.023	5
PEG17-Amine	$C_{34}H_{71}NO_{17}$	766.4795	10.9	766.4796	0.2	766.0232	-0.023	6
PEG18-Amine	$C_{36}H_{75}NO_{18}$	810.5057	11.0	810.5059	0.3	810.0233	-0.023	6
PEG19-Amine	$C_{38}H_{79}NO_{19}$	854.5319	11.2	854.5327	0.9	854.0239	-0.024	3
PEG20-Amine	$C_{40}H_{83}NO_{20}$	898.5581	11.4	898.5581	0.0	898.0231	-0.023	3
PEG21-Amine	$C_{42}H_{87}NO_{21}$	942.5843	11.5	942.5846	0.3	942.0233	-0.023	3
PEG22-Amine	$C_{44}H_{91}NO_{22}$	986.6106	11.7	986.6114	0.8	986.0239	-0.024	3

Figure 4.9 shows an example of nine possible isomers for the PEG9-amine (nominal *m/z* 414). The chromatographic separation of the nine isomers indicates that other structures of the PEG9-amine must be present. The standard was only available in the terminal amine, not in the substituted forms, and can only be present as a single isomer. However, the chemicals used in hydraulic fracturing are industrial grade; thus, it is not surprising to find a mixture of isomers due to side reactions and production of not only the primary amine but also secondary and possibly tertiary amines. The putative assignment then is that earlier eluting compounds with the same accurate mass are substituted amines present in small amounts that would have a shorter retention time relative to the primary amine.

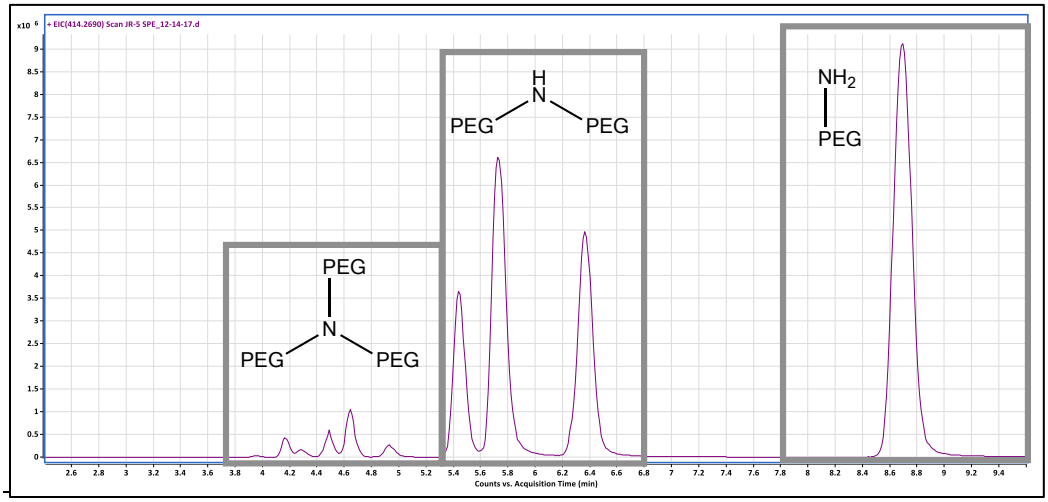

Figure 4.9: Extracted peaks for primary, secondary, and tertiary structures of PEG9-amine (*m/z* 414.2698 ± 0.0003, <1-ppm mass accuracy) in JR5. The largest and latest eluting peak is assumed to be the primary amine, followed by the secondary amines and then tertiary amines.

The postulated formation of secondary and tertiary amines was tested by MS-MS analysis of an isomer of PEG7-amine (*m/z* 326.2173, retention time = 3.6 min). The results of MS-MS are presented in Figure 4.10 and the unique fragmentation pathway is shown in Figure 4.11, which shows that the major ions are *m/z* 132.1018, 70.0649, and 45.0335, not the *m/z* 44.0495 and 88.0755 ions that are found in the primary amine (Figure 4.7). This different intensity of ions

would be expected for the secondary amine structures, thus confirming this finding for a secondary PEG-amine.

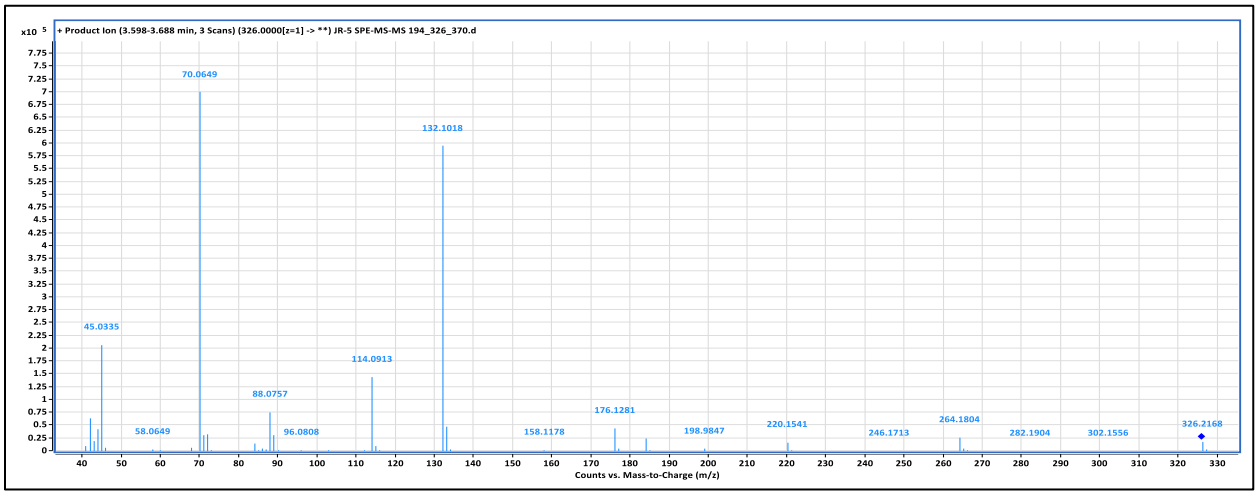

Figure 4.10: MS-MS spectrum and fragmentation pathway for isomer of PEG7-amine (*m/z* 326.2173) containing secondary amine.

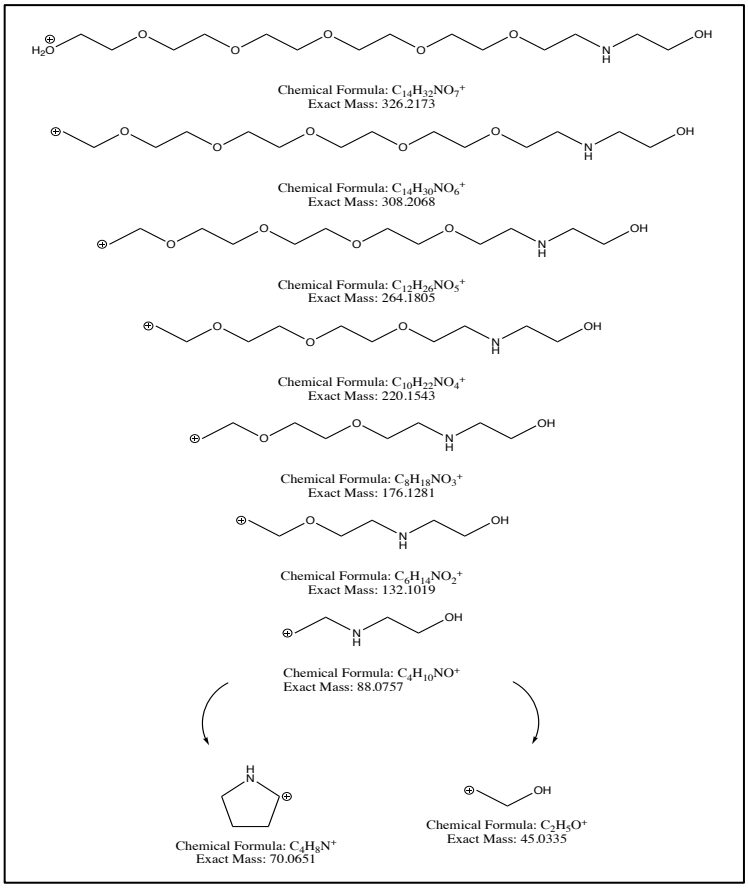

Figure 4.11: Fragmentation pathway for PEG7-amine (*m/z* 326.2173) showing the termination as either protonated ethylene oxide (*m/z* 45.0355) or the 5-member ring 1-pyrolinium (*m/z* 70.0651).

4.3.3 Identification of polyethylene glycol amine carboxylates (PEG-amine-carboxylates)

By analogy, the less prominent peaks in the early region of the JR5 chromatogram were examined. A series of peaks with values of *m/z* 296.1706, 340.1969, 384.2231, and 428.2491, which differ by 44.0262 ± 0.0001, were analyzed for their Kendrick mass defect. Figure 4.12 shows these extracted peaks from JR5 and the extracted mass spectrum for this region (retention time = 3-11 min), highlighting their low abundance relative to the PEG-amines and early eluting PEGs and illustrating the utility of solid phase extraction for compound identification.

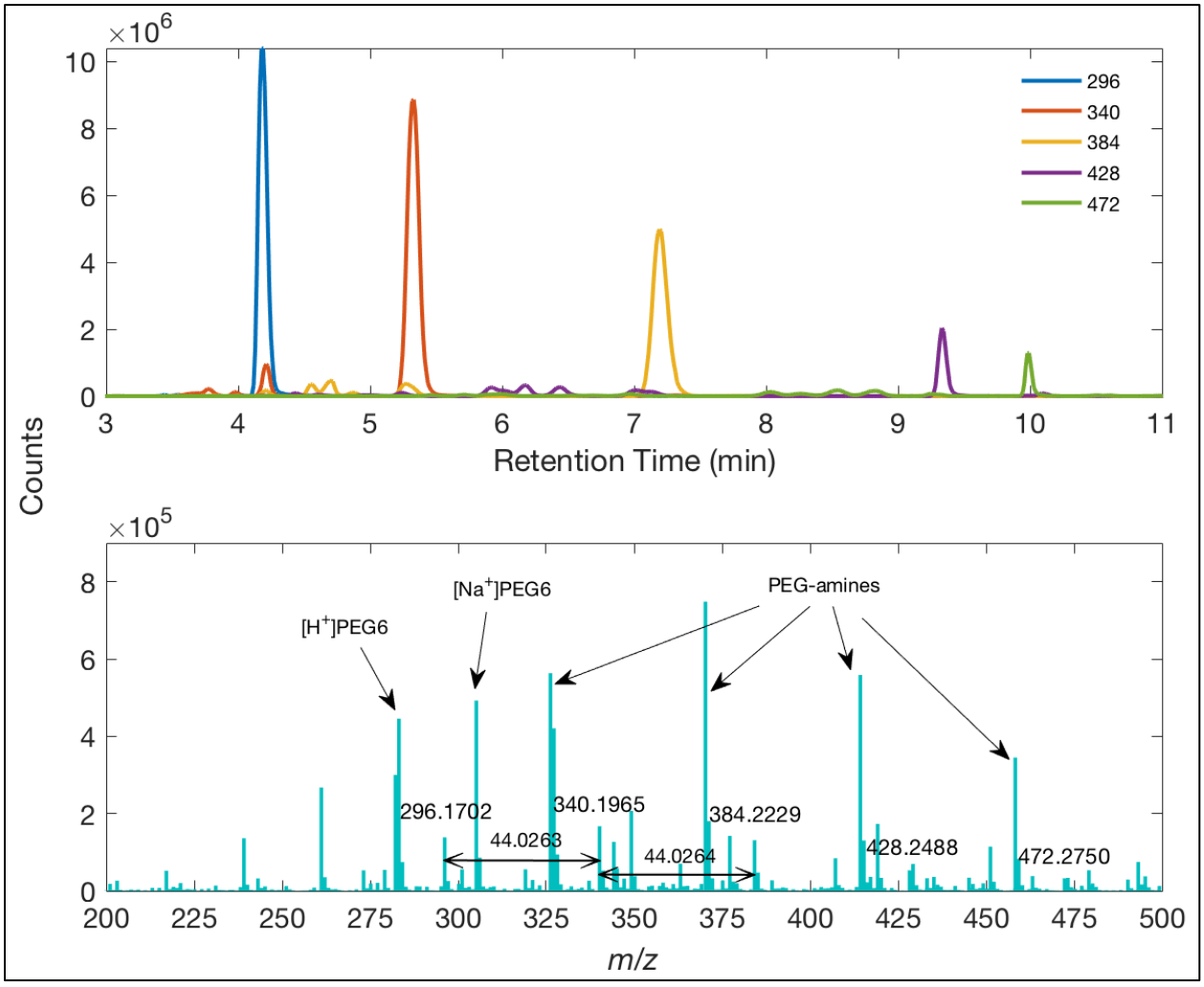

Figure 4.12: Extracted peaks from JR5 total ion chromatogram from 3-11 minutes showing unknown peaks and extracted nominal masses *m/z* 296, 340, 384, 428, and 472 (top panel). Extracted mass spectra of unknown peaks showing 44.0262 ± 0.0001 mass unit separation of unknown compounds, illustrating the low abundance relative to PEG-amines and PEGs (bottom panel).

Again, this result suggests another set of ethoxylated series with at least one nitrogen atom present, per the nitrogen rule. Furthermore, these ions differ from the previously identified PEG-amine series by 13.9789 ± 0.0007 mass units. It was hypothesized that this series is closely related to the PEG-amines. Because of the mass difference, i.e. 13.9789 mass units, it could not be the addition of a CH_2 group, which would have a mass difference of 14.0156. The formula generator gave a molecular formula of $C_{12}H_{25}NO_7$ for the *m/z* 296.1706 ion, which has one additional oxygen and two less hydrogen atoms than the PEG6-amine. This result suggests that the hydroxyl end of the PEG-amine was replaced with a carboxyl group. The neutral formula for *m/z* 296.1706 ($C_{12}H_{25}NO_7$) returned a putative identification by ChemSpider (ChemSpider ID: 13628845; IUPAC name: 17-amino-3,6,9,12,15-pentaoxahetadecan-1-oic acid; common name: PEG6-amine-carboxylate). These four peaks were tentatively identified as PEG-carboxylate-amines with ethoxylate chains from n=6-9 based on their accurate mass and Kendrick mass defect.

