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Hydraulic Fracturing and Organic Compounds – Uses, Disposal and Challenges

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Abstract

Hydraulic fracturing has allowed oil and natural gas producers in the U.S. to effectively tap reservoirs that would otherwise be unfeasible to produce. In recent years, the natural gas industry has experienced a boost in production through the increased use of hydraulic fracturing in shale and tight sand formations. Despite its production advantages, the hydraulic fracturing process is not without its concerns. Hydraulic fracturing utilizes large quantities of water which, together with a number of chemical additives known as the 'fracturing fluid', are injected into underground formations. After being injected, between 5 and 60 percent of this fluid mixture flows back to the surface as produced water carrying with it any remaining chemical additives and naturally occurring material from the formation. Due to the complicated cycling of water and organic compounds during hydraulic fracturing and produced water treatment, the ability to independently identify and quantify chemicals associated with fracturing activities at different stages of the shale gas water lifecycle remains challenging. The ability to identify and quantify organics may be relevant both for maximizing efficiency during fracturing and water treatment, and for environmental management.

Continued analyses of both the 'hydraulic fracturing fluid' and the produced water have shown that not all organic compounds that were injected into the well return to the surface. This suggests that adsorption/desorption and/or chemical transformation processes are taking place within the formation. Determination whether organic compounds detected in produced waters are synthetic or naturally-derived from the reservoir is complicated by the number of compounds that exist both naturally in the formation, and are injected with the hydraulic fracturing fluid. Depending on the fracturing job, roughly 4 – 10 different synthetic organic compounds are added to the hydraulic fracturing fluid at one time. A survey of 1000 API registered wells hydraulically fractured in Western Pennsylvania and West Virginia showed roughly 150 different organic compounds used as ingredients in the fracturing fluids. This makes identification and analysis of these compounds in produced waters difficult.

Further complications for evaluating organics in the shale gas water life cycle stem from the use of recycled produced waters. Analysis of samples from produced water treatment facilities showed the presence of organic compounds in the inlet and effluent of the treatment facility. The effluent of many treatment plants is reused bringing with it the organic compounds that are still present to the next hydraulic fracture job. This paper looks into the different organic compounds used in the hydraulic fracturing process, their possible life-cycle after the process, the difficulties encountered when analyzing for these compounds, and possible challenges with site planning and environmental decision-making.

Introduction

Clean energy, energy independence and security have been the key issues regarding energy demands in the United States. In 2008, it was reported that natural gas, coal and oil supply about 85% of the nation's energy (US DOE 2009b; EIA 2008). Natural gas itself supplied about 22% of the U.S. energy needs in 2008 and 25% by 2011 (Rahm 2011; EIA 2008; EIA 2012). Most of the US natural gas reserves are present in tight sands, shale and coal beds and less in conventional wells (Arthur et al. 2009; Soeder 2012).

Shale formations have low permeability and require stimulation in order to produce enough natural gas to be economically feasible (Arthur el al. 2010; Rahm 2011; Suarez 2012). Although the process of hydraulic fracturing has been around for over 60 years (Rahm 2011), the recent advancements in horizontal drilling coupled with advanced completion technologies have allowed oil and natural gas producers in the U.S. to effectively tap reservoirs that would be impractical and inefficient to produce (Nicot and Scanlon 2012; Suarez 2012). The advancements have led to a boost in production of natural gas through

the increased use of hydraulic fracturing in shale and tight sand formations.

Water availability, water quality, and groundwater contamination are some of the water resources-related concerns associated with hydraulic fracturing. The process uses large quantities of water which are injected along with sand and chemical additives (Rahm 2011; Soeder 2012). Once the well is fractured some of the injected fluid flows back up the well carrying with it both the chemical additives and material from the formation. Recent studies have shown high levels of total dissolved solids (TDS) in the produced waters (USDOE 2009b; Lee et al. 2011; Haluszczak et al. 2013) and particular attention has been paid to their proper recycle and/or disposal (USDOE 2009b). Less attention has been paid to the organic fractions, however investigations into the organic compounds used in the fracturing fluids and the reactions that may occur during the fracturing process may allow for improved produced water treatment and recycling strategies. This paper focuses on the hydraulic fracturing process, the organic compounds used during the process, and their possible life-cycle after the process.

Hydraulic Fracturing Process

Hydraulic fracturing is used to create permeable fractures throughout a shale or tight sand formation. The produced fractures allow for the gases trapped in the shale pores to migrate out of the shale formation and into the wellbore environment, from which they can be produced. The hydraulic fracturing process utilizes high pressure and fluid flow rates in order to transfer the fracturing fluids from the surface to the formation depth where the fracturing will occur (Lee et al. 2011; Rahm 2011; Myers 2012, NDRC 2012). In order to control and continuously monitor the fracturing treatment, a well is usually fractured using multiple stages along the length of the horizontal well (USDOE 2009b; Rahm 2011). Each stage is monitored for wellhead and down hole pressures, fluid pumping rates and even the volumes of water used (USDOE 2009; Rahm 2011).

