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Research article

Characterization of the chemicals used in hydraulic fracturing fluids for wells located in the Marcellus Shale Play

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A R T I C L E I N F O

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A B S T R A C T

Hydraulic fracturing, coupled with the advances in horizontal drilling, has been used for recovering oil and natural gas from shale formations and has aided in increasing the production of these energy resources. The large volumes of hydraulic fracturing fluids used in this technology contain chemical additives, which may be toxic organics or produce toxic degradation byproducts. This paper investigated the chemicals introduced into the hydraulic fracturing fluids for completed wells located in Pennsylvania and West Virginia from data provided by the well operators. The results showed a total of 5071 wells, with average water volumes of 5,383,743 ± 2,789,077 gal (mean ± standard deviation). A total of 517 chemicals was introduced into the formulated hydraulic fracturing fluids. Of the 517 chemicals listed by the operators, 96 were inorganic compounds, 358 chemicals were organic species, and the remaining 63 cannot be identified. Many toxic organics were used in the hydraulic fracturing fluids. Some of them are carcinogenic, including formaldehyde, naphthalene, and acrylamide. The degradation of alkylphenol ethoxylates would produce more toxic, persistent, and estrogenic intermediates. Acrylamide monomer as a primary degradation intermediate of polyacrylamides is carcinogenic. Most of the chemicals appearing in the hydraulic fracturing fluids can be removed when adopting the appropriate treatments.

1. Introduction

Shale gas has become a very important energy resource in the United States (U.S.), due to the progresses made in hydraulic fracturing and horizontal drilling technologies (Struchtemeyer et al., 2012; Zhou et al., 2014). Hydraulic fracturing is a stimulation technique used to increase the production of oil and natural gas through the high pressure injection of fluids at high volumes to form fractures and small openings in shale formations (Struchtemeyer and Elshahed, 2012; Struchtemeyer et al., 2012; Obo, 2013). These fluids, known as hydraulic fracturing fluids, are usually composed of 98%–99.5% water and proppants (*i.e.* sand, resins, ceramics) with chemical additives making up the balance (Arthur et al., 2009; Gregory et al., 2011). The proppants are injected into the formation to hold the newly generated fractures open, maintaining the permeability (Gregory et al., 2011; Stringfellow et al., 2014). Chemical additives are used to reduce the friction, and bacteria growth, as well as inhibit scale buildup and corrosion of the well casing (Arthur et al., 2009; Gregory et al., 2011; Aminto and Olson, 2012).

Advancements in horizontal drilling has enabled hydraulic fracturing to become common practice for recovering oil and natural gas from shale formations (Arthur et al., 2009; Beckwith, 2010; Montgomery and Smith, 2010). However, the potential adverse environmental impacts of this technology on the groundwater and surface water and potential adverse health impacts on workers have prompted the concerns of many engineers and scientists in recent years (Arthur et al., 2009; Gregory et al., 2011; Bloomdahl et al., 2014; Paulik et al., 2015; Werner et al., 2015; Durant et al., 2016; Chen and Carter, 2017). One concern is the return of the injected hydraulic fracturing fluids to the surface once the pressure is released. This fluid is generically referred to as flowback or produced water; however, flowback commonly refers to hydraulic fracturing fluids that return to the surface immediately after fracturing and before production, while produced water relates to hydraulic fracturing fluids and formation fluids that return during production and can take place over long time periods (Barbot et al., 2013; Stringfellow et al., 2014). The composition of both the flowback and produced waters varies due to the differences in the amounts and types of chemical additives used in the hydraulic fracturing fluids, the location and the geological characteristics of

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sites the fluids are injected, as well as the chemical characteristics of the supplied water (Aminto and Olson, 2012; Barbot et al., 2013). Because of the differences and the potential for the chemical additives to be toxic or contribute to the formation of toxic byproducts, a careful and systematic examination of the chemicals added in hydraulic fracturing fluids is necessary for processing and managing the hydraulic fracturing fluids to avoid ecological damage (Stringfellow et al., 2014). This paper investigated the characteristics of hydraulic fracturing fluids in wells located in West Virginia and Pennsylvania including the number of wells, total water volume and the toxicity and degradability of the organic compounds introduced through the chemical additives.