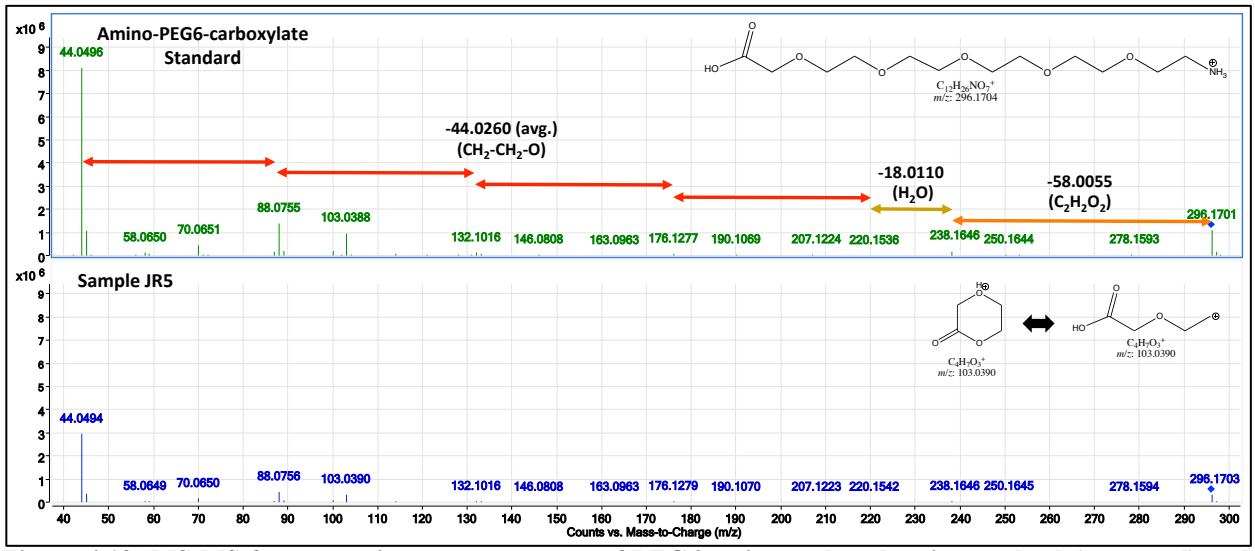

Figure 4.13: MS-MS fragmentation mass spectrum of PEG6-amine-carboxylate in standard (top panel) and JR5 (bottom panel).

An MS-MS experiment was performed on the putative PEG6-amine-carboxylate (*m/z* 296.1706) due to its sufficient abundance and availability of a standard (structure inset top of

Figure 4.13). The retention time for both the standard and the sample is 4.2 ± 0.05 minutes. The spectra are identical between the standard and the JR5 sample as seen in Figure 4.13. The dominant fragmentation pathway of the standard is the loss of acetolactone ($C_2H_2O_2$, exact mass 58.0055) from the parent compound to yield *m/z* 238.1649. Then, the ion loses water (*m/z* 220.1538) and proceeds to unzip with neutral ethylene oxide losses, yielding the *m/z* 88.0756 ion, and terminating at *m/z* 44.0495, which are the dominant ions similar to the PEG-amine fragmentation pathway. Alternatively, the compound will lose formic acid (CH_2O_2, exact mass 46.0055) to give *m/z* 250.1649, then lose formaldehyde (CH_2O, exact mass 30.0106) to *m/z* 220.1538 and follow the pathway above. The *m/z* 103.0390 ion (structure shown in Figure 4.13, bottom frame) is characteristic of PEG-carboxylates [76] and is present in both the standard and the sample. It most likely forms by direct neutral losses from the amine end of acetaldimine (CH_3-CH=NH, calculated exact mass 43.0432), water, and then three ethylene oxide units to terminate at the structure inset bottom in Figure 4.13.

Thus, comparison of the standard to the putative PEG6-amine-carboxylate in the JR5 sample confirmed the identification using MS-MS, matching accurate masses, and a retention time match with the standard. The Kendrick mass scaling factor was applied identically as before with a consistent defect of 0.006 and gave a series of sixteen PEG-amine-carboxylates (n=5-20) in sample JR5 with 84 observed isomers (Table 4.3).

As with PEG-amines, secondary and tertiary amines are also possible for PEG-amine-carboxylates and give a different fragmentation. Figure 4.14 shows six isomers for the PEG8-amine-carboxylate based on their accurate masses within a tolerance of ±0.0003 mass units (less than 1-ppm mass accuracy). Like the result for PEG-amines (Figure 4.9), the largest peak at 7.2 minutes is hypothesized to be the primary amine, with postulated secondary and tertiary amine structures eluting earlier.

Table 4.3: Formula, calculated exact mass (proton adduct), retention time, measured mass, mass accuracy, Kendrick mass, Kendrick mass defect, and number of isomers for PEG5-Amine-Carboxylate through PEG20-Amine-Carboxylate discovered in JR5. Measured mass and Kendrick mass is for the largest isomer present.

Name	Formula	Calculated Exact Mass ($M+[H^+]$)	Retention Time (min)	Measured Mass ($M+[H^+]$)	Mass Accuracy (ppm)	Kendrick Mass ($M+[H^+]$)	Kendrick Mass Defect	# Isomers
PEG5-Amine-C	$C_{10}H_{21}NO_6$	252.1442	3.5	252.1440	-0.6	251.9939	0.006	1
PEG6-Amine-C	$C_{12}H_{25}NO_7$	296.1704	4.2	296.1705	0.4	295.9941	0.006	1
PEG7-Amine-C	$C_{14}H_{29}NO_8$	340.1966	5.3	340.1969	0.9	339.9943	0.006	3
PEG8-Amine-C	$C_{16}H_{33}NO_9$	384.2228	7.2	384.2225	-0.8	383.9937	0.006	7
PEG9-Amine-C	$C_{18}H_{37}NO_{10}$	428.2490	9.3	428.2488	-0.5	427.9938	0.006	12
PEG10-Amine-C	$C_{20}H_{41}NO_{11}$	472.2752	10.0	472.2749	-0.7	471.9937	0.006	17
PEG11-Amine-C	$C_{22}H_{45}NO_{12}$	516.3015	9.8	516.3014	-0.1	515.9940	0.006	11
PEG12-Amine-C	$C_{24}H_{49}NO_{13}$	560.3277	10.2	560.3280	0.6	559.9944	0.006	6
PEG13-Amine-C	$C_{26}H_{53}NO_{14}$	604.3539	10.5	604.3542	0.5	603.9943	0.006	6
PEG14-Amine-C	$C_{28}H_{57}NO_{15}$	648.3801	10.4	648.3798	-0.5	647.9937	0.006	4
PEG15-Amine-C	$C_{30}H_{61}NO_{16}$	692.4063	10.6	692.4059	-0.6	691.9936	0.006	4
PEG16-Amine-C	$C_{32}H_{65}NO_{17}$	736.4325	10.9	736.4324	-0.2	735.9939	0.006	4
PEG17-Amine-C	$C_{34}H_{69}NO_{18}$	780.4587	11.0	780.4589	0.2	779.9942	0.006	2
PEG18-Amine-C	$C_{36}H_{73}NO_{19}$	824.4850	11.2	824.4853	0.4	823.9944	0.006	2
PEG19-Amine-C	$C_{38}H_{77}NO_{20}$	868.5112	11.4	868.5107	-0.5	867.9936	0.006	2
PEG20-Amine-C	$C_{40}H_{81}NO_{21}$	912.5374	11.5	912.5368	-0.6	911.9934	0.007	2

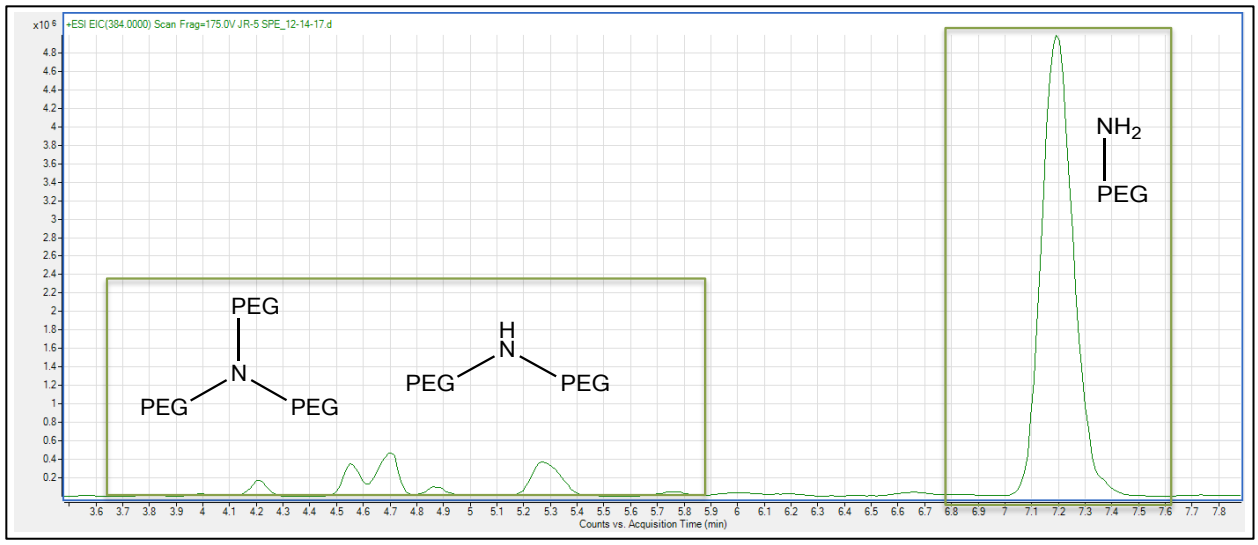

Figure 4.14: Extracted peaks for postulated primary, secondary, and tertiary structures of PEG8 carboxylate-amine (*m/z* 384.2228 ± 0.0003, <1-ppm mass accuracy) in JR5. The largest and latest eluting peak is assumed to be the primary amine, followed by the secondary amines and then tertiary amines.

An MS-MS experiment was performed on both the largest peak at 7.2 minutes and an early isomer of PEG8-amine-carboxylate at 4.5 minutes (Figure 4.14). The top spectra in Figure 4.15 is the fragmentation of the primary PEG8-amine-carboxylate (retention time of 7.2 minutes) and follows the same pathway as PEG6-amine-carboxylate (*m/z* 296.1704) based on neutral losses with dominant ions at *m/z* 103.0391, 88.0757, and 44.0495. The bottom panel of Figure 4.15 shows the MS-MS fragmentation spectra for a PEG8-amine-carboxylate that elutes at 4.5 minutes with dominant ions at *m/z* 190.1073, 114.0912, 70.0650 and 45.0333. One fragmentation scheme for this compound begins at the hydroxyl end of a secondary amine with a loss of water (*m/z* 366.2122) followed by losses of EO until *m/z* 146.0812, then either a loss of the secondary amine as aziridine (C_2H_5N, exact mass 43.0422) to the diagnostic ion *m/z* 103.0390, or the loss of acetolactone to *m/z* 88.0757 followed by a water loss to *m/z* 70.0651.

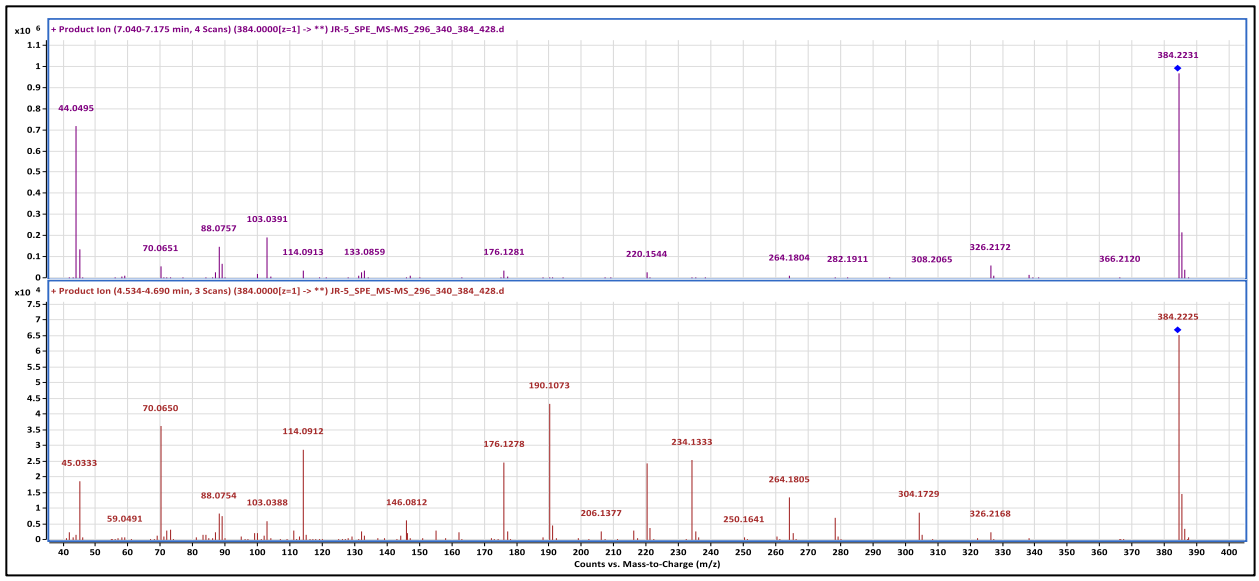

Figure 4.15: Top panel shows results of MS-MS experiment on the PEG8-amine-carboxylate isomer at 7.2 minutes; bottom panel shows results of MS-MS experiment on isomer at 4.5 minutes.

4.3.4 Identification of double amine polyethylene glycols (amino-PEG-amines)

After the identification of the PEG-amines and PEG-amine-carboxylates, we considered what other related ethoxylated structures may be present. One potential structure is the PEG-amine with the hydroxyl end replaced with a second amine (i.e. an amino-PEG-amine). Again, by analogy, masses of *m/z* 281.2070, 325.2334, and 369.2593 were present in the JR5 sample and could be candidates as the amino-PEG5-amine through amino-PEG7-amine, based on calculated exact masses of *m/z* 281.2071, 325.2333, and 369.2595. The formula generated for measured mass of *m/z* 281.2070 gave a molecular formula of $C_{12}H_{28}N_2O_5$ (the first of two possible formulas considering a mass error of ±5 ppm) and matched the formula for the drawn structure. The neutral formula for this ion returned a putative identification by ChemSpider (CAS no.: 72236-26-1; IUPAC name: 1,17-diamino-3,6,9,12,15-pentaoxaheptadecane; common name: amino-PEG5-amine).