Figure 1a is an example of a pressure rate curve used for monitoring the fracturing of a single stage. The pressure rating, flowrate and density of the fracturing fluid are monitored to ensure the appropriate pressure and proppant flowrate are reached. A line check is performed at the beginning of each stage. This is recognized by a sudden increase and immediate drop in pressure at the very beginning of a pumping curve. This is performed before the fracturing process begins to ensure that the equipment is working properly and can safely meet the pressure and flowrate requirements to fracture a stage.

Figure 1b is an example of the chemical pumping curve used to monitor the concentration of the different types of chemical additives. The chemical additives are introduced at different times and amounts are dependent on the formation the service company is fracturing. Each additive is a mixture of various chemicals with the main ingredient having a specific function (USDOE 2009b; Aminto and Olson 2012). The first chemical introduced is the acid package which is used to clean the perforations made in the wellbore allowing the proppant to access the formation. The clean rate is used to measure the amount of water and proppant (usually sand) used and is introduced after the acid package. As time goes on different amounts of friction reducer (decreases the friction in the pipes), biocide (eliminates bacteria) and scale inhibitor (prevents scale build up on the well casing) are added (USDOE 2009b; Spellman 2012). Towards the end of the treatment, a gel sweep with a time-release breaker, are injected to clean out the rest of the chemicals from the stage and break down the gel. The amount of each additive used at each stage will vary depending on how the process is going (USDOE 2009b; Aminto and Olson 2012). At times more of a particular chemical may be added during one stage while more of a different chemical is added during a later stage. After the formation has been fractured the pressure is released from the well which causes between 5 and 60 percent of the fluid mixture to flow back to the surface as produced water (USDOE 2009a; USDOE 2009b; Clark et al. 2012; Rahm and Riha 2012; Suarez 2012; NDRC 2012) carrying with it any remaining chemical additives and naturally occurring material, including organic compounds, from the formation (Veil et al. 2004; Soeder and Kappel 2009; Karbo et al 2010; Clark et al. 2012; Hickenbottom et al. 2012; Rahm and Riha 2012; Lutz et al 2013; NDRC 2012).

Water and Chemical Usage

A simplified diagram of the life-cycle path for the water and organic compounds used in hydraulic fracturing from the start of the process to the end is shown in **Figure 2**. The water is supplied by the company performing the fracturing of the well and is obtained through a number of sources including municipal, groundwater, surface water and recycled frac water sources (NDRC 2012). Hydraulic fracturing consumes 2 – 5 million of gallons of water for each fractured well (Lee et al 2011; Rahm 2011; Stephenson et al. 2011; Hickenbottom et al. 2012; Myers 2012; Nicot and Scanlon 2012; Suarez 2012). The water is mixed with sand and chemical additives making up what is known as the frack fluid. The composition of the fracturing fluid can be between 98 – 99% water and sand with the other 1 – 2% a combination of different acids, salts and organic compounds (USDOE 2009b; Lee et al 2011; Spellman 2012). The number of chemical additives used and their concentrations is dependent on the well that is being fractured (USDOE 2009b; Rahm 2011; Spellman 2012; Rahim and Holditch 2003; USDOA 2011), the chemicals supplier and service company mixing the fluids (US House of Representatives 2011). In most cases the formulations are closely guarded and may contain a variety of toxic and non-toxic chemicals (Kargbo et al 2010).

A survey of the Hydraulic Fracturing Fluid Product Component Information Disclosures was performed on over 1000 American Petroleum Institute (API) registered wells in Western Pennsylvania and West Virginia and focuses on wells fractured in the Marcellus Shale play. The information was gathered from www.fracfocus.org and includes data reported by oil service companies over this small region. It should be noted that at the time of this survey, which took place from August to December 2012, 33295 wells were registered on FracFocus.org throughout the United States. This number continues to increase along with the number of wells in the region that was the focus of this study; therefore some newer wells may have been added to the Frac Focus database since this paper was written.

Roughly 150 different organic compounds were used as ingredients in the hydraulic fracturing fluids for this region. **Figure 3** illustrates an overall view of the different organic compounds used, grouped according to their similar functional groups and classifications (for example: soaps and surfactants, carbohydrates or fatty acids). Not all compounds are used at one time; however, in one specific example 4 – 10 of these compounds were used as ingredients for a single well (Spellman 2012; Jenner and Lamadrid 2013). The most common ingredients used include glycols (ethylene and propylene), hydrotreated distillates, methanol and various ethoxylated compounds.

