

**PS An Overview of Trends within Hydraulic Fracturing in Louisiana  
with a Focus on Haynesville Gas Play\***

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**Abstract**

For 70 years, hydraulic fracturing has occurred but has come to public attentions due the massive amounts of water used for development of unconventional hydrocarbon deposits with long horizontal holes in the last decade. A few general studies considered volumes of water used and chemistry of fracturing water throughout the United States. For these studies, periods considered are broad, decades. For this study, hydraulic fracturing trends are considered on a year-by-year manner and for within Haynesville Shale Gas Play (HSGP). Data from two sources was analyzed. Louisiana Department of Natural Resources data of volumes of water used, source type and source location. Frac Focus has data for the chemistry of water used within the fracturing solution. Their chemical data, maximum concentrations, is split up by components of fracking by reason of use, such as: acid, acid/corrosion inhibitor, biocide, base carrier fluid (water), breaker, clay and shale stabilization control, crosslinker, friction reducer, gel, iron control, non-emulsifier, pH adjusting agent/buffer, propping agent, scale inhibitor, and surfactant. Often 10 to 20 different chemicals were used in addition to water and sand for each hydraulic fracturing job. Many of these are not identified for economic reasons. Within the HSGP there are over 100 different compounds used with fracking in solutions. However, for this study focus is on the thirty most commonly used compounds. Throughout the past decade, the median volume of water used for hydraulic fracturing has increased. The source of that water is nearly always surface waters. Usually a natural or artificial pond is nearby. However, an increasing share of sources is larger water bodies, example Red River. This is contractor response to general agreements between LDNR and frackers to use more regional surface water sources moving frack water demand from groundwater to local small ponds, indirect withdrawals of local groundwater, and ultimately to regional water bodies supplied by distant groundwater baseflow. In the past six years chemistry the fracture solutions are changing. Concentrations of hazard compounds methanol, naphthalene, or light/heavy petroleum distillates are decreasing. By contrast, concentrations of more benign compounds such as sand/quartz/silicon dioxide for proppant or guar gum are increasing.

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## ABSTRACT

For 70 years, hydraulic fracturing has occurred but has come to public attention due the massive amounts of water used for development of unconventional hydrocarbon deposits with long horizontal holes in the last decade. A few general studies considered volumes of water used and chemistry of fracturing water throughout the United States. For these studies, periods considered are broad, decades. For this study, hydraulic fracturing trends are considered on a year-by-year manner and for within Haynesville Shale Gas Play (HSGP) and a few other units in Louisiana.

Data from two sources was analyzed. Louisiana Department of Natural Resources data of volumes of water used, source type and source location. Frac Focus has data for the chemistry of water used within the fracturing solution. Their chemical data, maximum concentrations, is split up by components of fracking by reason of use, such as: acid, acid/corrosion inhibitor, biocide, base carrier fluid (water), breaker, clay and shale stabilization control, crosslinker, friction reducer, gel, iron control, non-emulsifier, pH adjusting agent/buffer, propping agent, scale inhibitor, and surfactant. Often 10 to 20 different chemicals were used in addition to water and sand for each hydraulic fracturing job. Many of these are not identified for economic reasons. Within the HSGP there are over 100 different compounds used with fracking in solutions. However, for this study focus is on the thirty most commonly used compounds.

Throughout the past decade, the median volume of water used for hydraulic fracturing has increased. The source of that water is nearly always surface waters. Usually a natural or artificial pond is nearby. Usually the source of water is either a small local pond or an intermediate size source of water. Regional sources such as Red River are usually less than 25% of sources by year. Contractors response to general agreements between LA DNR and frackers to use fewer groundwater sources by moving frack water demand from groundwater to local small ponds, indirect withdrawals of local groundwater.

In the past six years chemistry the fracture solutions are changing. Concentrations of hazard compounds methanol, naphthalene, or light/heavy petroleum distillates are decreasing. By contrast, concentrations of more benign compounds such as sand/quartz/silicon dioxide for proppent or guar gum are increasing or remain approximately constant.

## INTRODUCTION

Hydraulic fracturing is used to increase productivity of oil and gas fields. It has been referred to as hydrofracturing, hydrofracking, fracking or fracing (Suchy and Newell, 2012). Hydraulic fracturing (HF) is a four-step process. One, use fluid to pressure the reservoir rock creating fractures. Two, continue to pump fluids into fractures to grow them. Three, pump proppant mixture into fractures. Four, stop pumping and flowback to the well to recover fracture fluids while leaving proppant in place to keep fractures open (Canadian Society for Unconventional Resources, no date)

Enhancing the production of hydrocarbons by fracturing rocks started in the 1860s by explosives (Montgomery and Smith, 2010; Larkin, 2016; and Testa, 2017). Later in the 1930s acidizing treatments under pressure were used to increase rock permeability (Montgomery and Smith, 2010; Larkin, 2016; and Testa, 2017). Modern HF using a variety of chemicals has been used since 1947 in order to increase permeability and ultimate production of hydrocarbons deposits (Montgomery and Smith, 2010; Suchy and Newell, 2012; Larkin, 2016; and Testa, 2017). The first commercial application of HF occurred in 1949 (Khyade, 2016). By 1955, over 100,000 individual treatments of HF have been performed (Testa, 2017). Starting in 1973 massive HF involving 1.2 to 3.5 millions of gallons of water per well occurred in the western United States (Khyade, 2016). Approximately one million applications of HF by 1988 and more than 2.5 million applications were completed by 2016 (Testa, 2017). As of 2012, over 60% of all oil and gas wells drilled worldwide are fractured (Suchy and Newell, 2012). One benefit of HF is that it has increased estimated recoverable reserves of gas by 90% and oil by 30% (Montgomery and Smith, 2010; and Suchy and Newell, 2012).

The patent for the idea of non-straight line drilling, short radius drilling was filed in 1891 (Helms, 2008). In 1929, the first horizontal well was completed near Texon, Texas and few more wells that are horizontal were completed by 1957. However horizontal wells were not common into the early 1980s (Khyade, 2016; and Testa, 2017). First horizontal drilling for Barnett Shale west of Dallas, Texas occurred in 1991 (Khyade, 2016). In 2000, 6% of all wells drilled were horizontal wells. There was a major increase in technological development associated with the developing shale gases started in 2002 as indicated by a major increase in the number of patents filed yearly in the United States (Lee and Sohn, 2014). The patents come in seven clusters. Two of which associated with drilling: wellbore technologies, and hydraulic fracturing and drilling systems (Lee and Sohn, 2014). Just ten years later, 2010, 42% of all wells drilled were horizontal wells (Gallegos and Varela, 2014). This trend of rapid change in drilling type is reflected in rig type: vertical, directional, and horizontal between 1991 and 2017 (Figures 1 and 2). During the rapid increase in the share of well rig count that is horizontal development of technique went through several generations. During this development lateral lengths increased from 400 ft. to 8000 ft. (Helms, 2008).

One of the concerns about HF is the volume of freshwater used for it (Gallegos et al., 2015). Well orientation, date of HF and geologic basin influence the volume of water used (Gallegos et al., 2015). One of the basins, which has among the highest average volumes of water used for HF is the Haynesville-Bossier of Louisiana-Texas. Typically HF uses between 2 and 10 million gallons (Mgal) per water per well (Larkin, 2016). Others noted similar average volume of water used for HF elsewhere, Table 1. These large withdrawals in drier climates or highly stressed hydraulic systems can cause significant local water shortages, degradations of water quality, and lowering of stream flow in even wet areas (Vengosh et al., 2014).