Figure 4.16 shows the results of the MS-MS experiment performed on *m/z* 281.2070 in the sample and a standard for amino-PEG5-amine. This compound was not sufficiently abundant in JR5 to give a good MS-MS spectrum, so SWD was used due to a higher abundance of *m/z* 281.2070. The compounds in both the sample and standard are shown to lose aziridine (C_2H_5N, exact mass 43.0422) and then water to *m/z* 220.1543. The standard then continues to lose ethylene oxide until terminating at *m/z* 44.0495. The putative amino-PEG5-amine in the sample has a slightly different fragmentation, which suggests that it is a secondary amine. The compound loses two more ethylene oxide groups (*m/z* 132.1019), like the standard, until it reaches the secondary amine, at which point it loses the secondary amine as aziridine and then another ethylene oxide to terminate as protonated ethylene oxide. Furthermore, there is a secondary fragmentation pattern that gives more evidence of a secondary amine structure. In the MS-MS spectrum for the standard (Figure 4.16, top panel), *m/z* 264.1800 indicates the initial loss of ammonia (exact mass 17.0265) from the structure. If the sample compound had two primary amines like the standard, we would expect a similar loss. Instead we see *m/z* 263.1975, indicating the loss of water (exact mass 18.0106), which could only occur if an alcohol occupied the terminal position. The proposed dominant fragmentation pathways for both isomers are shown in Figure 4.17. Because of the slightly different elution time and fragmentation, but matching accurate masses and fragment ions, we assign a putative identification of a secondary amino-PEG5-amine to *m/z* 281.2070 in the SWD sample. A standard was not available for confirmation of this secondary amino-PEG5-amine.

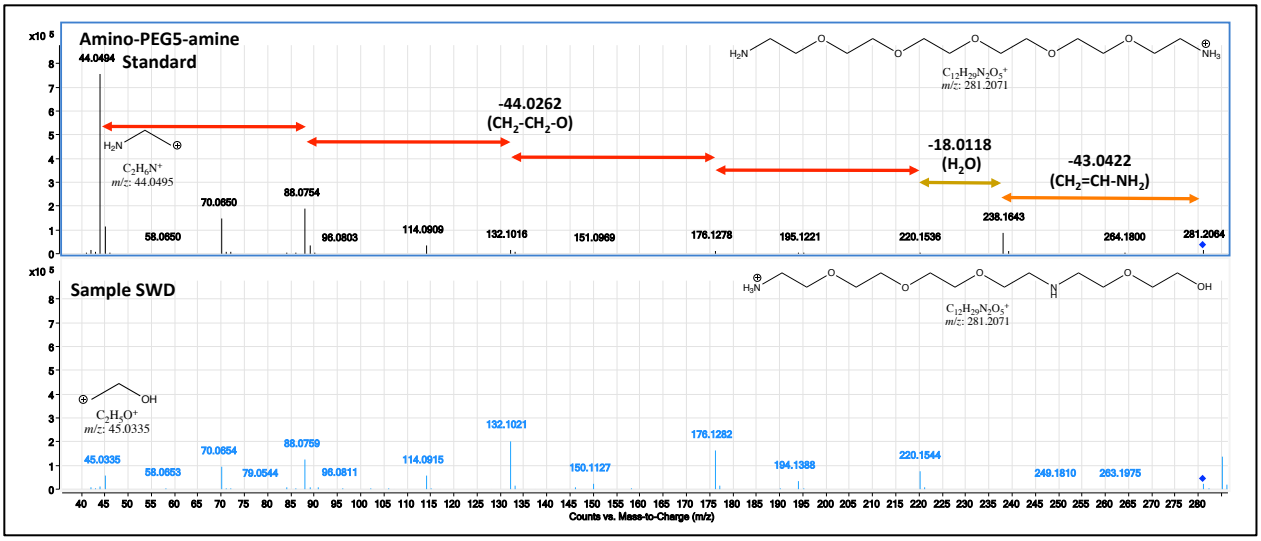

Figure 4.16: MS-MS fragmentation mass spectrum of amino-PEG5-amine in standard (top panel) and SWD (bottom panel).

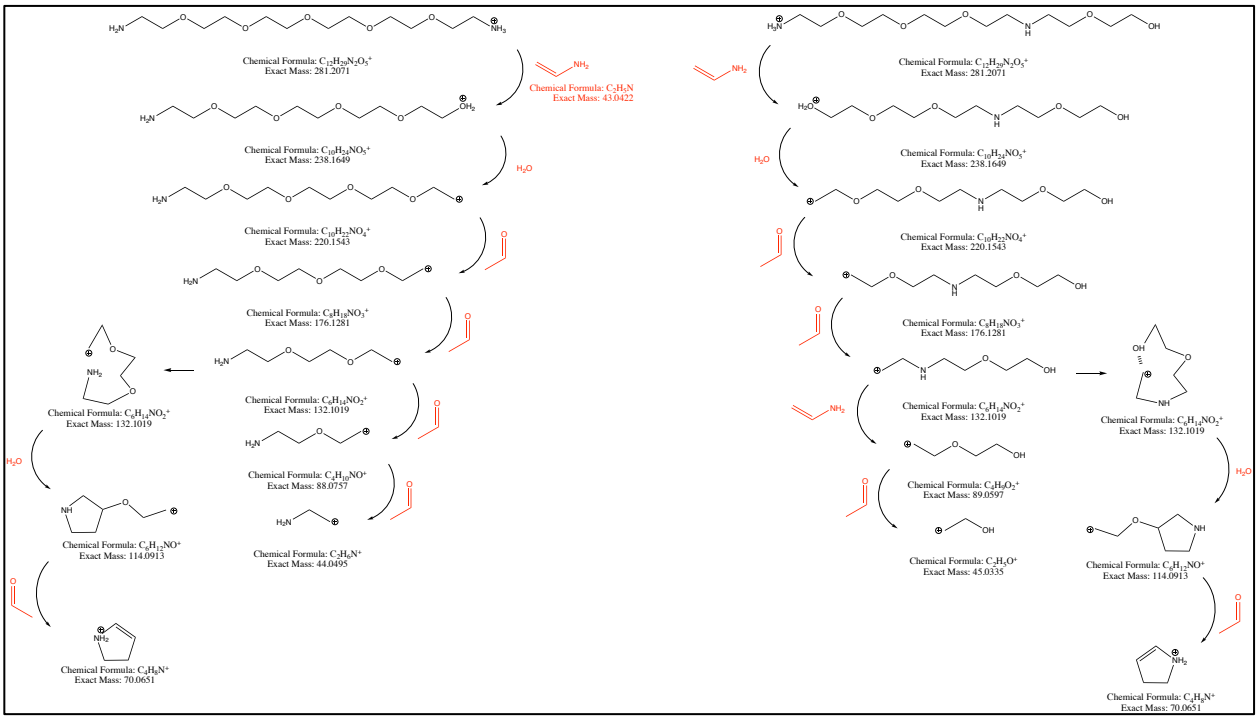

Figure 4.17: Proposed fragmentation pathway for the putative primary (left panel) and secondary (right panel) amino-PEG5-amine.

Notable ions that are present in the fragmentation spectrum for all the compounds discussed in this work are *m/z* 70.0651 and 114.0913. These are particularly abundant in spectra of

compounds that have been putatively identified to contain a secondary amine but exist in all spectra presented. We propose that these ions result from a charge migration and structure rearrangement that begins with *m/z* 132.1019. All ions presented in this paper are presented as if they are flat, two-dimensional confirmations. In reality, they are three-dimensional structures that bend and twist. As a result of this bending and twisting, the positive charge migrates from one end of the molecule to the other nearby end, causing a water loss to form the ion at *m/z* 114.0913 and then another ethylene oxide loss to form the ion at *m/z* 70.0651 (see Figure 4.17 for proposed fragmentation). These ions are particularly abundant because they contain a pyrrolidine ring that is difficult to fragment. Due to their presence in all spectra, they can be considered diagnostic ions for PEGs that contain an amine group.

The Kendrick mass scaling factor was applied identically as before with a consistent defect of 0.040 and showed a series of 13 amino-PEG-amines in SWD with 41 isomers (see Table 4.4). This series of compounds also has isomers with secondary and tertiary amines. Figure 4.18 shows five isomers for the amino-PEG8-amine based on their accurate masses within a tolerance of ±0.0003 mass units (<1-ppm mass accuracy). The largest peak at 3 minutes is assumed to be an isomer containing secondary or tertiary amines, with the primary amines assumed to elute last (based on elution of standard), similar to the pattern in PEG-amines and PEG-amine-carboxylates (Figure 4.9 and Figure 4.14). The occurrence and implications on the identification of these compounds in hydraulic fracturing fluids will be discussed in the following section.

Table 4.4: Formula, calculated exact mass (proton adduct), retention time, measured mass, mass accuracy, Kendrick mass, Kendrick mass defect, and number of isomers for Amino-PEG3-Amine through Amino-PEG14-Amine discovered in JR5. Measured mass and Kendrick mass is for the largest isomer present.

Name	Formula	Calculated Exact Mass ($M+[H^+]$)	Retention Time (min)	Measured Mass ($M+[H^+]$)	Mass Accuracy (ppm)	Kendrick Mass ($M+[H^+]$)	Kendrick Mass Defect	# Isomers
Amino-PEG3-Amine	$C_8H_{20}N_2O_3$	193.1547	2.0	193.1546	-0.4	193.0396	0.040	3
Amino-PEG4-Amine	$C_{10}H_{24}N_2O_4$	237.1809	2.1	237.1815	2.6	237.0403	0.040	1
Amino-PEG5-Amine	$C_{12}H_{28}N_2O_5$	281.2071	2.1	281.2070	-0.4	281.0396	0.040	2
Amino-PEG6-Amine	$C_{14}H_{32}N_2O_6$	325.2333	2.3	325.2332	-0.3	325.0395	0.040	4
Amino-PEG7-Amine	$C_{16}H_{36}N_2O_7$	369.2595	2.6	369.2596	0.2	369.0397	0.040	5
Amino-PEG8-Amine	$C_{18}H_{40}N_2O_8$	413.2857	3.1	413.2858	0.1	413.0397	0.040	6
Amino-PEG9-Amine	$C_{20}H_{44}N_2O_9$	457.3120	3.5	457.3119	-0.1	457.0396	0.040	4
Amino-PEG10-Amine	$C_{22}H_{48}N_2O_{10}$	501.3382	3.5	501.3382	0.1	501.0397	0.040	2
Amino-PEG11-Amine	$C_{24}H_{52}N_2O_{11}$	545.3644	3.5	545.3644	0.0	545.0397	0.040	2
Amino-PEG12-Amine	$C_{26}H_{56}N_2O_{12}$	589.3906	4.0	589.3905	-0.2	589.0396	0.040	4
Amino-PEG13-Amine	$C_{28}H_{60}N_2O_{13}$	633.4168	4.9	633.4166	-0.3	633.0394	0.039	4
Amino-PEG14-Amine	$C_{30}H_{64}N_2O_{14}$	677.4430	5.3	677.4424	-0.9	677.0390	0.039	4

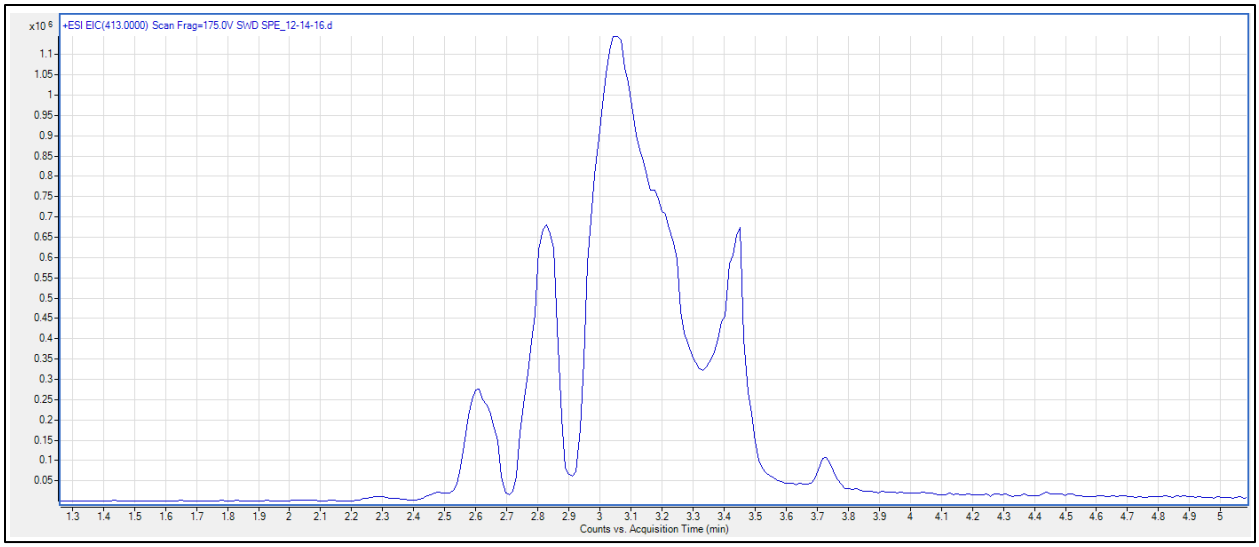

Figure 4.18: Extracted isomers of amino-PEG8-amine (*m/z* 413.2857).

4.3.5 Occurrence in Produced Waters & Use in Fracturing Fluids

Table 4.5 presents a summary of the compounds detected in each of the twenty samples examined and includes their state of origin and basin (if available), and their semi-quantitative concentrations. These samples are from five different regions (CO, OK, TX, WY, ND) collected at a wide range of times of production (<5 days to >230 days after production begins) and so are thought to be a good representation of produced waters from hydraulic fracturing. PEG-amines were detected in every sample, PEG-amine-carboxylates were detected in thirteen samples, while amino-PEG-amines were only detected in two.

Table 4.5: Approximate concentration of aminated PEGs found in various hydraulic fracturing samples from five western states (CO, ND, OK, TX, WY). N.D. = not detected.