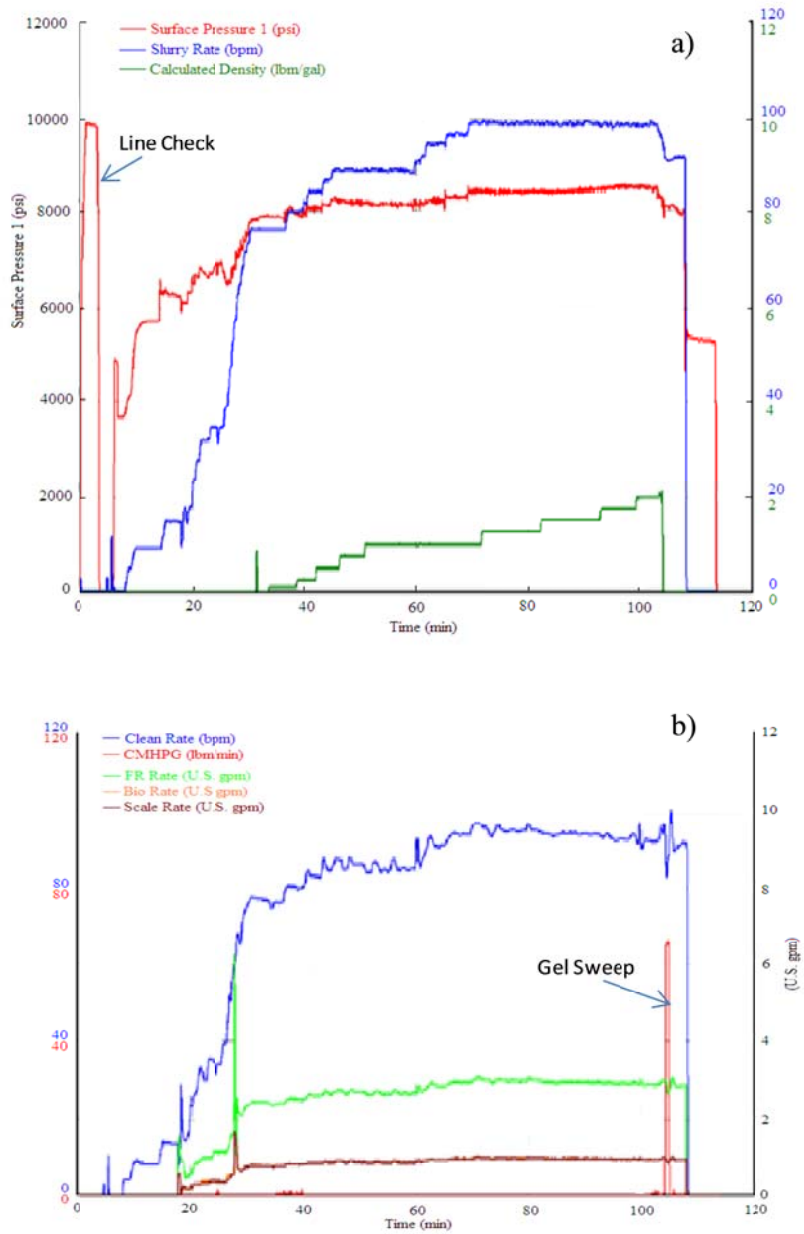

Figure 1. a) Pressure rate cure and b) chemical pumping curves used to monitor the hydraulic fracturing process of a single stage for well in the Marcellus Shale play.