There have been observed trends of increasing volume of water used for HF for other unconventional shales. Between 2000 and 2014, median volume of water used for HF increased from 0.17 Mgal to 4.0 Mgal for oil and 5.1 Mgal for gas fields throughout the United States (Gallegos et al., 2015). This is a result of both increasing volume for median horizontal well fracturing and the increasing share of wells fracture that are horizontal. The share of wells fractured that are horizontal increased from approximately 5% in 2000 to approximately 58% in 2014 (Gallegos et al., 2015). Increase has occurred for a single basin. Nicot and Scanlon (2012) observed that per well use of water for fracturing of the Barnett Shale increased from approximately 1.4 Mgal in 2000 to 2003 to approximately 2.0 Mgal in 2010 to 2011.

There have been changes in not only volume of water used per HF but the chemistry of HF fluid used. The first HF was treated with napalm in 1947 (Holditch, 2007). Through the decades, the chemistry of fracturing fluids has continued to change between the 1950s and 1990s. By the 1950s, fracturing involved the use of gelled oil and astringent, which progress to the 1960s use to linear gelled water. Cross-linked gelled water was used in fracturing by the 1970s. Foamed fluids and delayed cross-linkers were used for fracturing by the 1980s. In the 1990s, fracturing uses reduced polymer loading with advanced breaker technology (Holditch, 2007). In 1996, slickwater fluids were introduced (Khyade, 2016). The slickwater fluids include water-soluble gelling agents, for example guar gum, which increases efficiency of proppant intrusion into the formation rock that hosts oil and/or gas (Khyade, 2016). For modern fracturing solution, there are 11 different categories of compounds having different roles within the fracturing operation (Table 2). Many of these categories of compounds are used within other products that more familiar and used daily (Table 3).

The chemistry of fracturing fluids is one of the concerns about hydraulic fracturing, which could contaminate drinking water due to spills/leaks, stray gas migration, in adequate treatment of waste water or migration of hydraulic fracturing fluids or produced waters (Venosh et al., 2014; Gallegos et al. 2015; and Larkin, 2016). Typically, the HF solution is composed of 90% water and 9.5% sand/quartz (Khyade, 2016). Typically, there are 3 to 12 added compounds to the HF fluid for a single well HF job (Khyade, 2016). The other compounds are what creates public concern (Larkin, 2016). Concern is for a good reason, overall, approximately 2500 HF additives of which over 650 are possible human carcinogens under the safe drinking water act or listed as hazardous pollutants (Khyade, 2016). This concern about contamination of groundwater from leaks of fracturing solution based on what chemicals are in that solution (Table 2) such as petroleum distillates, methanol (wood alcohol), hydrochloric acid.

## METHOD

Companies have voluntarily reported the chemical additives used for HF on a web-based registry FracFocus (Suchy and Newell, 2012). FracFocus reports the maximum concentration of a chemical compound, within each of the general categories of use of compounds. They listed concentrations as a percentage within each category of compounds used and for the total solution used. The total values are the ones of interest for this study. For this study, it was assumed that category of compounds were added separately and that maximum reported are not additive for the total maximum for the fracture solution.

For analysis of volume trends a larger data set provided by the Louisiana Department of Natural Resources is analyzed. Collection of data started in 2009, approximately a year before first reports to FracFocus of chemical data. This data was collected to early 2018. Hence, the range of data included for volumes is approximately 18 months longer than the chemistry data.

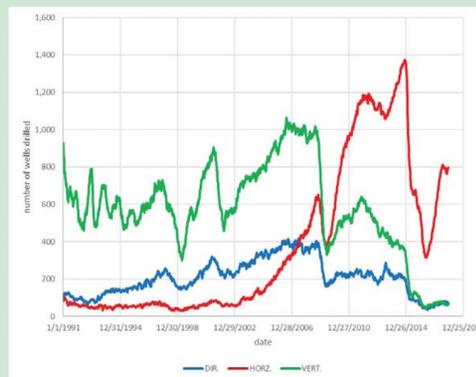


Figure 1. Rig count type, weekly counts between 1/4/1991 and 12/8/2017 (Baker Hughes, 2017).

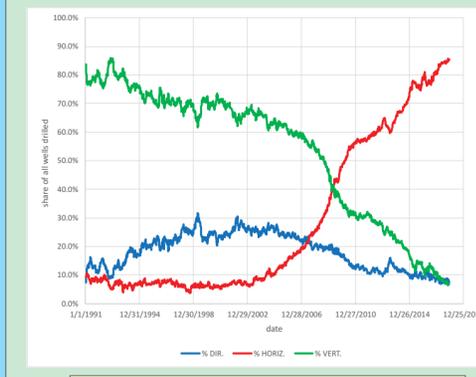


Figure 2. Share of rig type, weekly between 1/4/1991 and 12/8/2017 (Baker Hughes, 2017).

Table 1  
Average water use per well for HF (Vengosh et al., 2014).

Basin	Water use per well millions of gallons (Mgal)
Horn River Basin, British Columbia, Canada	13.21
Marcellus Shale, Pennsylvania (<2010)	2.03 to 10.04
Haynesville, Texas	5.70
Eagle Ford, Texas	4.25
Woodford Shale, Oklahoma	4.25
Marcellus Shale, Pennsylvania (2008-2011)	3.04 to 5.02
Niobrara, Colorado (2012)	3.43
Barnett Shale, Texas	2.64

Table 3  
HF solution as divided by category of purpose for chemicals and some examples of other uses of these chemicals (Larkin, 2016).

Category of use	Share of Frac solution	Other Uses
Acid	0.123%	Household cleaner, and swimming pool cleaner
Friction Reducer	0.088%	Water treatment, candy, and makeup remover
Surfactant	0.085%	Glass cleaner, antiperspirant, and hair color
Potassium Chloride	0.06%	Low sodium table salt substitute
Gelling Agent	0.056%	Toothpaste, baking goods, ice cream, sauces and cosmetics
Scale Inhibitor	0.043%	Household cleaners and deicing agent
pH Adjusting Agent	0.011%	Detergents, washing soda, water softener and soap
Breaker	0.01%	Hair cosmetics and household plastics
Crosslinker	0.007%	Soaps and laundry detergent
Iron Control	0.004%	Food additive, lemon juice, and food & beverage flavoring
Corrosion Inhibitor	0.002%	Pharmaceuticals and Plastics
Antibacterial Agent	0.001%	Disinfect used to sterilize medical equipment

Table 2  
HF solution as divided by category of purpose for chemicals and some examples of what chemicals are used (FracFocus, 2017a)

Category of use	Purpose in fracing solution	Example compound(s)
Acid	Helps dissolve minerals to initiate cracks in the rock.	Hydrochloric acid
Acid/Corrosion Inhibitor	Protects casing from corrosion	Formic Acid, Methanol & Isopropanol
Biocide	Eliminates bacteria in water that can cause corrosive by products	Guanaraldehyde & Quaternary Ammonium Chloride
Breaker	Allows a delayed break down of gels when required	Sodium Chloride & Magnesium Oxide
Clay and Shale Stabilization/control	Permanent or temporary clay stabilizer to lock down clays in the shale	Sodium Chloride & Tetramethyl Ammonium Chloride
Crosslinker	Maintains viscosity as temperature increases	Petroleum Distillate, Boric Acid, Borate Salts, Ethylene Glycol & Methanol
Friction Reducer	Reduces solution friction compared to water on pipes	Petroleum Distillate & Methanol
Gel	Thickens water in order to suspend the proppant	Guar Gum, Petroleum Distillate & Methanol
Iron Control	Helps prevent precipitation of metal oxides	Citric Acid & Acetic Acid
Non-Emulsifier	Break or separate oil/water mixtures	Isopropanol & Ethylene Glycol
pH Adjusting agent/Buffer	Maintains effectiveness of other additives such as crosslinkers	Sodium Hydroxide & Potassium Hydroxide
Scale Inhibitor	Prevents buildup of scale on pipes and formation	Phosphoric Acid Salt
Surfactant	Reduces surface tension of the treatment fluid in the formation and helps improve oil and/or gas recovery from the well after the frac is completed	Ethanol, Naphthalene & Methanol