2. Research methods

2.1. Database and tools

The Marcellus Formation (or Marcellus Shale Play) is currently the largest shale gas play in the United States (U.S.), with an estimated area of approximately 95,000 square miles (mi^2) and production depth ranging from 4000 to 8500 ft (National Energy Technology Laboratory, 2010). The formation crosses six states including West Virginia, Pennsylvania, Ohio and New York, and contains an estimated 1500 trillion cubic feet (Tcf) of original shale gas, 489 Tcf of which was reported to be technically recoverable (National Energy Technology Laboratory, 2010; Lee et al., 2011). The data in this paper was obtained from hydraulic fracturing fluid product component information disclosures found on the www.FracFocus.org website's Chemical Disclosure Registry (FracFocus, 2014). The registry is used by well-operators as a means of disclosing the chemicals and volumes of water injected into each gas and oil well. The data gives specific locations, volumes of water and dates of completion and includes wells to produce both gas and oil. The wells used for this study were completed between 2008 and 2014 with the last access date for wells in West Virginia and Pennsylvania was August 6 and August 22 of 2014, respectively.

MATLAB version R2014b (The MathWorks, Natick, MA) was used to read the data from each well after the downloaded files were converted from portable document format (PDF) into Excel (Microsoft Office 2013, Microsoft Corporation, Redmond, WA) using Adobe Acrobat X Pro (Adobe Systems Incorporated, San Jose, CA). After importing the data into the database, it was determined that there were 111,264 observations and 20 variables including: Fracturing date, State, County, API Number, Operator Name, Well Name and Number, Longitude, Latitude, Long/Lat Project, Production Type, True Vertical Depth (ft.), Total Water Volume (gal), Trade Name, Supplier, Purpose, Ingredients, CAS Number, Max Additive Concentration (%), Max Concentration In Hydraulic Fracturing Fluids (%), and Comments. The correlation between the true vertical depth (ft.) and the total volume of water (gal) for the wells reported in these states was determined using Pearson's product-moment correlation test in RStudio Desktop version 1.0.44 (Boston, MA, USA). Combining MATLAB with the Statistics Toolbox, analysis and calculations were carried out and the data was then stored using Microsoft Excel 2013. Two wells in Pennsylvania, were considered as outliners due to their water volumes and vertical depths therefore, empty values were assigned to their Total Water Volume and True Vertical depth, respectively.

2.2. Characteristics of disclosed chemicals

2.2.1. Number of wells and frequency of chemical observation

Observations for each compound were separated according to their CAS numbers. Observations without CAS numbers but with the same ingredient name were considered to be either the same chemical or a compound belonging to a group of similar chemicals. Many of the compounds were observed more than once on the operators' chemical disclosure lists causing the frequency in which the chemical was disclosed to be greater than the number of wells.

Observations with different values in the categories of Fracturing date, States, County, API Number, Operator Name, Well Name and Number, Longitude, or Latitude were considered to be different wells. The total number of wells was 5071. However, when considering observations with different values in States, County, API Number, Well Name and Number, Longitude, or Latitude, there were 5048 wells. Of those 5048 wells, 23 wells were fractured on two different dates, which means they have the same values in States, County, API Number, Well Name and Number, Longitude, and Latitude, but different values in Fracturing date or Operator Name, therefore increasing the number of wells from 5048 to 5071 (See Table S1 in the supplementary information). Because operators use different hydraulic fracturing fluid formulations, the first method for identifying the wells was adopted in the following analysis.

The value in “Num. of wells” pertains to the number of wells containing a specific chemical in their hydraulic fracturing fluid formulation. The frequency with which a chemical occurs in this paper refers to the number of incidences a specific chemical appeared in the disclosures for the hydraulic fracturing fluids of all the wells. Since some chemicals occurred more than one time in one well, the Number of Wells is expected to be less than or equal to the Frequency with which the chemical occurs.