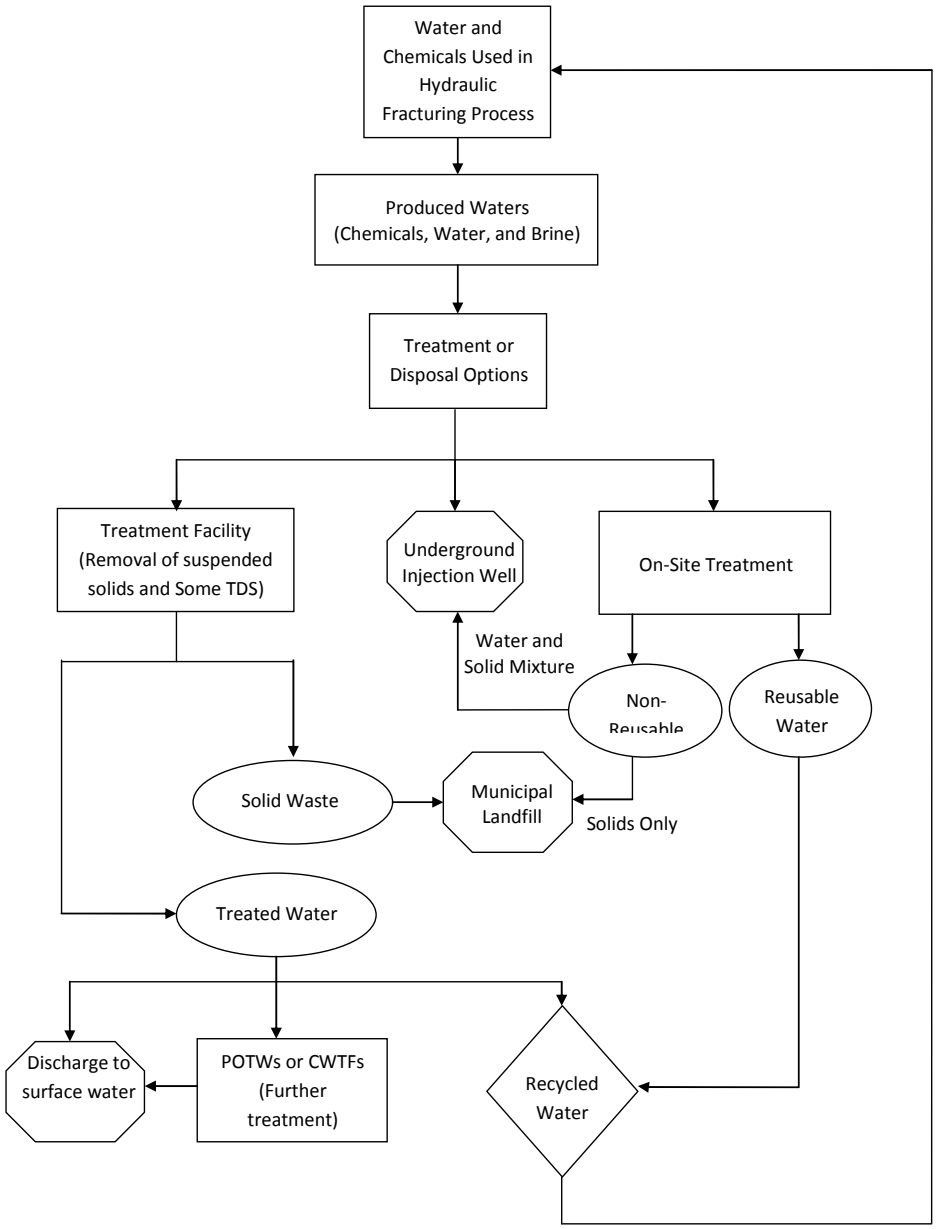

Figure 2. Simplified flow diagram of the process that is involved from the beginning of a hydraulic fracturing job to the treatment of the wastewater produced by the service companies.

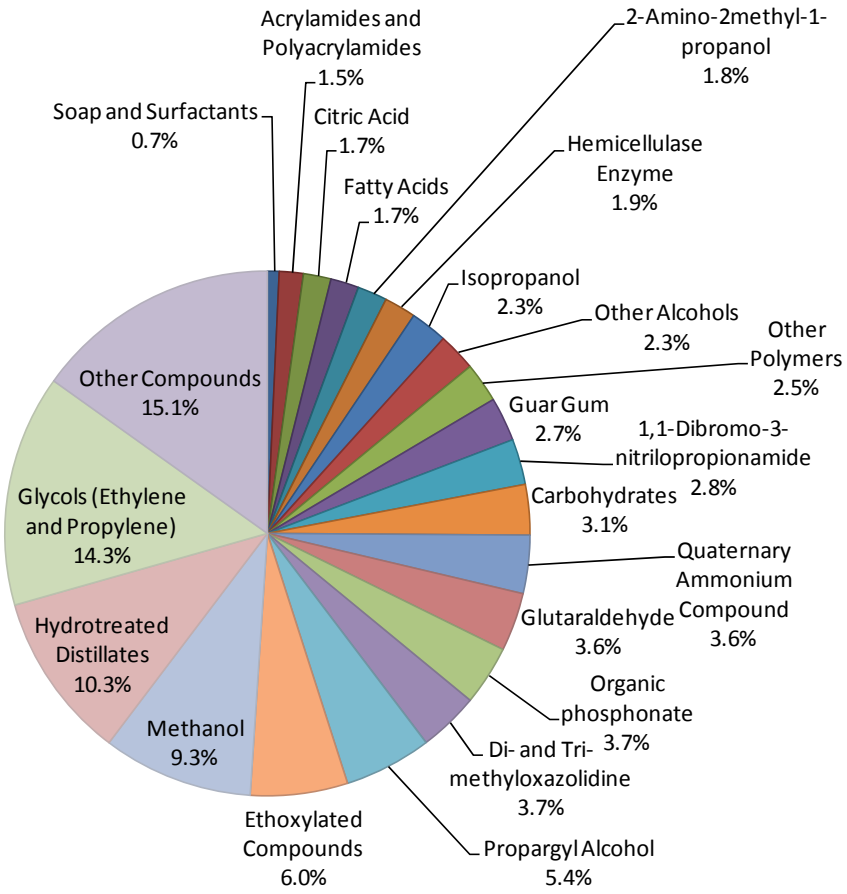

Figure 3. Organic compounds used in the chemical mixtures that make up the hydraulic fracturing fluids

The different organic compounds are usually ingredients in the chemical additives used for various purposes. **Figure 4a** shows the compounds found in the friction reducer. The most common of these compounds is the hydrotreated light distillate followed by ethoxylated alcohols. **Figure 4b** shows the occurrence of compounds found in the biocide. The different ingredients are used in the same frequency. However, the most repeatedly used compounds were glutaraldehyde, 1,1-dibromo-3-nitrilopropionamide and polyethylene glycol. **Figure 4c** includes the compounds used in the scale inhibitor which can consist of ethylene glycol, organic phosphates and methanol. **Figure 4d** displays the chemicals used in the gel sweep and breaker. The most common compound used in the gel sweep was the guar gum followed by hemicellulose enzyme and other carbohydrates. Other chemical packages include the corrosion inhibitors, iron control, surfactants and non-emulsifiers which contain a number of ingredients including oxyalkylated alcohols, methanol, formaldehyde, ethanolamine, sodium erythorbate and citric acid.

Figures 4a – 4d illustrate the number of chemicals, the different classes of compounds, and the many mixtures used in a sub-region of the area undergoing Marcellus Shale development. Some of the organic compounds are found in more than one chemical package, and may be used for a different purpose in each mixture. For example, ethylene glycol was found to be an ingredient in friction reducers, biocide, scale inhibitor and gel sweep. Polyethylene glycol was found in the friction reducer and biocide. Methanol was an ingredient in scale inhibitor, biocide and gel sweep. Some compounds were listed under generic compound names, while others were not specifically identified and listed as proprietary ingredients.