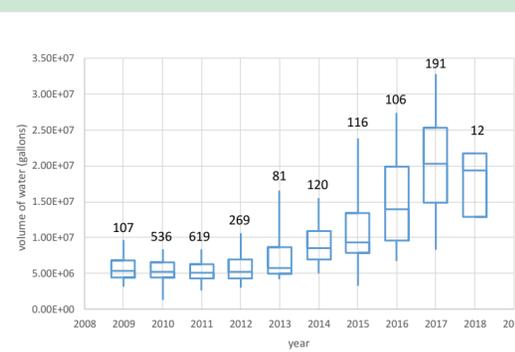


Figure 3. Distribution of the volume of water used for HF of wells within the Haynesville Formation in Louisiana. Source of volumes is Louisiana Department of Natural Resources (2018a). Number above each box and whiskers is total observations for the distribution of values. The bottom whisker is the 5% rank, bottom of the box is the 25% rank, median value bisects the box, top of the box is the 75% rank and top whisker is the 95%. This convention holds for all box and whiskers plots that follow. The results for 2018 for this and following plots is for approximately the first two months.

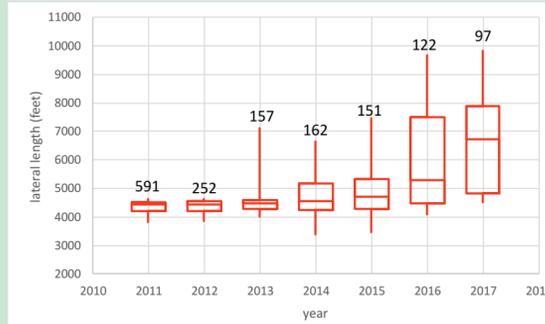


Figure 4. Length of perforated horizontal lateral for Haynesville wells in Louisiana between 2011 and 2017. Perforated zone data in 2017 is mainly prior to July. Source of lateral length data is Louisiana Department of Natural Resources (2018b).

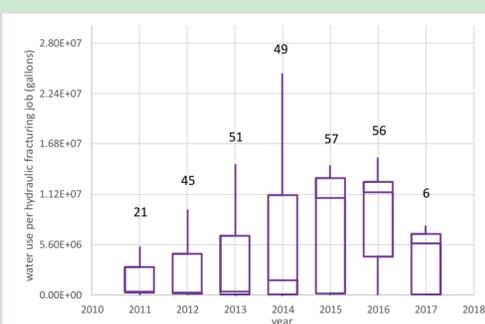


Figure 5. Distribution of the volume of water used for hydraulic fracturing of wells outside the Haynesville shale gas play. Source of volumes is Frac Focus (2017c)

Number of Hydraulic Fracturing Jobs 2009 to 2018

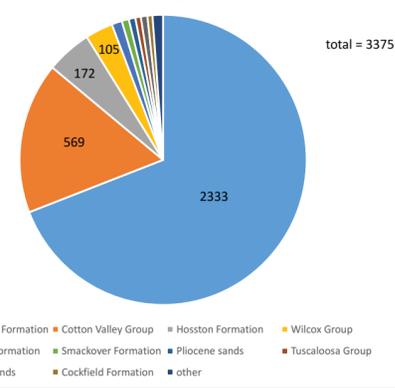


Figure 6. Distribution of hydraulic fracturing of wells by the unit that is fractured (Louisiana Department of Natural Resources, 2018a).

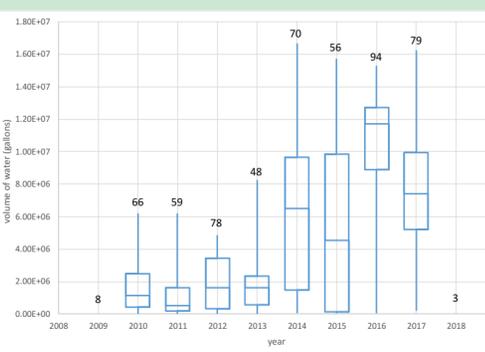


Figure 7. Distribution of the volume of water used for HF of wells within the Cotton Valley Group in Louisiana, mainly lower Cotton Valley-Bossier Shale. Source of volumes is Louisiana Department of Natural Resources (2018a). If there were between 10 and 19 wells within a unit HF only a box appears. Lastly only number of HF is noted near X-axis if HF is under 10. This is true for this and for other plots which for which some years lack 20 HF in a unit.

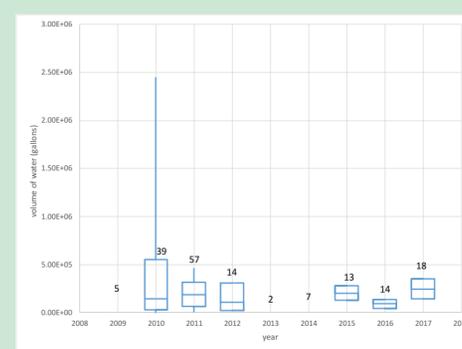


Figure 8. Distribution of the volume of water used for HF of wells within the Hosston Formation in Louisiana. Source of volumes is Louisiana Department of Natural Resources (2018a).

# An overview of trends within hydraulic fracturing in Louisiana with a focus on Haynesville Gas Play

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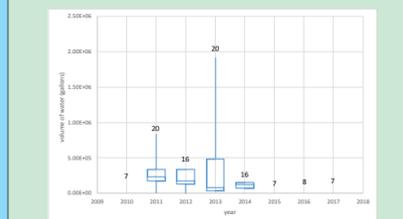


Figure 9. Distribution of the volume of water used for HF of wells within the Wilcox Group in Louisiana. Source of volumes is Louisiana Department of Natural Resources (2018a).

## RESULTS

### Volume of water used

For HSGP parishes (Bienville, Bossier, Caddo, De Soto, Natchitoches, Red River, Sabine, and Webster) the median volume of water used for HF was approximately constant between 2008 and 2014, approximately 5 Mgal per well (Figure 3). This is similar to the Texas side of the Haynesville where average volume of water used for HF during 2010-2011 is 5.7 Mgal (Nicot and Scanlon, 2012). After 2014 there has been a major increase of median volume of water used for fracturing jobs in northwest Louisiana up to approximately 20 Mgal (Figure 3). These large values of HF volume are in line with Elliott et al (2017) which noted volumes of 15 to 100 million liters (3.8 to 25 million gallons). The rate of increase is larger but similar to what Nicot and Scanlon (2012) noted for the Barnett Shale for 2001-2003, 1.4 Mgal, and 2010-2011, 2.8 Mgal. They noted doubling of water used in nine years, which is similar to the quadrupling of water used for HF of the Haynesville in Louisiana between 2011 and 2017-2018 (Figure 3). Haynesville results are similar to those noted by Ceres.org (2017) for their study of five major plays: Marcellus, Eagle Ford, Midland, Bakken, and Barnett between 2011 and 2015. The average HF volume increased from approximately 2 Mgal to 4.5 Mgal. There was variation among the fields. Only for Barnett did the average HF volume decrease from 4.5 Mgal to 3 Mgal, 33% decrease. For the other four fields HF volume increased between 2011 and 2015: Eagle Ford from 4.2 Mgal to 7.4 Mgal, 76% increase, Marcellus from 4.2 Mgal to 9 Mgal, 115% increase, Bakken from 2 Mgal to 4.4 Mgal, 120%, and Midland from 1.2 Mgal to 6.8 Mgal, 470% increase (Ceres.org, 2017). For the Haynesville an approximately doubling of median HF volume was observed from 5 Mgal to 9 Mgal between 2013 and 2015 and then another doubling occurred between 2015 and 2017. One study with a similar length of time observing HF volumes for 10 years, 2005 to 2014, for the Bakken Play displays an increase of mean volumes from 400,000 gallons to 3.6 million gallons (Eagle and Scanlon, 2016) for the ten years considered.