Sample	PEG-Amines (ppb)	PEG-C-Amines (ppb)	Amino-PEG-Amines (ppb)	Origin	Time of Collection
JR5	1,000-10,000	100-1,000	1-10	CO	<30 days
JR8	1-10	1-10	N.D.	CO	>30 days
K01D0	1	1-10	N.D.	CO	<5 days
K31D4	1	1-10	N.D.	CO	<5 days
G2D	1,000-10,000	1-10	N.D.	CO	<5 days
KAD0	1	1-10	N.D.	CO	<5 days
K10D	1-10	1-10	N.D.	CO	>30 days
SLY	1,000-10,000	1-10	N.D.	CO	unknown
S3D	10-100	N.D.	N.D.	CO	<5 days
WK14	10-100	1-10	N.D.	CO	<30 days
YAL	10-100	N.D.	N.D.	CO	<30 days
MM	100-1,000	1-10	N.D.	OK	>90 days
PV	100-1,000	1-10	N.D.	OK	<30 days
SWD	100-1,000	1-10	1,000-10,000	OK	various
VL	1	N.D.	N.D.	OK	>90 days
CR	1	N.D.	N.D.	OK	>230 days
PAL	1	N.D.	N.D.	WY	unknown
BGA	1	1-10	N.D.	TX	unknown
NRT4X	1-10	N.D.	N.D.	TX	unknown
MAJ3	1-10	N.D.	N.D.	ND	unknown

One way to view the compounds that were used to mix a fracturing fluid is by checking the FracFocus report for that well, which is made publicly available online. In many FracFocus reports, there are several entries that do not have an associated CAS number and are rather listed as being “proprietary” or a “trade secret”. Of the 20 samples analyzed for these compounds, we obtained FracFocus reports for 12 of them. The FracFocus report for one well has nine entries listed as “proprietary”: one with a listed purpose as “friction reducer” and eight with the purpose of “acid corrosion inhibitor”. Another has the “permanent clay stabilizer” listed as being a “trade secret” and “amine salts” listed as “proprietary” with no stated purpose. Internet search for a standard for the PEG-amines showed that they are reagents for preparation of “pH responsive self-

healing hydrogels formed by boronate-catechol complexation", which may be used in hydraulic fracturing. This is reasonable application in hydraulic fracturing because gel-based fluids are often cross-linked with boron compounds and catechol has been used as an oxygen scavenger to help stabilize gel formulations at high temperatures [133]. Patents for compounds with similar formulas and structures, and with both single and double primary and secondary amines, indicate that they have been used as a shale hydration inhibition agent [134], friction reducers [135], and thickeners [136]. Their purpose is to prevent clay swelling and plugging of the wells, which is a common problem that requires re-fracturing of the well.

These compounds have also been identified as being useful as clay stabilization agents because they can sorb onto the surfaces of clay minerals, thus reducing the number of active sites for water molecules leading to a decrease in swelling [63]. The swelling of clay containing formations during production can cause wellbore instability, borehole closure, and casing placement and is an expensive issue for operators [137]. The fundamental concept of clay swelling inhibitors is the displacement of cations between clay mineral layers so as to restrict their interaction with water and, thus, reduce swelling. Inhibitors with a PEG or PPG backbone and two primary amines were introduced in the last two decades and are stable under a wide range of pH and temperatures [137]. Suter et al. [138] performed computer simulations on the mechanism of action of several clay swelling inhibitors to develop a rule-based design approach. They found that the ideal swelling inhibitor should be able to displace sodium ions, possess a water soluble, hydrophobic backbone (e.g. alkyl, PEG, PPG), have primary or mono-quaternary amine functionality, and have little alcohol functionality. The amino-PEG-amines described in this work meet all these requirements, but the PEG-amines and PEG-amine-carboxylates have the alcohol functionality that increase hydrophilicity and, thus, encourage water intercalation to clay mineral layers. Additionally, a patent has been filed for the amino-PEG-amines with a primary and

secondary (and possibly tertiary) amine for the purpose of clay hydration inhibition [139]. Amino-PEG-amines and amino-PPG-amines have been shown to be effective clay swelling inhibitors, with amino-PPG-amines performing slightly better [140, 141].

No literature could be found regarding PEG-amine-carboxylate utility in a hydraulic fracturing fluid, but references are made to "amphoteric amines" for use as clay and shale stabilization additives, suggesting these compounds could be used for this purpose [133, 142]. However, previous research on PEGs (i.e. those without an amine) showed that carboxylation of the alcohol end was part of their aerobic biodegradation pathway [127], but further additional research is necessary to confirm this pathway for PEG-amines. In the absence of a sample of a proprietary surfactant blend from one of these producers or their suppliers, we cannot definitively know the function of the compounds discovered in this work. However, previous research and patent filings suggest that they may be used for shale hydration, friction reduction, thickening, and/or clay stabilization.

CHAPTER 5: AEROBIC BIOLOGICAL DEGRADATION OF ORGANIC COMPOUNDS IN HYDRAULIC FRACTURING WASTEWATERS

This chapter describes the efficacy of biological treatment experiments on reduction of bulk organic carbon and common hydraulic fracturing fluid additives.

This work will be published following manuscript review by co-authors and the addition of a section on microbial community analysis that is not included in this dissertation:

Sitterley, K.A., Silverstein, J., Rosenblum, J.R., Linden, K.G., Aerobic Biological Degradation of Organic Compounds in Hydraulic Fracturing Wastewaters, (*in preparation*, 2019).

5.1 Introduction

Hydraulic fracturing simultaneously requires and generates millions of gallons of water. The amount of water use per well varies from play to play and has been increasing in every major play. As of 2016, water use per well ranged from 21.6 million L (5.7 million gal) per well in the Bakken play to 42.5 million L (11.3 million gal) per well in the Permian play [23]. Several attempts have been made to quantify the amount of flowback and produced water generated from hydraulic fracturing using publicly available data and modeling [23, 47-53]. A recent estimate for 2016 production shows that the total amount of flowback and produced water in the major plays in the United States ranged from 2.3 million L (610,000 gal) in the Niobrara to 75.0 million L (19.8 million gal) per well in the Permian, with projections that these values could double in the next 15-20 years [47].

The majority of this water is managed in one of two ways: injection in Class II disposal wells or treatment at a centralized facility for reuse or discharge [1, 56, 85]. Injection in disposal wells is still the dominant methodology, but treatment and reuse are growing trends in the United States [143] and is expected to dominate in Europe due to a paucity of suitable injection wells and regulations [144]. There are no well-defined water quality parameters that treatment facilities can target when treating for reuse in hydraulic fracturing because fluid formulations vary widely [94, 110]. Treatments are primarily concerned with reduction of suspended solids, oil and grease, and scale causing ions, but removal of fracturing fluid additives is not considered and can negatively impact water resources [143, 145]. Recently, companies have determined that reduction of TDS is not necessary to mix an adequate hydraulic fracturing fluid and have been developing formulations that use high TDS waters [91] or diluted flowback and produced water [92]. Removing organic matter prior to reuse is beneficial, as high levels of organic matter can cause microbes to thrive and lead to microbial induced corrosion in transport lines, pumps, and drilling equipment [95].

Further, high levels of organic matter in recycled fracturing fluid yielded gel-based fluids with lower peak viscosities [96], which is a crucial characteristic for an effective fracturing fluid [97]. Thus, targeting removal of organic matter rather than inorganic constituents may increase in future management approaches.

Centralized and mobile treatment facilities use physical/chemical treatment technologies like flocculation/sedimentation basins, bag filtration, aeration, evaporation and crystallization, chemical precipitation, oil/water separation, reverse osmosis, and thermal distillation [56, 143]. They achieve removal of organic compounds as an ancillary benefit of the primary inorganic treatment targets. Because of the highly saline nature of some flowback and produced waters, biological treatment was precluded from consideration as a treatment technology [88]. Recently, treatment of flowback and produced water with biologically active filtration (BAF) has been examined at the bench- and pilot-scale for DOC reduction prior to ultra- and nanofiltration membranes [101, 103, 104]. These studies generally achieved >90% DOC reduction in <72 hrs in waters with 36-723 mg/L DOC and 12,600-31,100 mg/L TDS. Analysis of treated and untreated flowback and produced waters presented alongside these studies showed the importance of biological treatment as a pretreatment technology, highlighting that biological degradation accounted for the majority of DOC removal [105]. Microbial mats were investigated as a biological treatment approach for real and synthetic flowback and produced waters with some success up to 200,000 mg/L TDS [108]. Aerobic degradation in conjunction with activated carbon of flowback water with 103,000 mg/L TDS and 649 mg/L DOC was shown to be preferential over ozonation for removal of low molecular weight compounds and achieved 83% reduction of DOC in 48 hr [109].

An important component that was missing from previous biological treatment studies was the impact on specific compounds commonly used as fracturing fluid additives. Polyethylene

glycols (PEGs) and polyethylene glycol amines (PEG-amines) have been identified in flowback and produced waters across the country [57, 65, 67]. Therefore, they are almost certain to be in any water received at a facility for treatment. Additionally, research is needed on the utility of biological treatment and on flowback and produced waters that encompass the full spectrum of organic and salt content found in these waters and the degree and rate of removal over several treatment cycles. Therefore, the objectives of this study were to (1) determine the extent of DOC removal from flowback and produced waters with a wide range of organic and salt content, (2) evaluate the rate of DOC removal and the impact of residence time and, (3) investigate the extent to which familiar fluid additives are removed.

5.2 Materials & Methods

5.2.1 Sample Collection and Water Quality

The samples used for these experiments were collected from hydraulically fractured wells in Oklahoma, USA accessing the Meramec and Osage formations. Samples were collected directly from the separator into new PTFE 15-gal barrels and immediately sealed for transport to the University of Colorado Boulder. Upon arrival, samples were placed into storage at 4°C. Relevant water quality parameters for each sample are provided in Table 5.1.

Table 5.1: Age, DOC, TN, and TDS for samples used for biological treatment experiments.

Sample	Age	DOC (mg/L)	TN (mg/L)	TDS (mg/L)
PR	<30 days	350	70	26,400
VL	>90 days	180	220	96,400
CR	>230 days	22	140	157,100

5.2.2 Biological Reactors

Each reactor was operated as a sequencing batch reactor (SBR) and had a total volume of 4L with 3L of liquid and 1L of headspace. They were seeded with activated sludge collected from 75th Street Wastewater Treatment Facility in Boulder, Colorado and aerated via diffuser stones at the bottom of the reactor with breathing air from the lab supply.

5.2.2.1 Acclimation Cycles

Acclimation occurred in two-day cycles with TDS of the feed water increasing by 4,000 mg/L for every cycle until it reached the full strength of the wastewater. At the end of two days, air to the reactors was turned off and the reactors were allowed to settle for 30 minutes. Then, 2L would be decanted and the reactors were fed with the next cycle of feed water. This meant that the acclimation times were proportional to the TDS of the sample. Samples were not filtered or otherwise treated prior to being introduced into the reactor. TDS and MLSS samples were taken periodically throughout the acclimation and treatment phase and analyzed with Standard Methods [146]. MLSS was maintained between 3,000-5,000 mg/L in each reactor. Feed water was supplemented with yeast extract (Beckton, Dickinson and Company; Franklin Lakes, New Jersey) and potassium hydrogen phosphate (Alfa Aesar; Ward Hill, Massachusetts) to aid in acclimation.

5.2.2.2 Treatment Cycles

After acclimation, three treatment cycles for each sample were carried out and the cycle time for each reactor was chosen in proportion to the total DOC in each sample and based off of previous experience with biological treatment of flowback and produced water. This was done to ensure adequate time for degradation of as much of the DOC as possible. Samples for DOC, LC-

MS, and GC-MS were taken at regular intervals and analyzed promptly. Blank experiments were conducted that did not include inoculum in both an aerated and non-aerated configuration.

5.2.3 DOC Analysis

The DOC samples collected were filtered through 0.45 μm nylon filters (VWR International; Radnor, Pennsylvania) and diluted prior to analysis with a Shimadzu TOC-V_{CSH} (Shimadzu Corp.; Kyoto, Japan) using the combustion/NDIR method. Each sample was analyzed in duplicate.

5.2.4 Fracturing Fluid Additive Analysis

Prior to analysis, samples analyzed for PEG degradation were filtered through 0.45 μm Acrodisc PTFE filters (PALL Corp.; Port Washington, NY). LC-MS analysis was performed with an Agilent 1100 series high performance liquid chromatography (HPLC) unit using a reverse phase 150 mm × 4.6 mm C8 analytical column with a 3.5 μm particle size (Zorbax Eclipse XDB-C8) coupled to an Agilent LC/MSD Ion Trap XCT Plus (Agilent Technologies Inc., Santa Clara, CA) with positive ion electrospray ionization. Mobile phase A was HPLC grade water (Honeywell Burdick & Jackson, Morristown, NJ) with 0.1% formic acid (Fluka, St. Louis, MO) and mobile phase B was HPLC grade acetonitrile (Honeywell Burdick & Jackson, Morristown, NJ). Gradient elution began with 90% A and 10% B, held for 5 minutes, and then increased to 100% B until 24 minutes with a linear gradient, after which it continued at 100% B for two additional minutes. Select samples were analyzed with ultrahigh-performance liquid chromatography (UHPLC) with liquid chromatography/quadrupole time-of-flight mass spectrometry (LC/Q-TOF/MS) for verification of accurate mass and compound identification using the method described in Sitterley et al. [67]. For quantitation, hydrogen, ammonium, and sodium adducts of PEG, PEG-

carboxylates, and PEG-dicarboxylates were extracted from samples analyzed on the Ion Trap and their peak areas were summed and compared over the course of each treatment cycle [130]. Due to the high salt content of these waters, samples analyzed for PEG-amine degradation were prepared with solid phase extraction (SPE). SPE was carried out with an Oasis HLB 500 mg cartridge (Waters Corporation; Milford, MA) using the method described in Sitterley et al. [67].

5.2.5 Degradation Kinetics Modeling

DOC degradation results were fit to a first-order reaction model:

$$C_t = C_0 e^{-kt} + C_f$$

Where C_t is the DOC concentration at time t, C_0 is the initial DOC concentration, t is time, C_f is the final DOC concentration, and k is the first-order degradation coefficient. The model was fit using the Curve Fitting Toolbox in the MATLAB programming environment (MathWorks, Inc.; Natick, Massachusetts).

5.3 Results & Discussion

5.3.1 DOC Degradation

Figure 5.1A shows the DOC degradation for all three cycles of treatment for each of the three water samples examined. The PR sample, with low TDS and high DOC, saw 84% reduction in DOC in the first 12 hours of the first cycle, but degradation slowed in the second and third cycle, reaching similar amount of degradation in 72 hours (85%) and 144 hours (78%), respectively. The first-order rate constants for these cycles reflect this slowing degradation, starting with k_{PR1} = 0.260 ± 0.037/hr (95% confidence interval) in cycle 1, but slowing 79% to k_{PR2} = 0.056 ± 0.011/hr in cycle 2 and 93% to k_{PR3} = 0.019 ± 0.004/hr in cycle 3. For an 80% reduction in DOC, these results

indicate that 20% of the DOC (approximately 50 mg/L) in this sample is not biodegradable under these conditions. Both the aerated and non-aerated blank saw no considerable decrease in DOC concentration over the course of the treatment cycle (Figure 5.2A).