Water Treatment

Some concerns associated with water treatment or disposal includes the available infrastructure for underground disposal and water quality after treatment (Rahm and Riha 2012). The produced water contains 100,000 mg $\cdot$ L^{-1} or more of total dissolved solids (TDS) (Rahm and Riha 2012; Haluszczak et al. 2013), other material from the formation and the compounds from the

fracturing fluid (Soeder and Kappel 2009; Mitchell and Casman 2011; Rahm and Riha 2012). Due to the high TDS levels the produced water cannot be sent directly to municipal wastewater treatment plants. Therefore, the produced water has to be treated or recycled using other means or methods.

Onsite treatment can be performed a number of ways. Some service companies will mix the produced waters with enough fresh water to minimize the effects the TDS may have on the chemical additives used in the subsequent fracturing jobs (Jenner and Lamadrid 2013; NDRC 2012). Other companies will treat the water by removing enough solids and organics using flocculation with filtration so that it can be reused for fracturing new wells (USDOE 2009a; USDOE 2009b; Veil 2010; Lutz et al. 2013). Some companies will store the waste in lined pits (USDOA 2011) in order to allow the water to evaporate off and then dispose of the solid waste in municipal landfills (Chen et al. 2007; Soeder and Kappel 2009; Aminto and Olson 2012; NDRC 2012), which is mostly efficient in arid areas of the U.S. including Texas, New Mexico and some part of Oklahoma.

A number of companies will send the wastewater offsite to be disposed of by injecting it into the subsurface. In these cases the water is not treated but injected into underground formations located below any groundwater formations (USDOE 2009a; USDOE 2009b; USDOA 2011; Rahm 2011; Spellman 2012; Jenner and Lamadrid 2013; NDRC 2012). In other cases the water will be evaporated off to minimize the amount of waste and then injected into the storage well. However, this method is limited by the lack of suitable geology for underground injection in certain regions (Lutz et al. 2013).

Offsite treatment involves sending the produced water to a dedicated treatment facility that is equipped to handle the high concentration of TDS. The water is treated to remove a number of contaminants including iron, barium, salt, oil and grease to a specified amount depending on the purpose of the effluent (Jenner and Lamadrid 2013; Lutz 2013; NDRC 2012). Some companies will treat the water using microfiltration, reverse osmosis or ion exchange to attain water that can be used for other purposes such as irrigation or land application. In some cases the treated water can be sent to a publicly-owned treatment works (POTW) or a centralized wastewater treatment facility (CWTF) (depending on state regulations) for further treatment (Veil 2010) and then released into surface water. In other instances the water is treated to a point where it can be recycled or reused in further fracturing processes.

Challenges in Understanding the Risks, Environmental and Health Implications

The challenge in understanding the risks and environmental implications associated with the chemical usage comes from the variety of chemicals used by different operators and drilling companies. Each company will use a specific mix for each well that is being fractured due to the dynamics of the shale at that well location. The service companies that provide the chemical additives that go into a fracturing fluid will have a number of compounds with similar properties to be used for the same purpose (US House of Representatives 2011; Spellman 2012). Some of the chemical additives will have the same ingredients but with different concentrations (USDOE 2009b; Spellman 2012).

While the EPA is probing the effects that hydraulic fracturing has on the environment, few federal regulations concerning this industry's practices are in place (Rahm 2011; Spellman 2012); therefore, states have provided guidelines for companies to follow (Kargbo et al. 2010). Though some states require companies to disclose what chemicals and ingredients are used in the fracturing fluids (Kargbo et al. 2010; PA DEP 2010; LADNR 2011; OCC 2011; Lee et al. 2011; ODNR 2011; Rahm 2011; Clark et al. 2012), not all states have mandated the disclosure, making it voluntary. Not all information can be found in the disclosures either. Some of the ingredients may be absent from the list (although they are present in the chemical mixtures) since their properties are not required for any specified use (Spellman 2012). Some ingredients are not listed since the chemicals they make up are labeled as proprietary or trade secret chemicals (Chen et al. 2007; Soeder and Kappel 2009; Clark et al. 2012; Spellman 2012) which belongs to the manufacturer of the products not the service companies (U.S. House of Representatives 2012). Some companies may list all chemicals that are on the well pad during the hydraulic fracturing of a well though some of the chemicals were not used in the actual fracturing fluid; therefore, there is no way to determine the accuracy of the disclosures (Spellman 2012). This creates a degree of uncertainty in determining the chemicals that may be present in the produced water when it returns to the surface.

Another difficulty in understanding the risk results from the reuse or recycle of produced water. Most companies reuse the produced water (USDOE 2009a; USDOE 2009b; Veil 2010; Spellman 2012; Jenner Lamadrid 2013; Lutz et al. 2013) by mixing it with the fresh water. Unfortunately, the produced water, whether treated or not, can still contain organic compounds from a previous fracturing job (Hickenbottom et al. 2012). **Figure 5** is the mass spectra of the a) inlet and b) effluent of a centralized water treatment facility that treats produced water from hydraulically fractured wells. The spectra are the same for both the inlet and the outlet indicating that the organic compounds have not been removed from the water. The effluent of this treatment plant is recycled by the service companies and comprises some of the water used to fracture new wells.