Ceres.org (2017) noted that most likely the increasing lateral length used to increase contact with shale formation is the cause of increasing HF volume. For the Haynesville, increasing HF volume was partially caused by increasing median length of lateral from 4,419 feet in 2011 to 6,711 feet in 2017 a 52% increase (Figure 4). The increasing length of horizontal laterals in Haynesville is similar to what occurred in the Barnett Shale where average lateral length increased from 1900 ft. in 2004 to 3800 ft. in 2011 (Nicot et al., 2014). Increasing lateral length also occurred between 2005 and 2013 from approximately 7200 ft to 9500 ft in the Bakken Field (Scanlon et al., 2014). A longer study of the Bakken Field notes a change in mean lateral length from 5,000 ft. in 2005 to 7,700 feet in 2014 (Eagle and Scanlon, 2016). Motsey Field in British Columbia experienced an increase in average lateral length from approximately 3,900 to 5,900 feet between 2005 and 2011 (Johnson and Johnson, 2012).

Outside the Haynesville parishes, the increase of median fracturing jobs is from less than 500 thousand gallons per well for 2011 to 2013 to approximately 5 to 10 million gallons for 2015 to 2016 depending on year (Figure 5). The results are more variable than for Haynesville parishes because the data sets are far smaller. The full years for Haynesville have been 143 fracture jobs in 2016 and 673 fracture jobs in 2011 (Figure 3). By comparison number of fracture jobs outside the Haynesville parishes for full year is between 21 in 2011 and 56 in 2015 (Figure 5).

Haynesville is not the only unit fractured in Louisiana. A larger data set of HF volumes from LA DNR than FracFocus is used to examine HF within other units. Within FracFocus data considered only 18% of HF jobs are for other units. By comparison LA DNR has approximately 31% of HF jobs for other units (Figure 6). The reasonable question is: Is there an increase in HF volumes for other units? The answer is yes for Cotton Valley Group (Figure 7), and no for Houston Formation (Figure 8), and Waxahouche Group (Figure 9). The increase for Cotton Valley is similar to that for Haynesville in that there was major increase in volume of HF water used. However, the relative change is even greater. In 2010-2011 Cotton Valley Group median HF volume is approximately 1 million gallons (Figure 7). By 2017 the HF volume for Cotton Group increased to approximately 7 million gallons (Figure 7), an increase of approximately 600%, which is even more than the 300% for the Haynesville Formation during the same time interval. By contrast for Houston Formation the median HF volume is approximately 250,000 gallons for both 2011 and 2017 (Figure 8). Lastly the trend appears between 2011 and 2014 that median HF volumes are decreasing for Wilcox Group (Figure 9). The number of individual HF jobs is too small to yield meaningful statistics for the last several years so it is difficult to determine and includes a great deal of uncertainty hence is not determined and boxes are noted plotted.

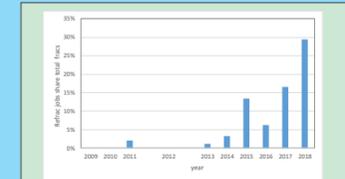


Figure 10. The share of HF each year within the Haynesville Formation that are re-fracturing. Source of volumes is Louisiana Department of Natural Resources (2018a).

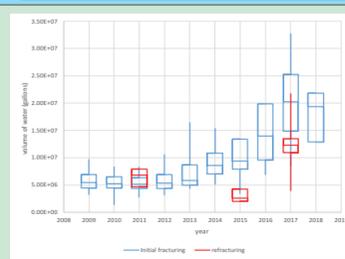


Figure 11. A comparison of initial and re-fracture volumes within the Haynesville Formation. Source of volumes is Louisiana Department of Natural Resources (2018a).

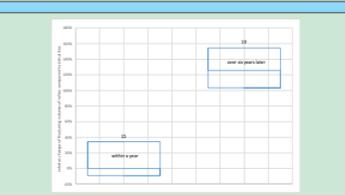


Figure 13. A comparison of initial and re-fracture volumes for a single well for re-fractures within a year and over six years after the initial fracture. Source of volumes is Louisiana Department of Natural Resources (2018a).

## RESULTS

### Re-fracturing compared to initial fracturing

The Haynesville shale is a unit that will in time have fractures collapse and in turn reduce permeability (Yawei and Ahmad, 2012) and resulting in an over 80% reduction of gas production in a year from initial production (Kaiser and Yu, 2011; and Wang, et al., 2013). Thus there is a need to HF the well again. This has started to happen for the Haynesville. The number of HF is small number but the share of total HF jobs is increasing (Figure 10). In general, the resulting volumes are smaller than initial HF within each of the year (Figure 11). The results of comparison between initial and re-fracture volumes for 2011 yield approximately similar volumes while re-fracture volumes are clearly smaller in 2015 and 2017. This is probably a result of short perforated lateral lengths for older wells than for newer wells (Figure 4).

However, if one considers an initial and re-fracture volume for a single well rather than the overall mix of results an interesting pattern appears. For a single well re-fractures are larger than the initial volume (Figure 12). This is especially true for re-fractures that occur approximately 6 years after the initial fracture. Then the volume is typically twice the initial volume (Figure 13). By comparison, if a re-fracture occurs within a year the volume is very similar to initial volume (Figure 13).

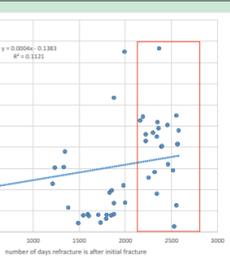


Figure 12. A comparison of initial and re-fracture volumes for a single well within the Haynesville Formation. Relative size of re-fracturing volume compared to initial fracturing volume for a single well as a function of days between the two fracture events. Source of volumes is Louisiana Department of Natural Resources (2018a).

Table 4  
Top ten compounds other than water and quartz for frequency of use for hydraulic fracturing in Louisiana. A total of 1847 hydraulic fracturing reports are included in Louisiana set of data, through June of 2017. All concentrations in ppm.

Compound	number	Share of all fracs	25% rank	median	75% rank
Petroleum distillates	1588	77%	309	309	493
Methanol	1201	58%	1.3	7.6	68.5
Guar gum	1145	55%	258	780	1870
Sodium chloride	982	48%	1.99	56.7	135
Isopropanol	936	46%	0.9	3.2	13.7
Sodium hydroxide	911	44%	30.2	48.3	122
Potassium hydroxide	745	36%	4.1	13.9	65.3
Ethylene glycol	635	30%	13.3	40.6	125
Ethanol	627	30%	2	9	145
Sodium Chloride	613	30%	7.6	16.8	47

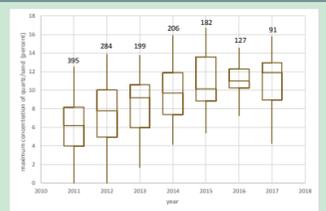


Figure 14. Maximum concentration of quartz/sand within the fracture solution used for a well. Source of concentrations is FracFocus (2017c).