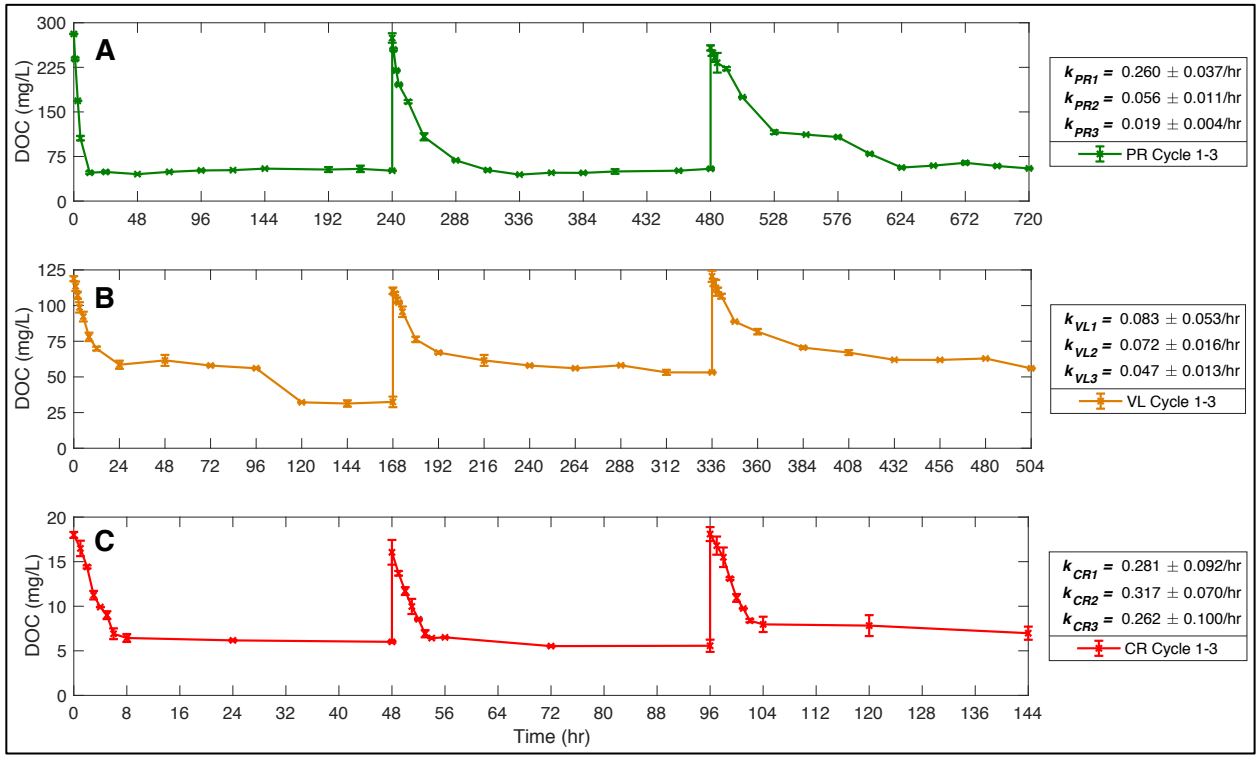

Figure 5.1: DOC degradation for three treatment cycles for (A) PR – high DOC, low TDS; (B) VL – mid DOC, mid TDS; (C) CR – low DOC, high TDS. Error bars represent standard deviation of replicate measurements.

VL degradation (Figure 5.1B) was slower and had a maximum DOC reduction at 74% only in the first cycle. In the second and third cycle, it only reached 52% and 54% degradation, respectively, indicating that between 25% and 50% of the DOC (30 to 50 mg/L) is not biodegradable in the treatment time period of 168 hours. The first-order rate constants for each of three VL treatment cycles are k_{VL1} = 0.083 ± 0.053/hr (95% confidence interval), k_{VL2} = 0.072 ± 0.016/hr, and k_{VL3} = 0.047 ± 0.013/hr. Degradation did slow in subsequent cycles but not as drastically as it did for PR treatment. In contrast with PR treatment, both the aerated and non-

aerated blanks for VL saw some amount of degradation (Figure 5.2B); the aerated blank showed a 61% reduction in DOC over 168 hours and the non-aerated blank saw a 24% reduction in DOC over 168 hours.

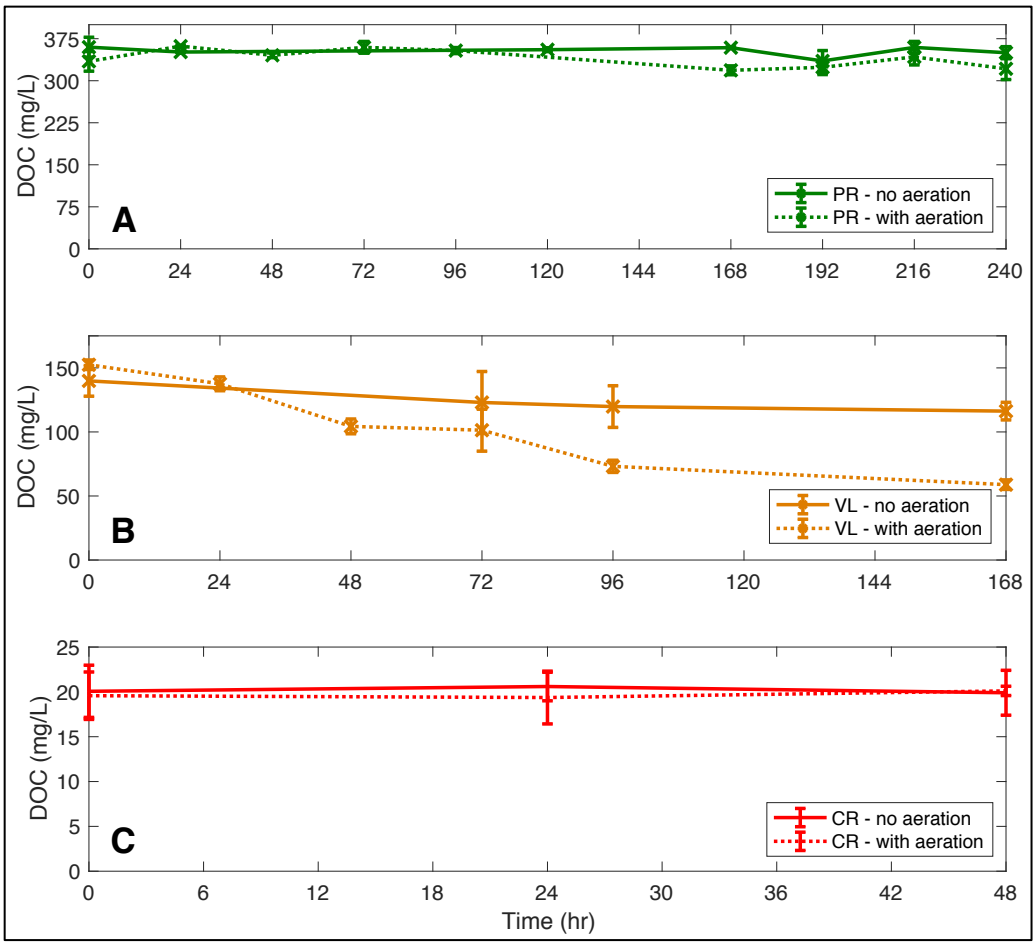

Figure 5.2: DOC results of unseeded treatment blanks both without aeration (solid line) and with aeration (dashed line) for (A) PR – high DOC, low TDS; (B) VL – mid DOC, mid TDS; (C) CR – low DOC, high TDS.

In CR, the high TDS and low DOC sample, the maximum DOC degradation was 67% and this was achieved in all three treatment cycles in the 48-hour treatment cycle, suggesting that approximately one-third of the DOC, or 7 mg/L is not biodegradable. Notably, CR had the most consistent treatment kinetics of the three samples considered with k_{CR1} = 0.281 ± 0.092/hr, k_{CR2} =

0.317 ± 0.070/hr, and k_{CR3} = 0.262 ± 0.100/hr. Similarly with PR treatment, the aerated and non-aerated blanks for CR saw no reduction in DOC over the course of 48 hours (Figure 5.2C).

This study demonstrates the ability of a well-acclimated culture to degrade between 50-80% of the total DOC in a hydraulic fracturing wastewater sample. Considering that the highest TDS sample tested saw similar normalized reductions to the other two samples, it also shows that the high TDS content of some of these waters is not an impediment to microbial degradation. However, there is still a sizeable portion, on a mass basis, of DOC that would be present if the water were to get reused, discharged to a surface water body, or transferred to another treatment technology for further treatment. In all cases, the treatment cycle could have been shorter and achieved a similar result for DOC removal because the data shows long plateaus in DOC degradation. PR has the highest DOC first-order degradation rate in the first cycle and had all of the degradation occur in the first 12 hours, so this sample would benefit from a residence time of 12 hours or less. The long treatment time provided no benefit to DOC degradation. The same could be said for CR - while it did not experience the decrease in DOC degradation rate in successive cycles, it did reach maximum DOC degradation in the first 6 hours of treatment. VL was different in that it did not reach maximum DOC degradation until the end of its treatment cycle, but about 50% of the DOC degradation occurred in the first 12 hours for each treatment cycle.

From an application standpoint, if aerobic treatment were to be used in a water management approach for hydraulic fracturing flowback and produced water, the effluent could go one of a few places. Often when operators include treatment in their water management strategy, it is to get the water to a quality that would enable reuse as base water for hydraulic fracturing fluids to reduce the cost of water sourcing. Though the amount of DOC degradation achieved here may not be sufficient to enable reuse as a base fluid, it could find utility as a supplemental treatment to a physical-chemical process. In that case, the treated effluent would be transported to the field and

sit in storage either in a pit or tank battery until it is used. Rather than applying a biocide, base water in storage with lower DOC would reduce bacterial growth. Lower bacterial growth would reduce the impact of microbial induced corrosion in the storage, drilling, and pumping equipment. Even if the water is captured and stored on site, introducing percolation to the storage pits could be enough to reduce DOC to some extent. In this study the aerated blank of VL saw 61% DOC reduction over one week. In these results, the fracturing fluid performed best when mixed with a base fluid with <5 mg/L DOC, a level that was not achieved in any of the trials here.

5.3.2 PEG Degradation

Figure 5.3 shows the results of PEG degradation for the VL sample over the 168-hour treatment cycle. This figure shows the sum of the peak area for each of the PEGs, PEG-carboxylates (PEG-Cs), and PEG-dicarboxylates (PEG-diCs) for five 168-hour treatment cycles.

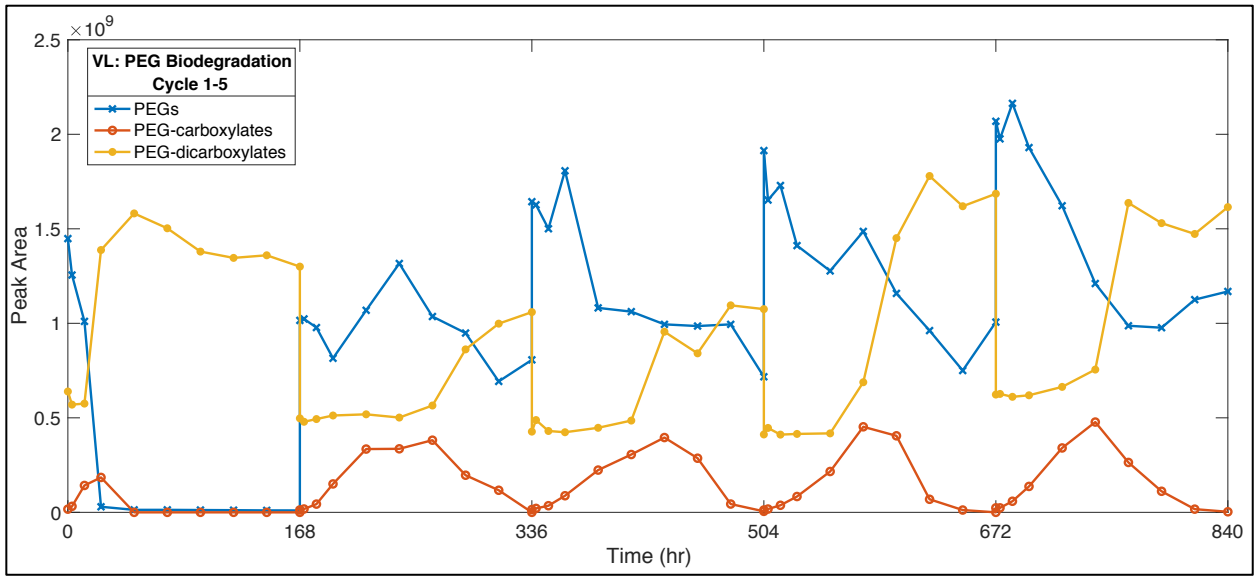

Figure 5.3: Sum of the peak area for the PEGs (blue trace), PEG-carboxylates (red trace), and PEG-dicarboxylates (yellow trace) in VL over five treatment cycles.

The pathway for aerobic biodegradation of PEGs has been proposed before [127] and includes oxidizing the terminal alcohol groups to carboxylic acid groups via alcohol and aldehyde dehydrogenase and then cleavage of the terminal ether bond to produce a shorter PEG (termed "PEG shortening") [125]. Figure 5.3 demonstrates this pathway: as the PEG concentration decreases, singly carboxylated PEGs concentration rises and then falls as the doubly carboxylated PEGs rises drastically. Then, the PEG-dicarboxylates persist for the remainder of the treatment cycle. This pattern is shown for every cycle but is much quicker in the first treatment cycle. This is likely due to the reactor coming off 48-hour acclimation cycles and could be considered a startup cycle; the pattern is consistent for cycles two through five. The first cycle is also the only cycle where the PEG presence in the reactor goes to almost zero and where the concentration of PEG-dicarboxylates start to decrease by the end of the cycle; in later cycles, the PEG-dicarboxylates show a steady increase or plateau by the end of the cycle. Figure 5.3 also shows that as PEG degradation slows after the first cycle, PEGs accumulate in the reactor and cause the initial concentration for each cycle to slowly increase. The aerated blank showed very minimal degradation in PEGs and the non-aerated blank showed no reduction, indicating that the microbial community present is responsible for the PEG degradation observed (Figure 5.4).