The recycled produced water is mixed with fresh water and a new mixture of chemical additives. This new fracturing fluid contains known and unknown compounds from a number of different wells and service companies. This poses a problem for being able to evaluate the composition of mixed recycled waters since there are over 150 different organic compounds that are known to be used in the Marcellus region, and anywhere between 750 - 930 known compounds present in the hydraulic fracturing fluids used throughout the United States. Complicating matters further are the proprietary blends used in preparing prior and new fracturing fluids.

Determining the fate of organic compounds used during fracturing is made difficult due to the number of possible compounds that can be present. **Figure 6a** is a mass spectrum for a fracturing fluid prior to injection, which was analyzed using liquid chromatography-mass spectrometry (LC-MS). The spectrum shows the masses of different organic compounds. Due to the

lack of chemical standards, both identification and quantification of the compounds are not possible. **Figure 6b** shows the mass spectrum of the produced water after a period of a few hours and roughly 1700 barrels of water produced water were collected. Looking at the two different spectra it appears to show a difference in composition from the fracturing fluid and the produced water. Masses present in the produced water are not present in the fracturing fluid suggesting either retention of the compounds in the formation, or transformation of the material from the fracturing fluid forms byproducts which may be detected through analysis. Naturally occurring (organic) material from the formation also may be present in the produced water. Degradation or reaction of both the synthetic and natural organic materials can make identification of the degradation byproducts a significant challenge since the various mechanisms and reaction pathways may exist.

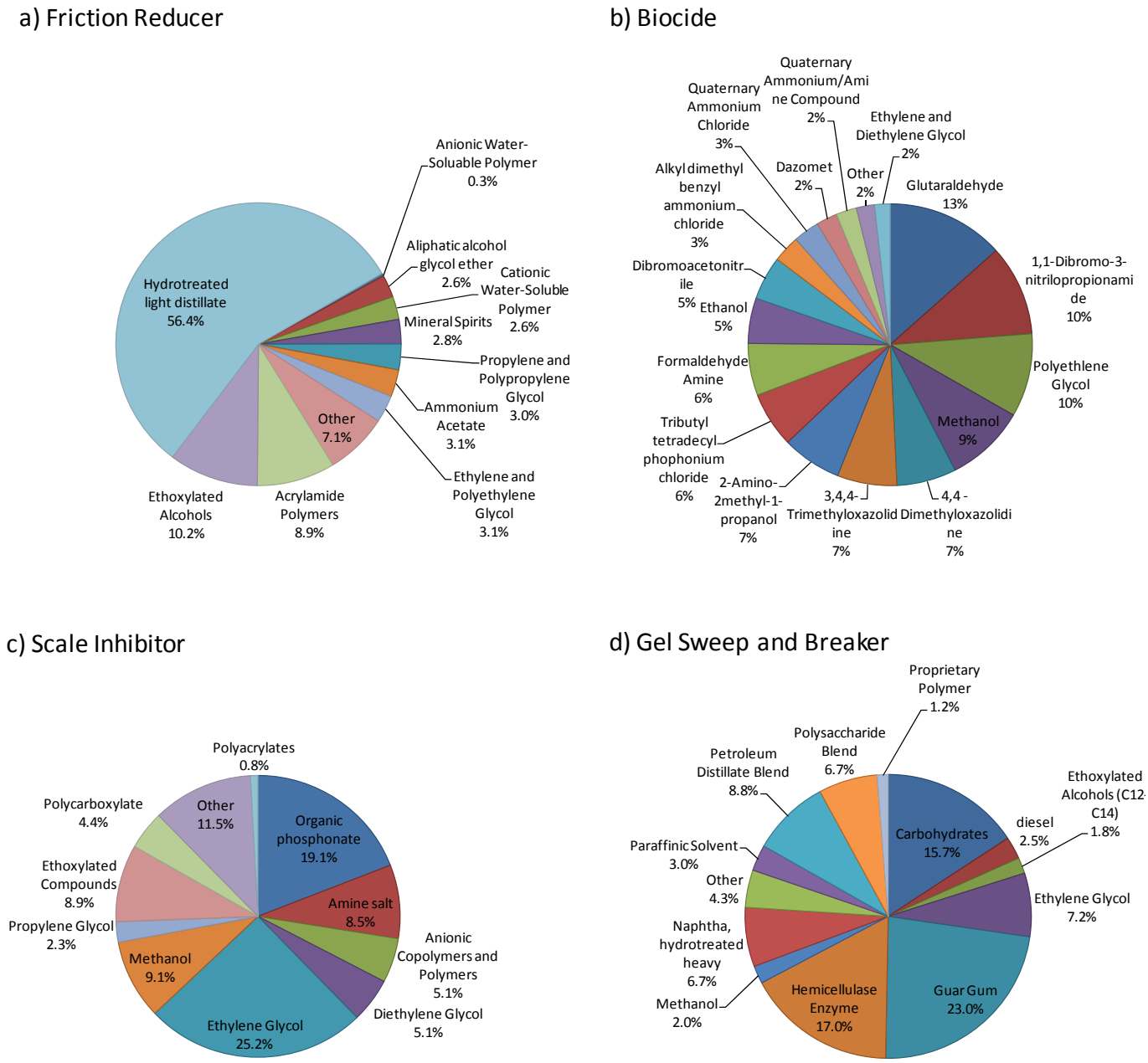

Figure 4. Breakdown of organic compounds used to make a) friction reducer, b) biocide, c) scale inhibitor and d) gel sweep and breaker