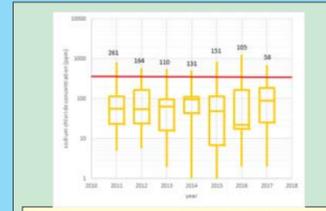


Figure 15. Maximum concentration of sodium chloride/table salt within the fracture solution used. Source of concentrations is FracFocus (2017c). Red line is a NaCl that would yield chloride concentration at U.S. EPA secondary drinking water standard.

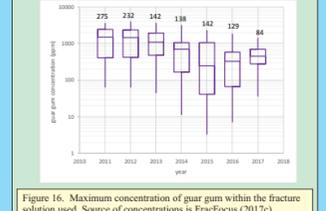


Figure 16. Maximum concentration of guar gum within the fracture solution used. Source of concentrations is FracFocus (2017c).

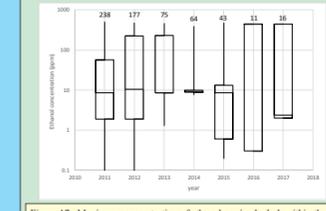


Figure 17. Maximum concentration of ethanol, grain alcohol, within the fracture solution used. Source of concentrations is FracFocus (2017c).

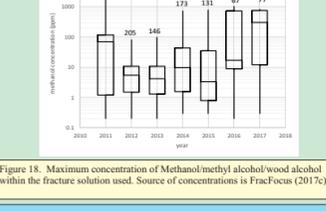


Figure 18. Maximum concentration of Methanol/methyl alcohol/wood alcohol within the fracture solution used. Source of concentrations is FracFocus (2017c).

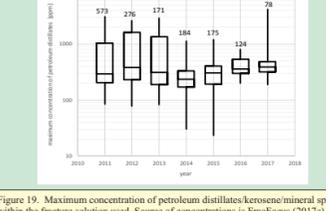


Figure 19. Maximum concentration of petroleum distillates/kerosene/mineral spirits within the fracture solution used. Source of concentrations is FracFocus (2017c).

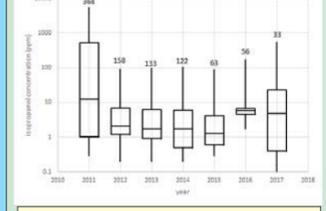


Figure 20. Maximum concentration of Isopropanol within the fracture solution used. Source of concentrations is FracFocus (2017c).



Figure 21. Maximum concentration of ethylene glycol, anti-freeze, within the fracture solution used. Source of concentrations is FracFocus (2017c).

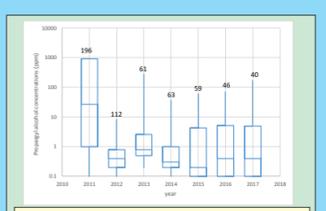


Figure 22. Maximum concentration of propargyl alcohol within the fracture solution used. Source of concentrations is FracFocus (2017c).

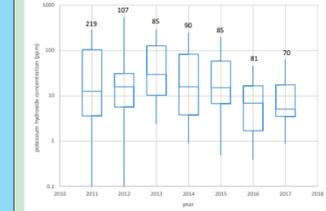


Figure 23. Maximum concentration of potassium hydroxide within the fracture solution used. Source of concentrations is FracFocus (2017c).

## RESULTS

### Water chemistry of fracturing water

There are hundreds of compounds that have been used for hydraulic fracturing (Banerjee, 2015; Ryan, 2015; and Chen and Carter, 2017). Some have noted that approximately 1000 chemicals have been used in HF fluids (Suchy and Newell, 2012; and Elliott et al., 2017). The bulk is water and sand (quartz) which typically is 99-99.5% of the HF fluid. The other 0.5-2% of which creates concern are toxic (Meyer, 2016; and Chen and Carter, 2017) and some are carcinogenic (Meyer, 2016; Chen and Carter, 2017; and Elliott et al., 2017). Meyer (2016) noted that 55, approximately 5% of compounds considered were carcinogenic. However, many HF compounds are generally safe (Suchy and Newell, 2012). The list of compounds within a fracture fluid will vary greatly as a result of reserve properties, rock and hydrocarbon type, pressure, temperature, and sensitivity of reservoir system to water (Gallegos and Varela, 2014).

Past studies have considered the changes in frequency of use for different general types of HF fluid systems (Barati and Liang, 2014; and Gallegos and Varela, 2014). There have been changes in types of fracturing fluids used between start of 2011 and second quarter of 2013. Slickwater treatments decreased from 46% to 19% of all HF jobs. By contrast slickwater with crosslinked fluids increased from 28% to 44% of HF jobs. Conventional crosslinked fluid treatments changed little from 10% to 14% of HF jobs. Lastly hybrid fluids of linear gels and slickwater fluids increased slightly from 14% to 17% of HF jobs (Al-Munkasheri, 2014). All other fluid types increased from 2% to 6% of HF jobs. These studies appear not to consider changes in either frequency of use and/or concentrations of individual chemicals except proppant quartz/sand (Gallegos and Varela, 2014; and Scanlon et al., 2014).

This study appears to be the first to consider trends of frequency of use and concentrations of commonly used HF compounds in the Louisiana portion of the HSGP. Have there been trends in the use of various compounds in HF? Sixteen of the over 200 compounds used for HF in Louisiana are considered. Among the sixteen, considered quartz/sand, sodium chloride/salt, and guar gum are generally considered safe and three of these salt, ethanol (grain alcohol), and guar gum are used in food. Five compounds, ethylene glycol, isopropanol, methanol/wood alcohol, petroleum distillates/kerosene, are commonly used in hydraulic HF and are considered occupational hazards, largely due to being flammable (New Jersey Department of Health, 2011, 2012, and 2016). Two of the compounds are strong bases and can be caustic: potassium hydroxide, and sodium hydroxide. Two of the compounds are acids, formic acid and acetic acid glacial. There is also among the 16 compounds considered, one disinfectant sodium chlorite and a bleaching agent, ammonium persulfate. Lastly, three of the compounds are aromatic compounds benzyl chloride, naphthalene and 1, 2, 4 trimethylbenzene. For example naphthalene is a greater concern by OSHA as indicated by lower permissible exposure limits (PEL) standards than either methanol or petroleum distillates. The PEL for naphthalene is 10 ppm, for methanol is 200 ppm and petroleum distillates is 3500 ppm (New Jersey Department of Health, 2011, 2012 and 2016). In addition, Naphthalene identified as a carcinogenic compound (Christopher et al., 2005; and New Jersey Department of Health, 2012).

Quartz/sand/silicon dioxide is a proppant within hydraulic fluid (Suchy and Newell, 2012). Sand has been used in approximately 99% of all HF solutions between 1947 and 2010 (Gallegos and Varela, 2014). It is the second most common compound in almost all of the approximately 1850 FracFocus compounds lists for Louisiana wells considered in this study. The concentration of quartz within hydraulic fracturing fluid has generally been increasing as indicated by the median concentration of quartz, proppant, nearly doubling between 2011 when concentration is 6.21% to 2017 when concentration is 11.91% (Figure 14). Increasing concentration of proppant was observed elsewhere. In the Eagle Ford there was a general increase over time between 2011 and early 2012 in the proppant loading/concentration (Scanlon et al., 2014). There values are typical for slickwater solutions which have proppant concentrations of 0.25 to 3 lbs/gal, 3% to 26%, of the solution (Al-Munkasheri, 2014).