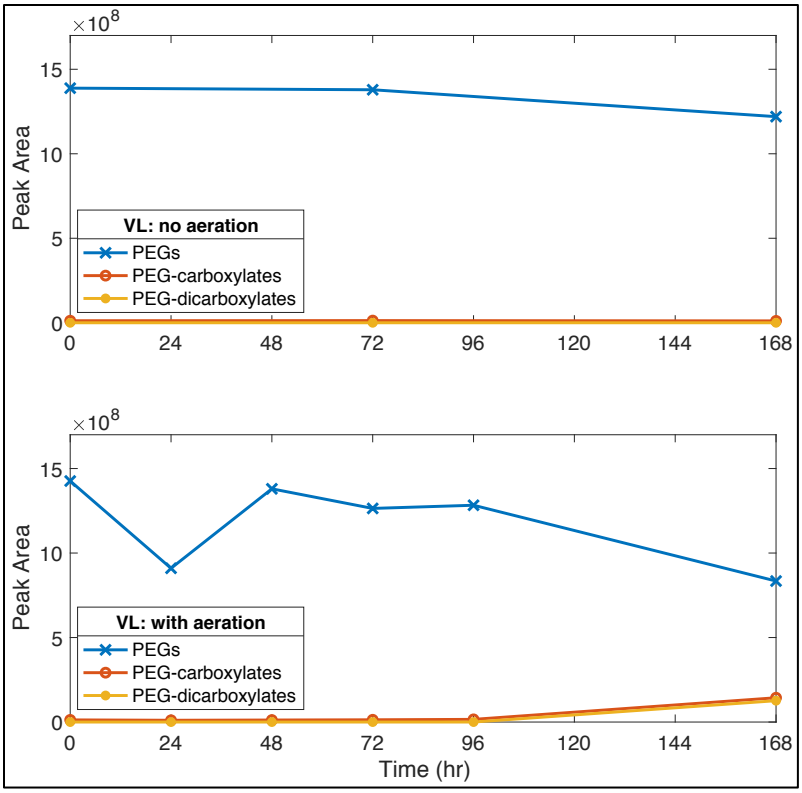

Figure 5.4: PEG, PEG-carboxylate, and PEG-dicarboxylate peak area in VL reactor with no aeration (top frame) and with aeration (bottom frame).

PEGs of different molecular weights were not degraded to the same extent. Figure 5.5 shows the degradation profiles for three PEG/PEG-carboxylate/PEG-dicarboxylate degradation pathways (i.e. PEG6 is carboxylated to PEG6-carboxylate which is then carboxylated again to PEG6-dicarboxylate). For the PEG6 combination, there is the same general pattern described above: PEGs decrease, PEG-carboxylates increase and PEG-dicarboxylates increase and plateau as PEG-carboxylates are decreasing. For the higher weight PEG11 combination, this pattern holds for the first cycle, but then for the remaining cycles, PEG11 shows less reduction and then plateaus. Then for the highest molecular weight, PEG16 starts to increase at t = 192 hours and surges at t = 240 hours and the rate of degradation slows. This increase in PEG abundance from t = 192-240 hours is seen in PEG combinations starting at PEG10 and becomes more pronounced as PEG

molecular weight increases up to the PEG16 combination, the highest molecular weight combination tracked in this work. Figure 5.6 shows the peak area of PEG4, PEG8, PEG12, and PEG16 as a fraction of the total PEG peak area. This figure illustrates how larger PEGs (i.e. PEG12 and PEG16) become a larger proportion of the total PEG abundance over the course of each treatment cycle, suggesting recalcitrance to treatment for larger PEGs.

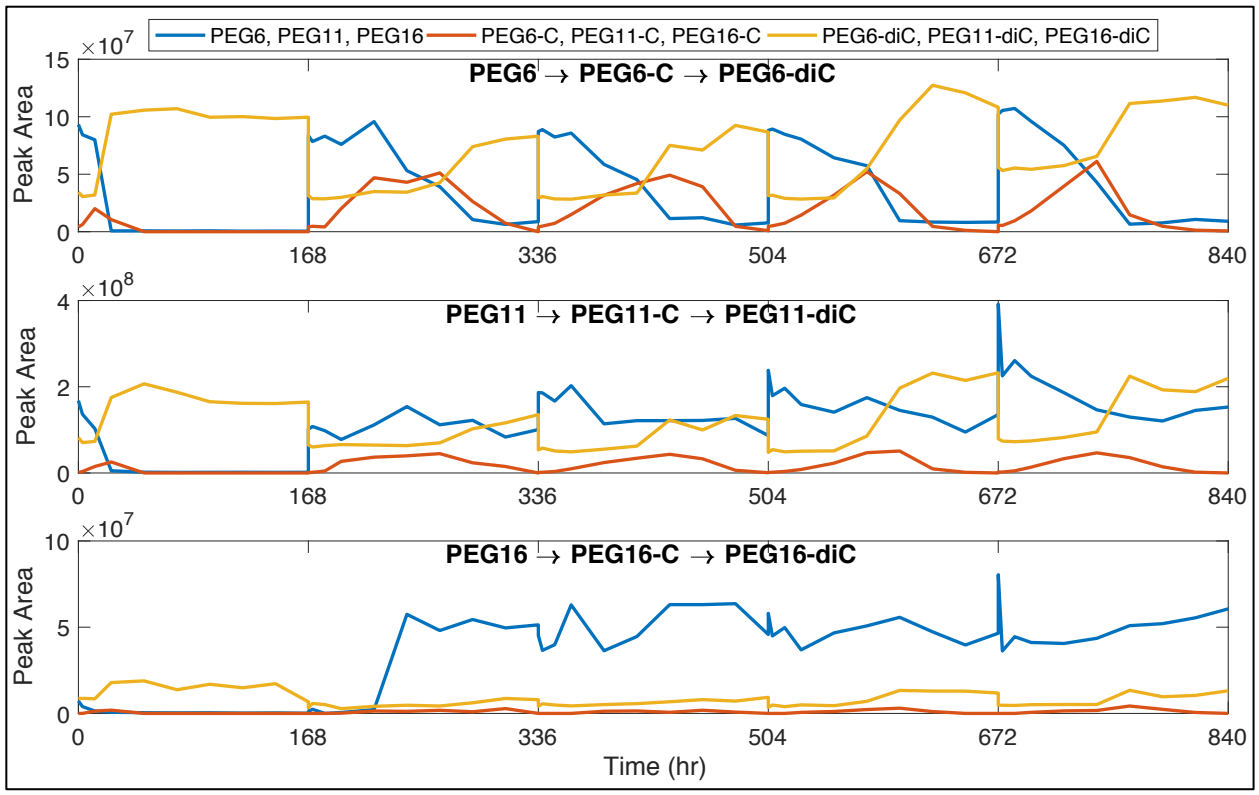

Figure 5.5: PEG/PEG-carboxylate/PEG-dicarboxylate peak area profiles for three different sized PEGs tracked in VL.

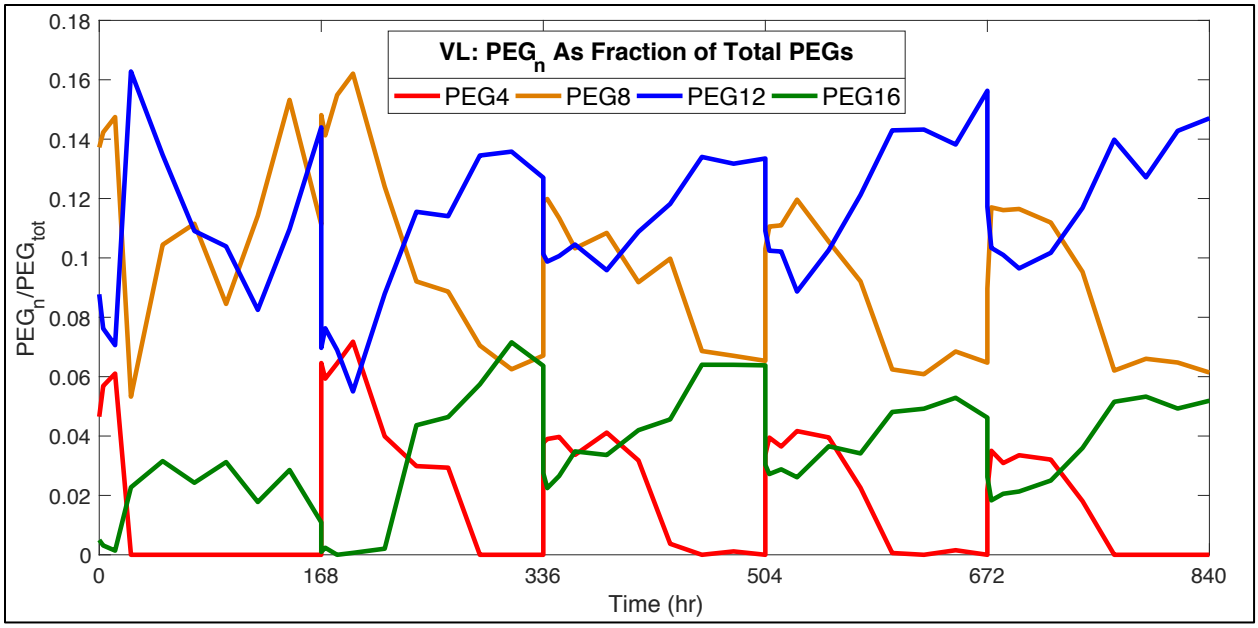

Figure 5.6: Fraction of PEG4, PEG8, PEG12, and PEG16 peak area of total PEG peak area in VL during the treatment cycles. Larger PEGs (PEG12 and PEG16) become a larger proportion of total peak area over the course of each 168 hour cycle.

The PEGs in these samples are not suspected to be a large part of the DOC; Thurman et al. [65] estimates them to be in the low mg/L range, but Nell and Helbling [78] estimate them to be <100 µg/L in their more thorough analysis. The persistence of PEGs and PEG-dicarboxylates is observed for all three samples despite the 50-80% reduction in DOC that is seen for each sample and literature demonstrating their biodegradability [127]. Figure 5.7 shows the normalized PEG and PEG-dicarboxylate peak area (PA_t/PA_0) for four PEGs of different molecular weight in each of the three samples for the third treatment cycle. Even with the long treatment times afforded in PR, the largest dicarboxylates are still present at 200× their initial abundance and persist through 336 hours of treatment (see Figure 5.8). This effect is less pronounced in VL and CR where the initial peak area was much lower, showing increases 2.5× the initial peak area. The full distribution of PEGs and their singly- and doubly-carboxylated byproducts for the third treatment cycle of each sample is shown in Figure 5.8 (PR), Figure 5.9 (VL), and Figure 5.10 (CR). These three figures

are important for demonstrating that PEG-dicarboxylates are present at the end of treatment for all three waters.

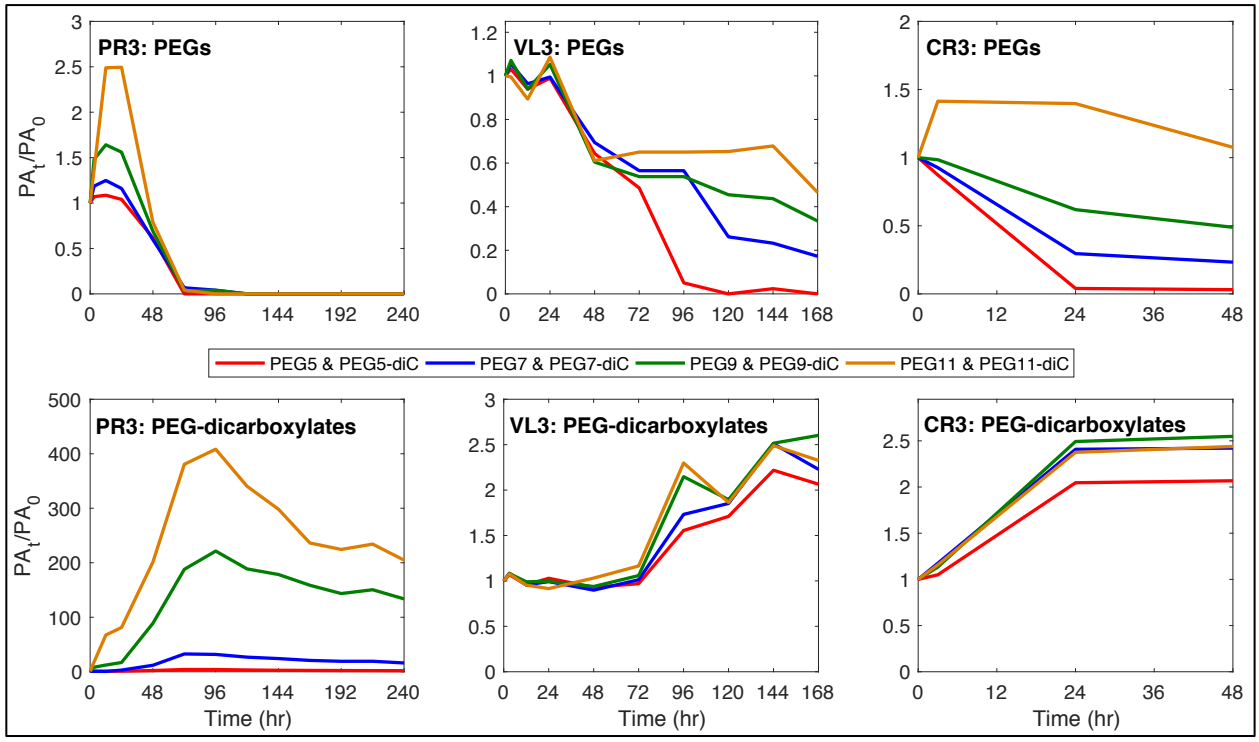

Figure 5.7: Normalized peak area (PA_t/PA_0) for PEG5 (*m/z* 239), PEG7 (*m/z* 327), PEG9 (*m/z* 415), and PEG11 (*m/z* 503) for the third treatment cycle of PR, VL, and CR.

The decrease in PEG degradation with increasing molecular weight could be related to a few different phenomena. The first is that slower biodegradation of higher molecular weight PEGs has been described before and is exacerbated by a saltier water matrix [127, 147, 148]. Bernhard et al. [147] demonstrated that complete degradation of PEGs with molecular weight between 250 and 57,800 Da took up to 65 days for the largest PEGs in freshwater. In seawater, complete degradation of the largest PEGs was not achieved in 180 days, and the smallest PEGs took between 15 and 37 days, which they partially attributed to a low abundance of low molecular weight PEGs.

Secondly, aside from the ethoxylated compounds presented in this work, there are other ethoxylated additives present in hydraulic fracturing produced water that fall outside of the mass

range observed in these experiments (m/z < 800 Da). PEGs with molecular weights >800 Da have been detected in all these samples with LC-QTOF-MS (data not shown), so these are likely partially responsible for feeding this higher molecular weight range over the course of treatment. Also, the FracFocus reports for these water samples and other reports of fluid additives [64] list several ethoxylated compounds: ethoxylated isotridecanol, linear alkyl ethoxylates (C_{10}-C_{16}), polyethylene glycol monooleate, polyethylene glycol sorbitan monostearate, polyethylene glycol sorbitan tetraoleate, alkyloxypolyethyleneoxyethanol (trade name "Tergitol"), among others, as well as several listed as "proprietary" with names like "oxyalkylated alcohol", "oxyalkylated fatty amine", "alkylene oxide block polymer", "ethoxylated fatty alcohol", and "surfactant". Degradation pathways of these compounds could include biotransformation to straight chain PEGs. Indeed, PEGs have been identified as biodegradation products of linear alkyl ethoxylates following fission of the hydrocarbon bond from the ethoxylate [149-151]. In addition, Nowicka et al. [150] showed the two degradation products of LAEs (LAE-carboxylates and PEGs) are persistent throughout 30 days of exposure to *Microbacterium* strain E19. LAEs were detected in both PR and VL, so could be another source of PEGs in these waters. Since this study did not explicitly search for these compounds or explore their degradation pathways, their impact is unknown.