2.2.2. Mean concentration in hydraulic fracturing fluids

The mean concentration of a chemical in the hydraulic fracturing fluids (in ppm) was determined by the chemical's concentration in the hydraulic fracturing fluids of each well and the amount of water provided by the well operators for each well. In most cases the value in the variable of “Max Concentration In Hydraulic Fracturing Fluids (%)” was empty, zero, or greater than zero. Observations with empty values in the “Max Concentration In Hydraulic Fracturing Fluids (%)” or “Total Water Volume (gal)” were removed. The concentration of a chemical in hydraulic fracturing fluids of a well was calculated according to the following Equation (1):

$$C_{A,j} = 10^4 \times \sum_{i=1}^{m} C_{max,A,j,i} \tag{1}$$

Where: $C_{max,\ A,\ j,\ i}$ is the maximum concentration of chemical A in hydraulic fracturing fluids when occurring at ith in well j, % by mass; m, is the frequency of chemical A in well j; $C_{A,\ j}$ is the concentration of chemical A in well j, ppm or mg/l.

“Mean Conc. in Hydraulic Fracturing Fluids, ppm” of a chemical was calculated according to Equation (2) and was calculated after excluding the wells with zero mean concentration.

$$C_{mean,\,A} = \sum_{j=1}^{n} (C_{A,j} \times V_{water,j}) \Big/ \sum_{j=1}^{n} V_{water,j} \tag{2}$$

Where: $C_{A,\ j}$ is the concentration of chemical A in well j, ppm; $V_{water,\ j}$ is the water volume in well j, gal; n is the total number of wells containing chemical A in their hydraulic fracturing fluids; $C_{mean,\ A}$ is the mean concentration of chemical A in the wells, where chemical A was added in their hydraulic fracturing fluids, ppm or mg/l.

2.3. Chemical classification

Chemicals were separated into three groups: organic compounds, inorganic compounds (Table S2 in the supplementary information), and unknown compounds (Table S3 in the supplementary information). The organic chemicals were classified based on the functional groups of the chemical species and the potential for the different compounds to undergo similar chemical reactions (McMurry, 2010; Brown, 2013). In order to define their characteristics, the organic compounds were classified into hydrocarbons, benzyl, phenyl, organics containing oxygen, organics containing nitrogen, sulfur, or phosphorus, and polymers. Hydrocarbons were further divided into naphthas, alkanes, alkenes, and others. Organics containing oxygen were further separated into alkoxy, ethoxy, carbohydrates & enzymes, carboxylic acids & their salts, alcohols, aldehydes, anhydrides, and others. After classifying the compounds, duplication of the chemicals was avoided by setting the priorities as follows: Ethoxy > Alkoxy > Carbohydrates & Enzymes > Polymers > Naphathas > Benzyl > Phenyl > Nitrogen > Phosphorus > Sulfur > Carboxylic Acids & their Salts. Organics with frequencies greater than or equal to 25 are discussed in this paper, while organics with frequencies less than 25 are listed in Table S4 (supplementary information).

3. Results and discussion

3.1. Well information

3.1.1. Number of wells put into production from September 2008 to August 2014

From September 2008 to August 2014, there were 5071 reported wells located in Pennsylvania and West Virginia that were fractured; 23 of these wells were fractured twice, giving a total number of 5048 wells. Among these wells, 4342 and 729 are located in Pennsylvania and West Virginia, respectively. The number of wells in Pennsylvania was approximately six times greater than the number of wells completed in West Virginia. Fig. 1a shows the number of wells fractured in both of Pennsylvania and West Virginia, which increased from 2008 to 2014, while Fig. 1b shows the growth rate in the number of wells located in either Pennsylvania or West Virginia starts to decrease in 2012. The highest rates for hydraulic fracturing were 3.81 wells per day in Pennsylvania at the beginning of 2012 and 0.74 per day in West Virginia at the end of 2012.