Gallegos and Varela (2014) noted the general type of HF fluid throughout the United States for approximately 1.6 million fracturing treatments throughout approximately one million wells fractured included eleven classes: acid, crosslinked gel, foam, gel, fracturing, My-T Frac, oil, slick water, unknown, and water. Initially the most common type was unknown, 1947 to 1959. Water was the most common overall and for years of 1961 to 1970 and 1982 to 2008. My-T Frac was most common type between 1971 and 1980. Lastly, they noted that in last couple of years, 2009 and 2010 slick water was the most common type of fracture solution (Gallegos and Varela, 2014). Only approximately 19% of records note individual additive classes and almost no records prior to 1978 (Gallegos and Varela, 2014). Surfactants, for example petroleum distillates, came into common use only since 2005.

Sodium chloride has two uses within a fracturing solution: used as breaker and clay stabilizer (FracFocus, 2017b). The concentration of sodium chloride/salt has been approximately steady between 2011 and 2017 (Figure 15). The concentration has been declining, typically concentrating less than the U.S. EPA secondary drinking water standard for chloride is 250 mg/L / 250 parts per million (ppm). Secondary drinking water standards are not health concerns but are concentrations that affect taste/smell or cause staining of fixtures and cloths (U.S. EPA, 2003). Sodium chloride, NaCl when it dissociates yields Na and Cl ions. A concentration of NaCl must be over 412 ppm to yield Cl concentrations over the U.S. EPA secondary drinking water standard. Less than 25% of HF fluids for all seven years has a concentration of sodium chloride that could yield a chloride concentration exceeding the EPA secondary drinking water standard (Figure 15).

Guar gum is a thickening/gelling agent used in hydraulic fracturing fluid (FracFocus, 2017b). It helps suspend the proppant. Guar gum is also used as a thickening agent for cosmetics, food and toothpaste (Suchy and Newell, 2012). For Louisiana wells in the HSGP region, the concentrations of guar gum have generally been declining between 2011 and 2017 (Figure 16) as indicated by median concentration decreasing from 1510 ppm in 2011 to 445 ppm in 2017 a 71 % decline. The concentrations of guar gum used in the Haynesville between 2011 and 2013 are typical of values noted by Barati and Liang (2014) of 1200 to 1900 ppm. From 2014 to 2017 guar gum concentrations were typically less than half of the concentrations noted by Barati and Liang (2014).

Ethanol is used in HF as a surfactant (FracFocus, 2017b). The concentration of ethanol has remained fairly constant between 2011 and 2017 (Figure 17). The concentrations are far below the blood alcohol concentrations that are the legal limits for intoxication while driving, 0.8% or 8000 ppm (FindLaw.com, 2016). Ethanol like the other two previous compounds, guar gum and sodium chloride/salt, is often used in food, and have concentrations that have been fairly constant between 2011 and 2017 within the HF mixtures used in the HSGP region.

The concentration of the five compounds that are flammable but not carcinogenic generally have lower concentrations than more benign compounds previous noted (Chilcott, 2006; Cruzan, 2009; Department of Health and Human Services, no date; epa.gov, no date; and toxnet.nlm.nih.gov, no date). One of these compounds is methanol, also known as wood alcohol. Methanol is a volatile organic compound that is highly toxic to humans. It can cause depression of central nervous system and degenerative changes in the brain and visual system (National Toxic Network, 2013). This compound has many uses within HF, which include: corrosion inhibitor, friction reducer, gelling agent, and surfactant (FracFocus, 2017b). Methanol if ingested even in moderate concentrations can cause blurred vision while in high concentrations it can cause blindness and maybe death (Banerjee, 2015). Methanol median concentrations declined from 70 ppm in 2011 to less than 10 ppm in 2012 to 2015 then in concentrations to medians of 17 ppm in 2016 and 300 ppm in 2017 (Figure 18).

Petroleum distillates/kerosene are the third most commonly used chemical in hydraulic fracturing fluid in Louisiana behind only water and sand/quartz. The median concentration is typically fourth behind water, quartz, guar gum in most hydraulic fracturing fluids in Louisiana (Table 4). Petroleum distillates are used as a surfactant, which is used to facilitate pumping of the fluids and lower pressure than if water alone was used (Suchy and Newell, 2012). Other uses for petroleum distillates are crosslinker, friction reducer, and gelling agent (FracFocus, 2017b). There are two trends for petroleum distillates concentrations. One, a weak trend of decreasing median concentrations. The decrease is from 292-377 ppm for 2011 to 213-394 ppm from 2014 to 2017 (Figure 19). Two, a decrease in the scatter of results for concentration between 75% and 25% rank for the same set of years. This decrease is from 838-1381 ppm for 2011 to 2013 to 162-238 ppm from 2014-2017 (Figure 19).

Lastly, for some less commonly used alcohols: isopropanol, ethylene glycol and propargyl alcohol, there are a variety of concentration trends over the past nine years. Isopropanol is a reproductive toxin and irritant (National Toxics Network, 2013). Isopropanol is used in variety of ways with the HF solution as corrosion inhibitor, non-emulsifier, and surfactant (FracFocus, 2017b). For isopropanol there is an initial decline in median maximum concentration from approximately 10 ppm in 2011 to approximately 2 ppm between 2012 and 2015 (Figure 20). Then there was an increase in median maximum concentration to approximately 5 ppm in 2016 and 2017.

Ethylene glycol with HF solution is used for crosslinker, friction reducer, gelling agent, and non-emulsifier (FracFocus, 2017b). Ethylene glycol can on contact irritate eyes, nose and throat. It is a respiratory toxicant. It can also increase risk of spontaneous abortion and birth defects. Ethylene glycol is among 134 EPA priority chemicals as an endocrine disrupting substance (National Toxics Network, 2013). Ethylene glycol between 2011 and 2017 has a generally increasing median values for maximum concentrations from approximately 16 ppm in 2011 to 32 ppm in 2017 (Figure 21). The last alcohol considered was propargyl alcohol. The median value of maximum concentration has a pattern similar to that for isopropanol. There was a quick decrease from 2.5 ppm in 2011 to 0.4 ppm in 2012. The next five years 2013 to 2017 have similar values of 0.2 ppm to 0.5 ppm (Figure 22).

Two strong bases, sodium hydroxide and potassium hydroxide are often included within the mixture of compounds used for hydraulic fracturing in the HSGP region. Both of these compounds are pH adjusting agents (FracFocus, 2017b) which is reasonable because both are strong bases. For these two strong bases the median value of maximum concentrations are slowly declining between 2010 and 2017 (Figure 23 and 24). The median value of maximum concentration of potassium hydroxide has declined from approximately 11 to 4 ppm, an approximately 65% decline in concentrations (Figure 23). Results are similar for sodium hydroxide which median value of maximum concentration has declined from approximately 63 to 25 ppm, an approximately 58% decline in concentrations (Figure 24).