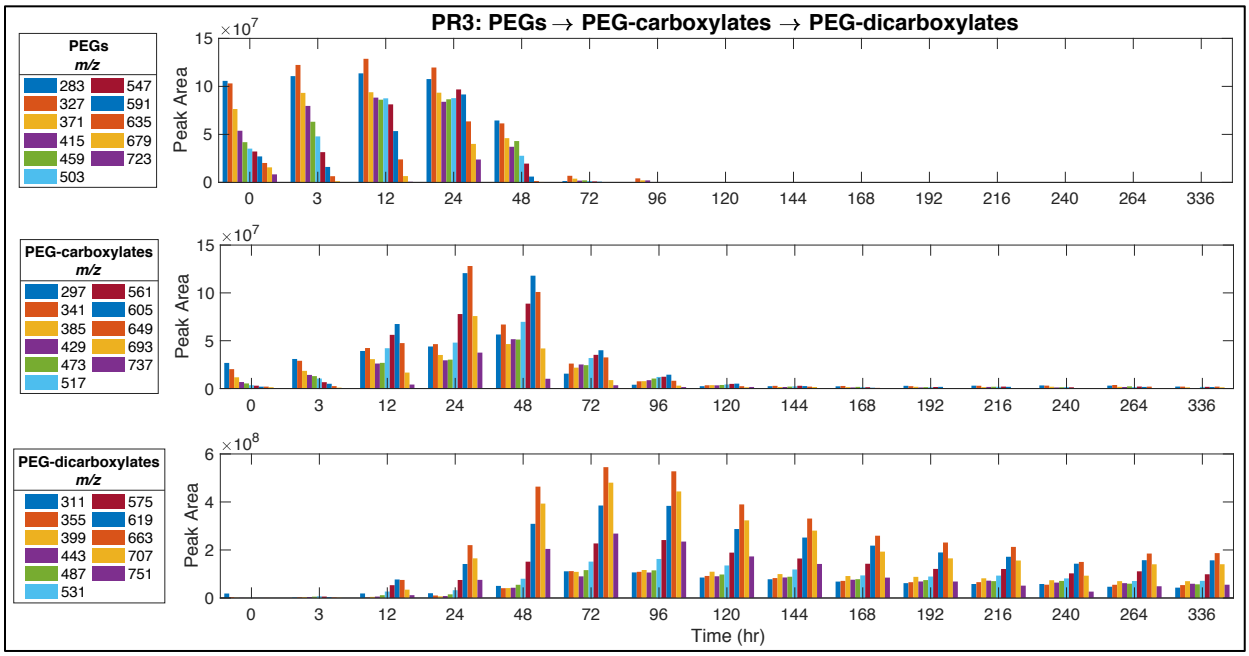

Figure 5.8: Distribution of PEGs (top frame), PEG-carboxylates (middle frame), and PEG-dicarboxylates (bottom frame) for the third treatment cycle of PR.

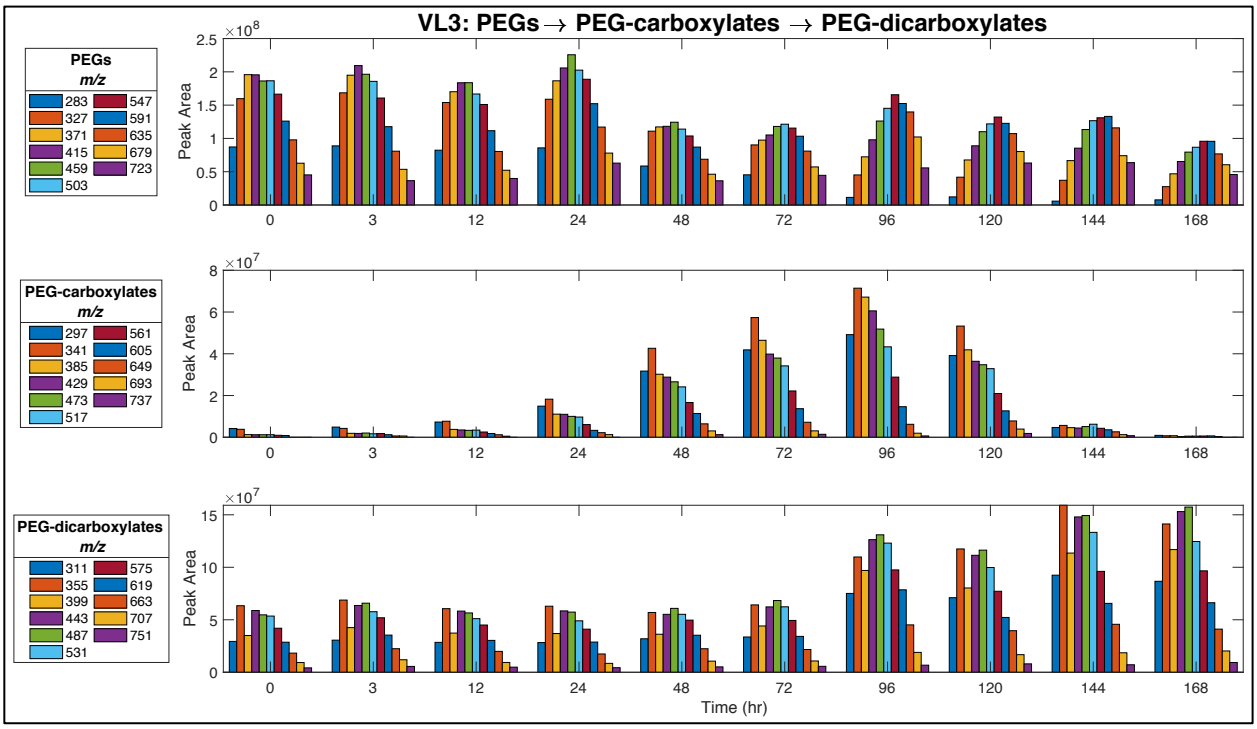

Figure 5.9: Distribution of PEGs (top frame), PEG-carboxylates (middle frame), and PEG-dicarboxylates (bottom frame) for the third treatment cycle of VL.

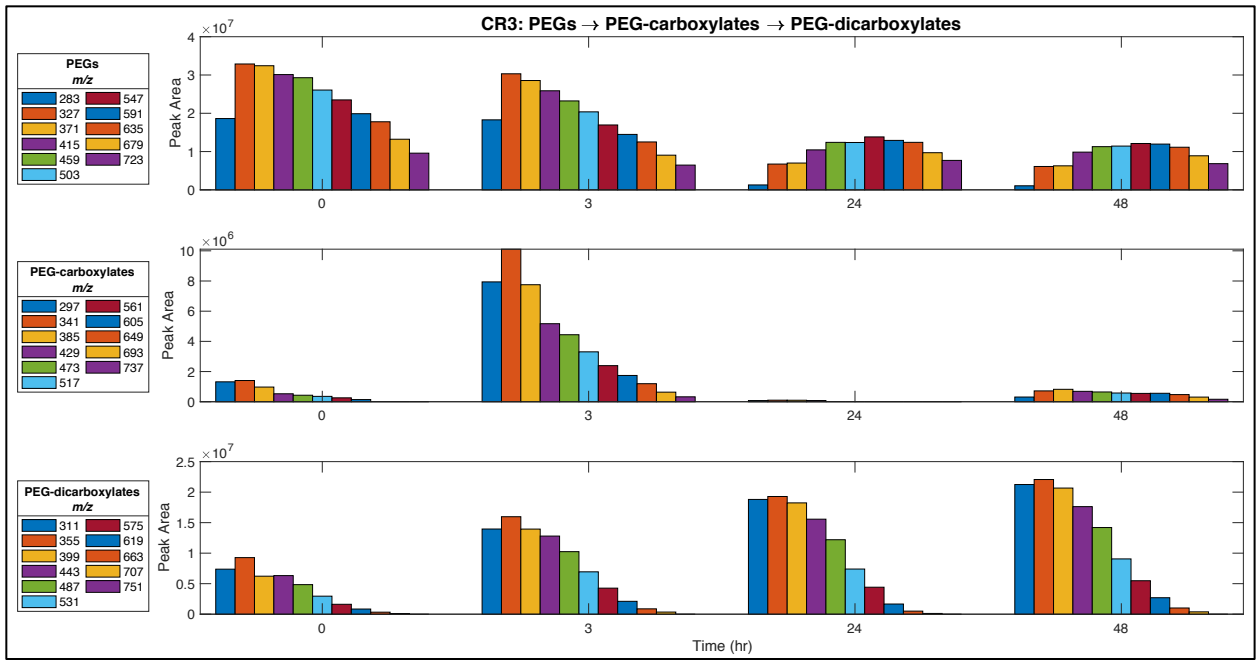

Figure 5.10: Distribution of PEGs (top frame), PEG-carboxylates (middle frame), and PEG-dicarboxylates (bottom frame) for the third treatment cycle of CR.

These results may preclude aerobic biological treatment to be used as a standalone technology to remove organic compounds from hydraulic fracturing produced water, and may require a second physical-chemical technology, such as membranes or sorption, that can more efficiently remove these surfactants. Riley et al. [105] tracked the concentration and composition of dissolved organic matter in flowback and produced waters through a biologically aerated filter → ultrafiltration → nanofiltration treatment scheme. They found the low molecular weight neutral compounds to be the most persistent, a group that would include the non-ionic PEGs. Rosenblum et al. [112] demonstrated that coagulation and 1 g/L powder activated carbon (PAC) are effective at near complete removal of PEGs and some removal of DOC, so could be a good pretreatment for biological treatment. Additionally, in the context of reuse for hydraulic fracturing, the presence of short chain fracturing fluid residuals in base water was shown to be a detriment to successful fluid

formulations due to their interactions with complexing ions [96]. Thus, additional treatment would be necessary for almost any reuse application.

In the event that this treated water was discharged to the environment, the PEGs could be persistent in sediments. PEGs have been detected in fresh and marine water sediments several miles from the discharge point at concentrations up to 10 mg/L [129, 130], and the sorption is enhanced with larger PEGs [152]. Biological PEG degradation in sediment was inhibited for >170 days in simulated synthetic fracturing fluid spills containing glutaraldehyde, salt, and other fluid additives [124], though this was not observed in a study using real produced water [125]. While PEGs themselves are only toxic at very high concentrations [153], the toxicity of PEG-carboxylates and -dicarboxylates is unknown. This presents the possibility that untreated PEGs and PEG-dicarboxylates may accumulate to dangerous levels if continually discharged from a facility.

Further studies should be performed to verify the results presented here and should include tracking of other ethoxylated compounds as they become identified in flowback and produced waters. Due to the ubiquitousness of PEGs and persistence of PEG-dicarboxylates in these treated waters, and because they can be a byproduct of degradation of other fluid additives, they could be considered a suitable indicator compound suite for biological treatment of fracturing fluid additives.

5.3.3 PEG-Amine Degradation

Figure 5.11 shows the results of biological degradation on PEG-amines in PR [67]. This figure represents the sum of the proton adducts of primary and (assumed) secondary (as suggested in Sitterley et al. [67]) PEG-amines from PEG5-amine through PEG16-amine and PEG5-amine-carboxylate through PEG16-amine-carboxylate isolated with solid phase extraction. No attempt

was made to distinguish biodegradability between the different isomers. In contrast with the PEGs, PEG-amines show to be more consistently biodegradable, achieving 95% removal in the first 72-96 hours in each treatment cycle. Similarly with PEGs and PEG-carboxylates, there is a rise in the PEG-amine-carboxylate after degradation of the PEG-amine begins. This result shows that the PEG-amine-carboxylate is a biodegradation product of PEG-amines rather than a fracturing fluid additive, as suggested in Sitterley et al. [67].

Figure 5.12 shows the total ion chromatogram for the results of a biodegradation test on a PEG7-amine standard (*m/z* 282). These results show that the primary degradation pathway for PEG-amines is similar to the PEGs. The terminal alcohol is on the PEG7-amine is oxidized to PEG7-amine-carboxylate (*m/z* 296), followed by cleavage of the carboxylate via the terminal ether bond to produce PEG6-amine (*m/z* 238). In Figure 5.12, the red trace is the chromatogram for 24 hours of degradation, and by this time the PEG6-amine had almost been fully oxidized to PEG6-amine-carboxylate, as is shown. The earliest eluting peaks (retention time 3-4 min) are smaller PEG-amines as a result of degradation. We considered the possibility that PEG-amines could be biotransformed to a PEG and thus contribute to the increased PEG abundance observed at later treatment times but found no evidence in the standard degradation experiment. We also considered that the compound could be oxidized to an amide (rather than a carboxylate) and that both ends could be oxidized to a carboxylate and amide (similar to a PEG-dicarboxylate) but found no evidence of these in the standard or sample degradation experiments, either. Thus, we can reasonably conclude that PEG-amines are not contributing in a significant way to the rise in higher molecular weight PEG concentration (Figure 5.8) and are more readily biodegradable than PEGs.

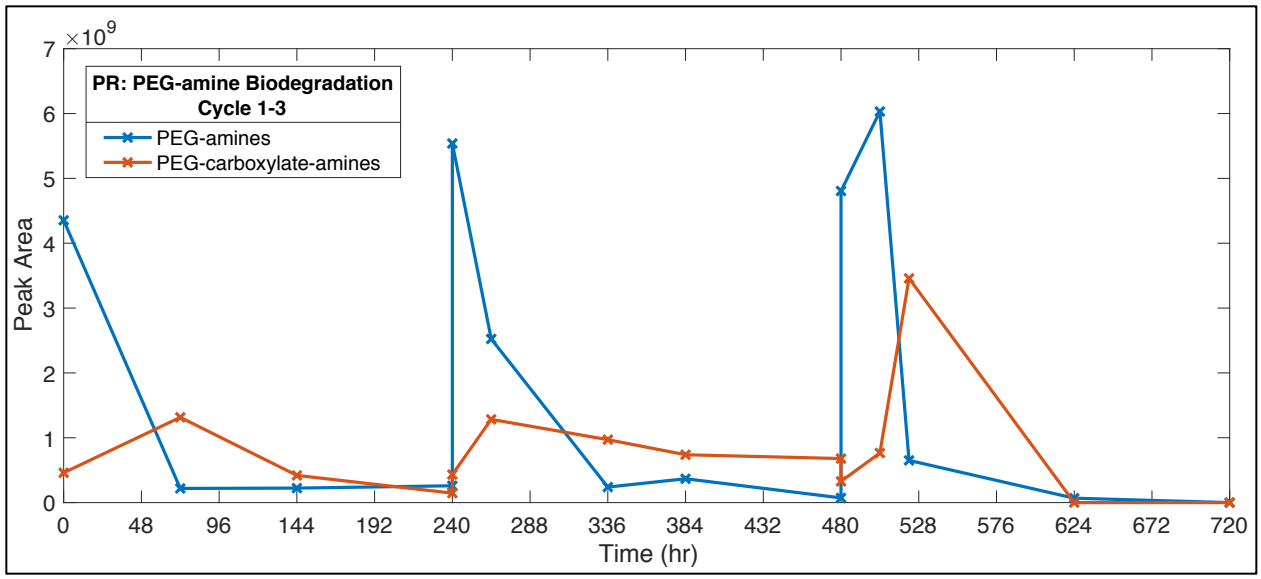

Figure 5.11: Sum of the peak area for the PEG-amines (blue trace) and PEG-amine-carboxylates (red trace) in PR over three treatment cycles.