There are various potential environmental implications associated with the organic compounds used in hydraulic fracturing. Chemicals used in the hydraulic fracturing process are stored onsite until ready for use. Leakages and spills, through rare, may contaminate the site, soil, shallow aquifers and surface waters near the fracturing site (Rahm and Riha 2012; NDRC 2012). Insufficient well and casing structure, along with fractures which might break upward, and improper completion may allow chemicals access to groundwater and drinking water sources (Mitchell and Casman 2011; Clark et al. 2012; Rahm and Riha 2012; Soeder 2012; Spellman 2012; Jenner and Lamadrid 2013), in turn contaminating a possible groundwater drinking water resource.

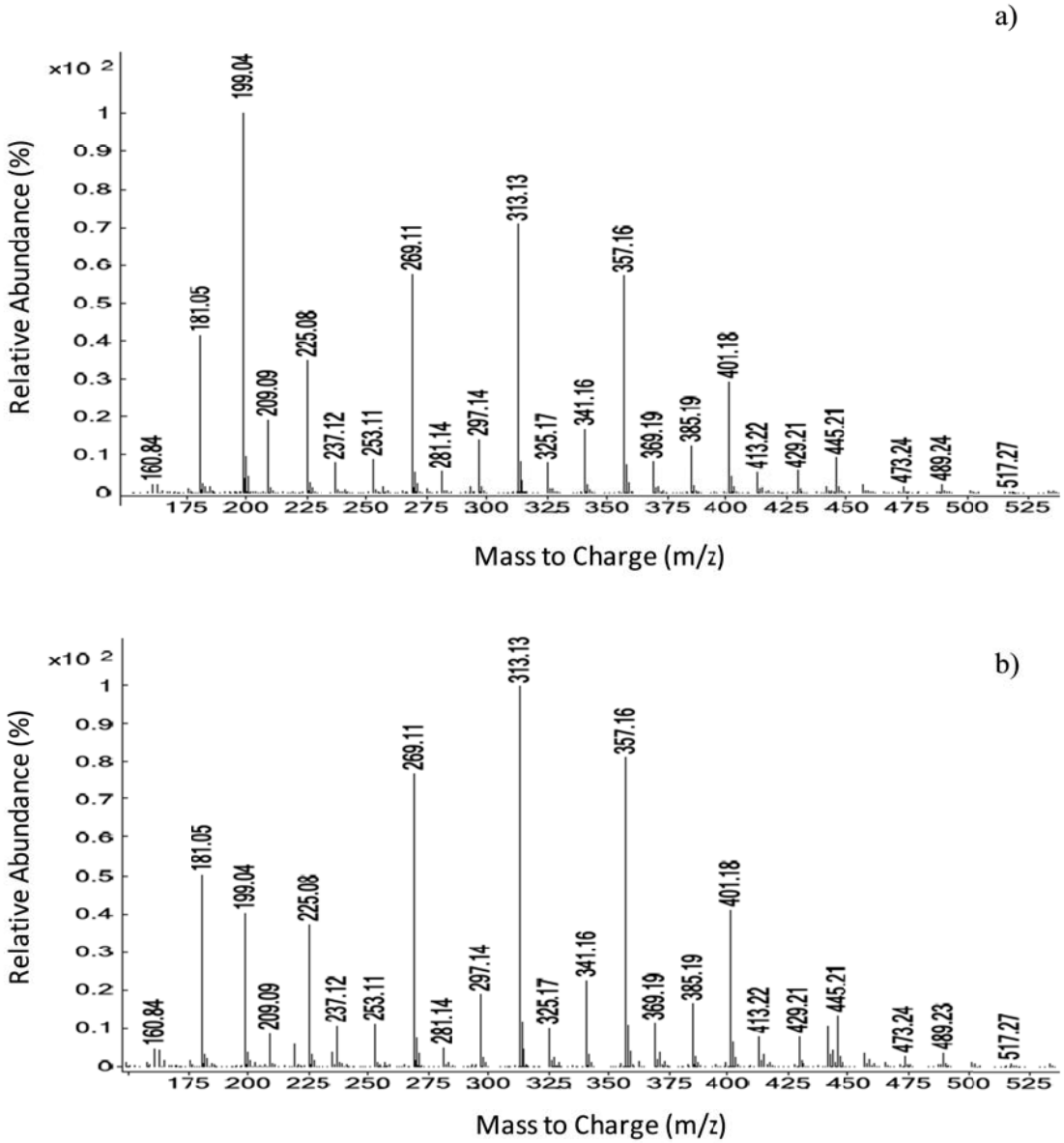

Figure 5. Mass spectrum of a) influent and b) effluent samples collected at a water treatment facility used specifically for the treatment of produced waters.