Two acids are commonly used within the solution of chemicals used for HF in HSGP, acetic acid and formic acid. Acetic acid is generally used for iron control and as pH adjusting agent (FracFocus, 2017b). In contrast to strong bases, potassium hydroxide and sodium hydroxide, the median value of maximum concentrations for acetic and formic acids have increased. Between 2011 and 2014 the median of maximum acetic acid concentrations remained approximately constant between 1.2 ppm and 2.7 ppm then there was a spike in 2016 and 2017 (Figure 25). However, the frequency of use has decreased from 30 % of all HF jobs in 2011 and 2012 to 6% of all HF jobs in 2016 and 2017. Like acetic acid formic acid is used as a corrosion inhibitor (FracFocus, 2017b). Between 2011 and 2017 median value of the maximum concentrations for formic has increased from approximately 6.3 ppm to 10 ppm, an approximately 50% increase (Figure 26).

A bleaching agent, ammonium persulfate and sodium chlorite a disinfectant are among the short list of compounds considered this study for the HF solution. The median value of the maximum concentration of sodium chlorite is between 13 ppm to 35 ppm (Figure 27). There appears to be no general trend of concentrations. By contrast, ammonium persulfate has a couple of trends, for this compound which has been used a beaker within a HF solution (FracFocus, 2017b). Between 2011 and 2015 there was a decrease of the median value of maximum concentration decreased from approximately 33 ppm to approximately 1 ppm (Figure 28). Then there was an increase to approximately 9 to 26 ppm during 2016 and 2017. So, between 2011 and 2017 there was a decrease from approximately 33 ppm to 9 ppm, an approximately 70% decrease.

Naphthalene is one of three compounds that is aromatic compound among the sixteen considered in this study. It has been used as a surfactant for the HF solution (FracFocus, 2017b). It is considered a possible human carcinogen (epa.gov, no date). Chronic exposure can cause cataracts and damage to the retina (National Toxics Network, 2013). For Louisiana wells fractured, both its median concentration between 2011 and 2017 and frequency of use are decreasing (Figures 29 and 30). The decrease in concentrations of naphthalene occurred first as median concentration decreased from 21.5 ppm in 2011 to 0.1 ppm in 2012, an over 99% decrease. Other years had higher median concentrations up to 0.4 ppm in 2016, which is still a 98% decrease from 2011 (Figure 29). After the concentration decrease came the decrease in frequency that naphthalene was included in the HF fluid from 26-36% in 2011 to 12 to 14-18% in 2014 to 2017 (Figure 30).

Benzyl chloride is another of the aromatic compounds considered for this study. It is considered a probable human carcinogen (epa.gov, no date c). For Louisiana wells fractured, both its 75% rank concentration between 2011 and 2014 and frequency of use between 2011 and 2017 are decreasing (Figures 30 and 31). The decrease in concentrations of benzyl chloride occurred first as 75% concentration decreased from approximately 16 ppm in 2011 to 0.16 ppm in 2014, a 99% decrease. After the concentration decrease came the decrease in frequency that benzyl chloride was included in the HF fluid from 20% in 2011 to 3% in 2017 (Figure 30).

The least toxic of the three aromatic compounds used often for Louisiana HF is 1, 2, 4 trimethylbenzene. It is uncertain if 1, 2, 4 trimethylbenzene is a human carcinogen. However, this is due to lack of studies indicate if it is or not a carcinogen (Epa.gov, 2016). For Louisiana wells fractured, the 75% rank concentration increased between 2011 and 2016 while the frequency of use between 2011 and 2017 are decreasing (Figure 30 and 32). The increase in concentrations of benzyl chloride occurred first as 75% concentration increased from approximately 4 ppm in 2011 to 7 ppm in 2016, an approximate 70% increase. As concentration increased there was a decrease in frequency that 1, 2, 4 trimethylbenzene was included in the HF fluid from 22% in 2012 to 7% in 2017 (Figure 30).

In addition to the list of compounds noted by their chemical names there are ones listed as proprietary compounds, unknown, or not available. These unknown compounds present a question in terms of the toxicity of HF fluid. Often in a FracFocus report there are compounds such as methanol or petroleum distillates that are listed more than once because they perform a variety of functions within the HF fluid. The assumption for this study's count of unknown compounds is that they are very specialized and tend to serve only one function within the HF fluid. The share of HF jobs with at least one unknown/proprietary/not available (UPNA) compound is over 83% every year. The lowest share is in 2016, 84% and highest in 2015, 98%. For the sum of 1846 HF reports, there is at least one UPNA compound for 90% of the reports. Initially, the number of UPNA compounds per FracFocus report increased from approximately four in 2011 to seven in 2014 to 2017 (Figure 33). These numbers are considerably higher than a more general study of more 39,000 FracFocus reports examined, which was 70% Banerjee (2015).

However, these compounds may only be the tip of the iceberg in terms of being carcinogenic. Meyer (2016) for a study of over 1000 compounds used to fracture the Marcellus shale noted that over 80% there was insufficient data to determine if they were carcinogenic compounds.

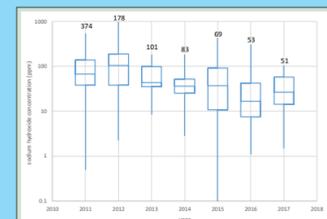


Figure 24. Maximum concentration of sodium hydroxide within the fracture solution used. Source of concentrations is FracFocus (2017c).

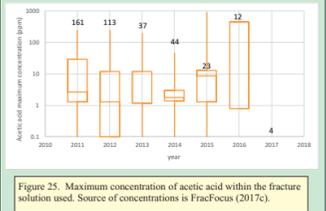


Figure 2

## RESULTS

### Target of hydraulic fracturing

Within Louisiana the share of HF jobs as indicated by FracFocus occurring in the seven HSGP parishes has been declining over the past six years from over 95% in 2011 to approximately 80% in 2017 (Figure 34). The majority of all wells fractured are of the Haynesville within both the seven-parish area (Figure 34) and all of Louisiana (Figure 33). The share of wells within the seven-parish area that are Haynesville wells decreases from 89% in 2011 to 78% to 80% in 2012-2014 (Figure 35). Later in 2016-2017 the share of wells in Haynesville increases back to 85% to 86%. As for the state as whole Haynesville shale always accounts for over 60% of all wells fractured. In 2011 87% of all wells fractured in Louisiana were Haynesville wells. In general, between 2013 and 2016 share of state wells that were fractured in Haynesville wells was between 61% and 63% (Figure 36). However, the more complete set of LA DNR HF data reveals the fact that generally a smaller share of HF jobs were completed in the Haynesville, compare figure 35 and figure 36. Typically less than 50% of all wells HF jobs were in the Haynesville between 2013 and 2016 (Figure 37). It all makes sense if one remembers that the bust for oil price followed gas (Figure 38) and that many of the other units, Hosston, and Wilcox are mainly oil producing units while deeper Haynesville and Cotton Valley (mainly lower Cotton Valley/Bossier shale) are gas producing units.