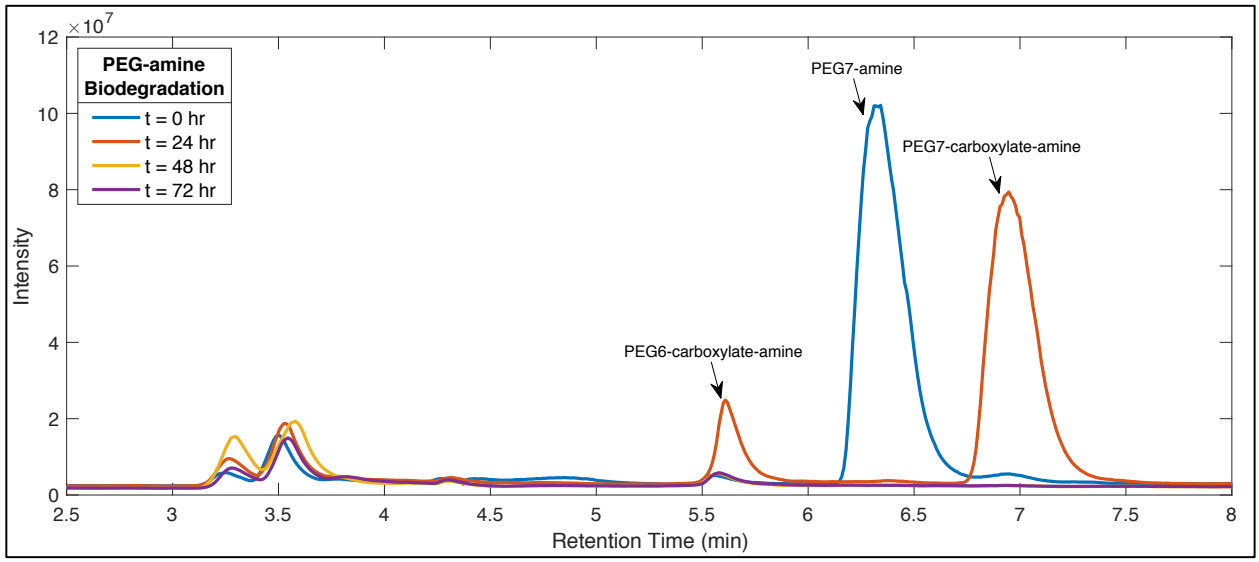

Figure 5.12: Total ion chromatogram of biodegradation test on PEG7-amine standard (*m/z* 282) for *t* = 0, 24, 48, 72 hours.

5.4 Conclusions

In this study, three hydraulic fracturing flowback and produced waters with a range of DOC and TDS concentration were treated with aerobic biological treatment. DOC degradation ranged from 50-80% of the total DOC in each sample and slowed with each treatment cycle. The high salt

content of these waters was not shown to be a hindrance to DOC removal, though complete DOC removal was not observed. In the flowback and early produced water samples (PR and VL), biological treatment left around 50 mg/L of DOC in the treated water. Practically, this means it is unlikely that biological treatment alone would meet the water quality needs for some sort of beneficial reuse application and would need to be coupled with a physical-chemical process. The long treatment cycle times provided no benefit to DOC removal because most DOC degradation occurred in the first 12-24 hours of treatment. However, PEGs were not removed in any reactor and only were transformed to PEG-dicarboxylates, which persisted throughout the length of the treatment cycle and accumulated throughout the experiments. Reporting on the presence and persistence of the PEGs and their metabolites through aerobic treatment has not been done before for hydraulic fracturing waters.

Thus, there is a conundrum for treating these waters: considerable DOC degradation in these complicated wastewaters is possible and occurs quite quickly, but does not come with complete removal of PEGs, which are ubiquitous in flowback and produced waters. Due to the persistence of PEGs and their dicarboxylated metabolites, we believe they are good contenders for indicator compounds for the extent of fracturing fluid additive removal in biological processes. Additionally, this research demonstrated the superior biodegradability of PEG-amines over PEGs and showed that PEG-amine-carboxylates are metabolites of PEG-amines, rather than fracturing fluid additives.

CHAPTER 6: CONCLUSIONS AND FUTURE DIRECTIONS

Overall, the research presented here aims to move the water management approach in hydraulic fracturing to more sustainable practices by experimenting with fluid additive detection (mass spectrometry) and a conventional treatment technology (aerobic biological degradation). First, the research supplements the understanding of mass spectrometric detection of common hydraulic fracturing fluid additives and the impact that the complex matrix of this wastewater has on their detection. The developed method was shown to be effective in pure and dilute samples and was the foundation for a deeper look at compounds that are suppressed by the high salts and organic content of these waters. Second, with the developed solid phase extraction method and learned analytical approach, undisclosed fracturing fluid additives were identified, and their purposes posited, revealing that they are ubiquitous fluid additives. These compounds are hydrophilic portions of the fracturing fluid additive mixture and thus represent an important fraction to monitor in the environment and treatment. The first two points of research outcomes combined suggest a sample preparation approach and suite of additives that would increase and enable detection of these compounds in pure, environmentally dilute, and treated fracturing flowback and produced water samples. Third, aerobic biological treatment was shown to be capable to achieve moderate to massive reductions in DOC, but significant concentrations on a mass basis still remain. PEGs and their degradation products were also shown to be persistent in all three waters considered, suggesting their use as indicator compounds for biological degradation. Though the research presented here represents advances made in characterization and management of flowback and produced water since the beginning of the research project, there are many unanswered questions.

6.1 Hypothesis 1: Method Development

The research in Chapter 3 demonstrated that a simple solid phase extraction method was useful (and often necessary) to detect and identify the suite of common hydraulic fracturing fluid additives. Several solid phase extraction sorbents were considered for their retentive capacity for the bulk DOC in four flowback and produced waters with a spectrum of salt and organic contents. For all sorbents, the reduction of salts from the analyzed matrix made for increased signal and detection of ethoxylated and propoxylated surfactants, particular those with longer chains. The selection of HLB as the preferred sorbent is based off its demonstrated superior recoveries of all examined additives over the other sorbents and its utility in diluted samples. The excellent recoveries of HLB may be due to increased mass transfer that occurs as a result of the integrated *N*-vinylpyrrolidone moiety into the polymeric structure, which helps water penetrate the solid phase. The enhanced detection of these compounds in dilute samples is of particular environmental importance because fluid additives are not monitored in the discharge of facilities that release treated effluent to the environment. Specifically, the carboxylated metabolites were detected well, which is notable since they are present at much lower concentrations than their parent compounds.

With the anticipation that hydraulic fracturing is a permanent fixture in our energy landscape, it may be expected that more stringent regulations come to pass that require managing and monitoring these common fluid additives in treatment and the environment. Many of the further research directions are synergistic to the research presented here, but there are aspects that concern only the described method. There are unknown additives with unknown degradation products that were not evaluated in this research. For example, as demonstrated in Chapter 5, dicarboxylated PEGs are persistent degradation products of PEGs, so investigations into their recovery will further inform the utility of this approach. The identification of new additives may require adjusting the solid phase extraction procedure outlined in this work and may require

additional sample preparation (e.g. pH adjustment, different eluting solvent) to provide adequate recoveries. Quantification of these additives with this method will be relevant for establishing a limit of detection in treatment and environmental samples and will help in setting limits for regulation and realistic treatment outcomes. A limitation of this method is that it requires the use of a mass spectrometer for detection, which requires specialized knowledge and instrumentation that may not be available in all laboratories. Thus, research into the possibility of detecting these additives without mass spectrometry is warranted.

6.2 Hypothesis 2: Compound Identification

The research in Chapter 4 chronicled the detection and enhancement of three new classes of fracturing fluid additives. Over 230 new compounds were identified with a combination of standards, MS-MS experiments, and application of the Kendrick mass defect. These newly identified surfactants were present in several fracturing fluid samples and their purpose in fracturing fluids is postulated to be as friction reducers, thickeners, and/or shale inhibition agents. All three classes of newly identified additives elute at the beginning of the chromatogram, indicating that they are hydrophilic and may be relatively mobile in the environment. Thus, these additives add to the suite of fracturing fluid additives previously identified and complete the spectrum of compound polarities one would expect to see in a fracturing fluid. Additionally, this research provides insights into the fragmentation pathways and diagnostic ions for these ethoxylated compounds, isomers, and their metabolites, and will provide insights for future researchers to make additional compound identifications.

The most obvious direction for future research is to continue to pick these samples apart and identify additional fluid additives that are ubiquitous in hydraulic fracturing flowback and produced waters. The method developed in Chapter 3 was instrumental in this work and will aid

in future discoveries. Further identifications will add to the knowledge base for fracturing fluid additives and give additional fingerprints for environmental contamination via treatment discharges or accidental releases. Additionally, further identifications will lead to identifications of their degradation pathways, which are important in determining how the compounds will be removed in the environment or a treatment system. However, it is not lost on the author that making additional identifications is a tedious and difficult process, so tools should be developed that make new identifications more likely with non-targeted analysis. For example, it is possible that a tool could be developed to exploit the Kendrick mass defect. Anecdotally, observations in making these discoveries showed that ions separated by a repeating unit (in this case, ethylene oxide) appeared to be fairly common. Indeed, in examining a FracFocus report, most of the additives are not single compounds but are surfactants and hydrocarbons with distinct repeating units. Screening tools (e.g. algorithms) for non-targeted analysis of these waters that exploit the Kendrick mass defect and other pattern-based methods of identification may prove to be useful in identifying new compounds.

6.3 Hypothesis 3: Biological Treatment

The study in Chapter 5 demonstrates that aerobic biological treatment with an acclimated culture is capable of degrading a sizable portion (50-80%) of the DOC and that high salts are not an impediment to this degradation. Further, it showed that this degradation occurs in the first 12-48 hours of treatment and that extended treatment times provided no benefit to DOC degradation. However, it is not capable of completely removing ethoxylated surfactants common in flowback and produced water; PEGs and PEG-dicarboxylates were shown to be present in the effluent of all three water samples considered, and that larger PEGs were more resistant to degradation. Since these additives are persistent, they could be considered good indicator compounds for biological

treatment of these waters. Due to the high occurrence of ethoxylated compounds on FracFocus reports, a possible explanation for the persistence of PEGs is that PEGs are biodegradation products of other fracturing fluid additives. Thus, the results indicate that biological treatment would need to be coupled with an additional treatment technology to fully remove the organic compounds present in these water samples.

The extent of treatment of these waters should be dictated by the intended end use, which would suggest the treatment removal goals for DOC. In any realistic treatment scheme, biological treatment would likely not be a standalone technology, but would be coupled with at least a pretreatment clarification technology (e.g. coagulation/flocculation) and possibly a polishing technology to remove some dissolved solids (e.g. membranes). Further characterization of the DOC that is being removed would help making decisions about which technologies to consider for these crucial treatment steps. There has been considerable research done into the utility of individual treatment technologies to achieve their specific goal (e.g. coagulation/flocculation to achieve sample clarification), but there is still a need to investigate the synergistic impacts of these technologies in tandem. To fully evaluate the potential to integrate biological treatment in a complete treatment train, bench- and pilot-scale studies should be conducted with different technologies in tandem. This will give better evidence for if biological treatment can fit in the overall management scheme, or if another technology is better suited. This research also showed that PEGs are persistent in biological treatment and could be a good indicator compound for this technology. To support this proposal, additional degradation experiments of other ethoxylated fluid additives not considered in this work would indicate if their degradation products include PEGs and if they are contributing to the persistence of PEGs seen in this research. Further, the ability of other technologies to remove PEGs should be better understood before developing a treatment train.

However, perhaps the most important question to answer before endeavoring any other treatment research is: what is necessary? An overarching theme to the treatment research conducted in this work and this project in general is that the experimenters do not have well-defined treatment goals. Since the majority of the water reused in hydraulic fracturing is used for hydraulic fracturing itself, better communication with industry and academic research would be incredibly useful in helping direct research objectives. It is simply not possible to know if the extent of DOC degradation and persistence of PEGs observed in this (and other) research is acceptable or not. In essence, optimizing a treatment train for DOC degradation and PEG removal might be ultimately unnecessary for the intended reuse purpose. For example, while there is research that indicates high levels of DOC are detrimental to fracturing fluid mixtures, an acceptable concentration range would help researchers direct their future efforts. Ultimately, releasing their fracturing fluid preparation methods and additives to academic research institutions would enable academic researchers to determine the quality of water necessary to mix a successful fracturing fluid. If researchers are bound by the legal mechanisms necessary to ensure confidentiality and have this information, much more progress could be made on addressing the issue of water management in hydraulic fracturing. Of course, confounding the issue further is that fracturing fluid formulations vary from play to play and even from well to well, so understanding the requirements for one fluid may not translate to another; this conundrum is illustrative of the complexity of the water matrix and water management problem in this industry.

6.4 Summary

This research adds to the growing body of knowledge surrounding hydraulic fracturing flowback and produced water characterization and treatment. The objective is to enable a better understanding of the water matrix and the fluid additives contained to help direct treatment and

management efforts and integrate them into future policy and regulations for this industry. The methods developed and described here should be seen as a starting point for further development of standardized methods for detection and quantification of these common fluid additives if and when they are subject to additional regulations in the future. Biological treatment was shown to be a useful technology for DOC reduction, but unable to remove the common fluid additives of PEGs and the dicarboxylated metabolites. However, with further optimization and understanding, biological treatment could be a valuable piece of produced water management. Continuing research into this complex water matrix should beget a realistic and sustainable management strategy for this industry.

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