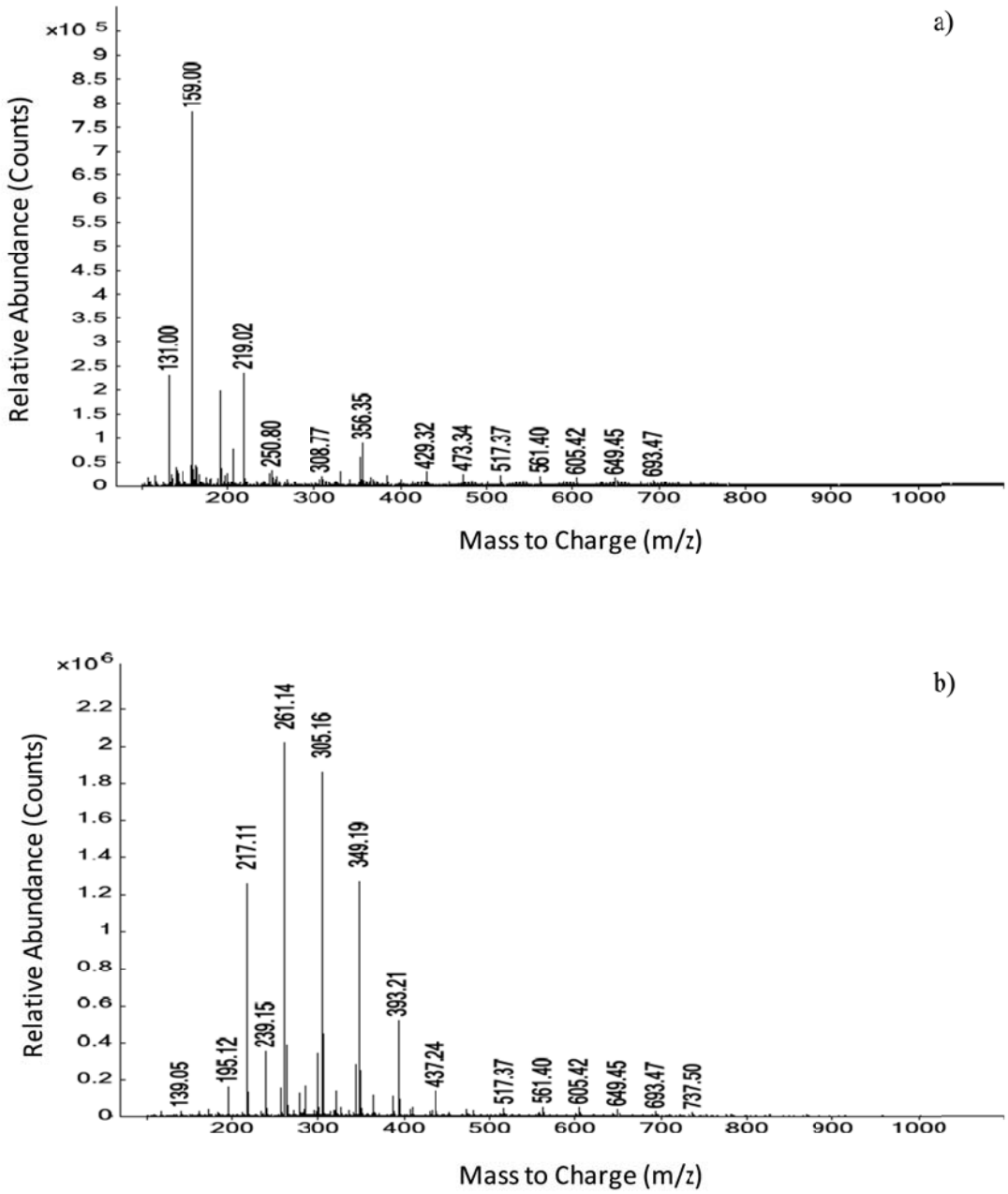

Figure 6. Mass spectrum for a) hydraulic fracturing fluid and b) produced waters obtained from a gas producing company. The samples were monitored for organic content prior to fracturing and after produced waters were recovered.

Another source of contamination is the roughly 2 million – 5 million gallons of produced water that may be used in the hydraulic fracturing of one well depending on the formation. Once the process is complete and the pressure is let off, 5 – 60% of this water will return to the surface carrying with it a number of chemical species. Failure of well casing can lead to a possible release of the produced water into other more permeable formations or groundwater resources in the vicinity of the well. Once the produced water reaches the surface, potential spills may occur when transporting to onsite holding tanks or offsite treatment facilities (Soeder 2012). If released into the environment, groundwater, surface water and soil may be contaminated (NDRC 2012).

Another potential concern is the class of the chemical additive used. Some of the chemical additives are considered hazardous materials and carcinogenic (NDRC 2012). Degradation or reaction of the compounds used in the hydraulic fracturing fluids can form byproducts which can be hazardous or toxic to humans and ecological systems. The produced water that flows back

to the surface can contain a number of different compounds. Some compounds do not degrade and may accumulate in natural systems if released into the environment (NDRC 2012).

Conclusions and Possible Future Studies

There are a number of organic compounds used in hydraulic fracturing with a variety of different functions. A number of these compounds are unknown due to the trade secret and proprietary formulations protected by intellectual property laws, making risk assessment and detection difficult. Environmental implications are complicated by the number of compounds used and possible contamination pathways. Degradation or reaction of these compounds further convolutes the issues regarding risk assessment by forming products that may be hazardous to the environment and human health. Studies should be performed to determine the fate of these compounds in the formation and possible products that may form as a result of degradation or reaction.

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