There have been a number of trends within hydraulic fracturing of Louisiana gas and oil wells:

1. There has been a significant increase in median volumes of water used for HF of wells that are both open to the Haynesville Gas Shale and other formations in Louisiana.
2. The share of HF jobs in Louisiana that are within the Haynesville has declined.
3. The median HF job in the Haynesville has increased by approximately 300% between 2011-12 and 2017-18.
4. The increase for other units is larger than for Haynesville that had median volume of water increase from 5 Mgal in 2011 to 20 Mgal per well in 2017. Increase of median water volume used per well for other units is from <0.5 Mgal in 2011 to 5 Mgal well in 2017. This is probably partly due to different mix of other units through time.
5. It appears the trend of increasing HF volumes is occurring not only for the Haynesville formation but also and the Cotton Valley group. Median HF volume has increase for the Cotton Valley group from approximately 0.5 Mgal in 2010 to approximately 8 Mgal in 2018 as result of increasing share of Cotton Valley HF in the lower Cotton Valley/Bossier shale.
6. For other units such as Hosston and Wilcox HF volumes have been relatively constant. This probably due to only vertical holes within these units are drilled and fractured.
7. Part of the increasing volume used of HF water for Haynesville well is due to an increase in median length of horizontal laterals from approximately 4400 feet in 2011 to 6700 feet in 2017, an approximately 50% increase in median length of laterals.
8. Even when refracting the same well the volume of water has increased by approximately 100%
9. The median portion of hydraulic fracturing fluid that is proppant, quartz/sand, has increased from approximately 6% in 2011 to 12% in 2017. Increasing proppant share appears to be similar to what is occurring in other shale gas plays.
10. median concentrations of other compounds in the HF fluid changes through the past six years.
11. For compounds such as sodium chloride/table salt, and guar gum that are used within food tend to have a fairly steady and larger median concentrations than other compounds that more hazardous.
12. Hydrocarbon compounds such as methanol/wood alcohol, and petroleum distillates/ kerosene, have median concentrations that are relatively steady with small increases in the case of methanol, or small decreases in the case of petroleum distillates.
13. More toxic compounds such as naphthalene tend to have major decreases in concentrations and are less frequently used between 2011 and 2017.

If present trends continue larger and larger volumes of water will be used for HF. The share of wells fractured that are in the Haynesville is likely to remain similar to the past six years unless there is a major change of the ratio of oil/gas price. As for water quality for the HF fluid there are some trends although not as clear. One, the concentration of proppant would likely to increase. Two, more-toxic compounds such as naphthalene are likely in the future to be used less frequently and at lower concentrations. As for other compounds that are occupational hazards such as methanol/wood alcohol and petroleum distillates the trends depend on what compound is considered and could be either be increases or decreases if current trends continue.

The risk to surface and near-surface aquifers from HF is due to: 1) leakage of drilling fluids from the well boring, 2) poor cement jobs on well bore casings, 3) excessive fracturing pressure causing cracks in casing, 4) accidental spills of fluids or solids on surface of drill pad and nearby, and 5) subsurface blow outs (National Toxics Network, 2013). Leakages and spills are rare but they will contaminant soil, surface unconfined aquifers and near surface aquifers due to fracturing near well site (Carter et al., 2015). Carter et al (2015) noted the possible avenue of contamination from poor cementing between annulus and poor well casings failing. Two of these have already happened in the Haynesville shale play. In April 20, 2010 a blow-out occurred southeast of Shreveport. A spill occurred earlier in Caddo Parish resulting in the death 16 cows in a nearby dairy farm (Lustgarten, 2010). This rate of 2 accidents for approximately 2000 Haynesville wells drilled and fractured is similar to the general rate of spills throughout the U.S. Between 2006 and 2012 the US EPA documented 457 fracking-related spills (Horvitt, 2016). During the same years in US, 304,390 oil and gas wells were drilled (Independent Petroleum Association of America, 2014). Assuming all wells drilled today are fractured there are approximately 1.5 fracking-related spills per 1,000 wells drilled in the U.S., which is slightly higher than the less than 1 accident per 1,000 wells within the Haynesville set. Something to keep in mind is risk 3 would probably increase with each re-fracturing that occurs years to decades after the steel casing was initially completed. During the years-decades of the Haynesville production (Browning et al., 2015) corrosion will occur due to contact from highly saline waters (Brondel et al., 1994). For example TDS mean values for some of the units fractured in Louisiana (Figure 6) are approximately: 28,000 mg/L for Nacatoch, which is similar to sea water's TDS value of 35,000 mg/L. However several units fractured in Louisiana have water that is far more saline: approximately 89,000 mg/L for Tuscaloosa Formation, 126,000 mg/L for Cotton Valley Group; and approximately 144,000 mg/L Hosston Formtion (Blondes et al., 2016).

In summary trends indicate HF will have increasing impacts on water supplies as the amount of water is clearly increasing over the past decade: quadrupling for the Haynesville Formation and by a factor of ten for Cotton Valley Group, which has mainly HF jobs located in lower Cotton Valley -- Bossier shale. Size of potential contamination area has increased due to increasing volumes of HF water used and many contaminants are being used in higher concentrations than in the past. Both of these trends indicate greater thought and care must take place when developing unconventional wells in the future in order to avoid unnecessary negative impacts from development on other users of groundwater within unconventional hydrocarbon play regions.



Figure 34. Share of wells fractured in northwest Louisiana parishes where the Haynesville shale gas play is versus in the rest of Louisiana. Source of data FracFocus (2017c).

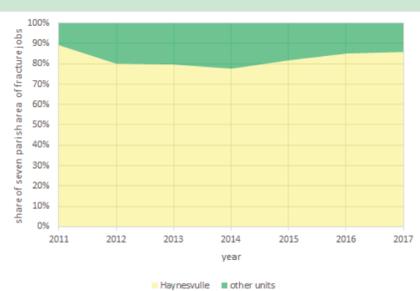


Figure 35. Share of wells fractured in northwest Louisiana parishes that are of Haynesville shale gas play is versus other units in the seven-parish area. Source of data FracFocus (2017c).

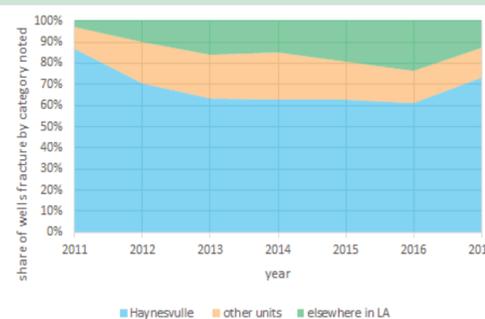


Figure 36. Share of wells fractured that are in Haynesville shale gas play, other units in Northwest Louisiana seven-parish area and elsewhere in Louisiana. Source of data FracFocus (2017c).

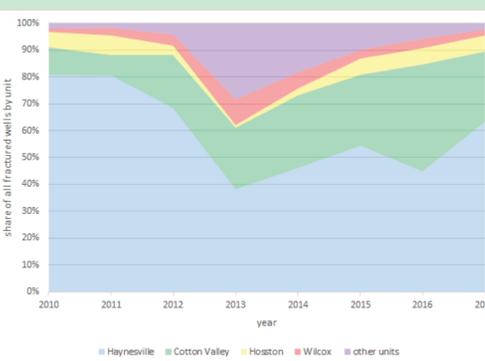


Figure 37. Share of well fractured that are in Haynesville shale gas play, and other units throughout Louisiana. Source of data Louisiana Department of Natural Resources (2018 a).

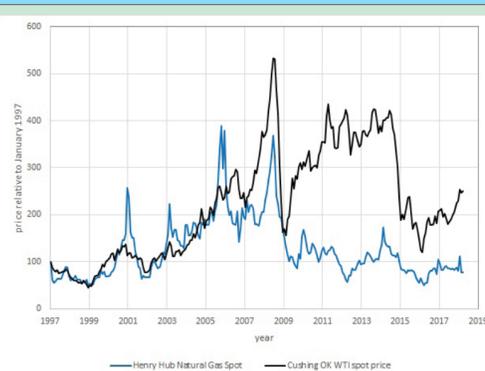


Figure 38. Relative price of oil and gas over the past decade. Source of information is the Energy Information Administration (2018)

## CONCLUSIONS

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