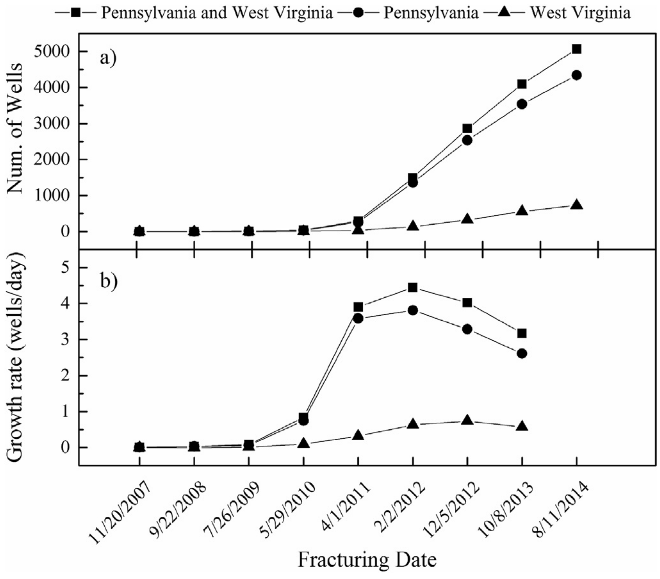

Fig. 1. Growth in number of wells is shown over time. The number of well put into production increased over time until 2012. Towards the end of 2012 a slow decline in the number of well was exhibited.

The growth rate of wells in Pennsylvania and West Virginia decreased from 2013 to 2014. The decreased growth rate of hydraulic fracturing wells may reflect the development trends of the shale gas in the Marcellus shale play in recent years due to cost of productivity and the demand for natural gas (Kerr, 2010; Sovacool, 2014). Furthermore, the expensive cost for environmental remediation of water and soil contamination, health costs, and air quality, which are considered as priority issues for Marcellus Shale Formation production decisions may have also contributed to the decreased development of shale gas in this region (Coulson et al., 2011).

3.1.2. Total water volume for wells put into production

Statistical analysis showed the average Total Water Volume (gal) was 5,383,743 ± 2,789,077 (mean ± standard deviation, s.d.) with the median of 4,911,362, while the True Vertical Depth (ft.) is 7061 ± 1069 with the median of 7054 (Table S5 in the supplementary information). The medians for both parameters were close to their means, indicating both the total volume of water (gal) and vertical depth (ft.) are evenly distributed around their means.

Further analysis showed the total water volume in West Virginia was 6,778,925 ± 3,108,758 gal, which was higher than the 5,153,736 ± 2,663,905 gal used in Pennsylvania. This is consistent with the U.S. EPA (2015) report that also found the median value of total water volume reported between January 2011 and February 2013 was 5,012,238 gal in West Virginia, which was higher than 4,184,936 gal in Pennsylvania. The standard deviation of the Total Water Volume (gal) is almost 50% of its average value, indicating fluctuations in the Total Water Volume (gal) from well to well. One reason for the differences in water usage are the 5071 completed wells belonged to 63 operators, and were distributed among 56 counties in Pennsylvania and West Virginia, which are displayed in Fig. 2 listed in Table S6 (in the supplementary information).

While the water usage varied, the true vertical depth was 7085 ± 1125 ft and 6921 ± 620 ft in Pennsylvania and West Virginia, respectively, which were considered similar depths as the wells in both states are located in the same Shale Play (Chen and Carter, 2016). Further correlations between the true vertical depth and the total water volume were tested using Pearson correlation to determine if a relationship existed between these parameters for the wells in Pennsylvania and West Virginia. The correlation between the true vertical depth (ft.) and the total volume of water (gal) showed no obvious linear relationship exists between these two variables ($r = 0.040$, p-value $= 0.0054$, $n = 5071$), indicating that the total water volume may not depend on the vertical depth of the well, which was previously determined in the authors' previous study of all wells in the US (Chen and Carter, 2016).

Flowback and produced water consists of hydraulic fracturing fluids and formation water that returns to the surface during oil or gas production (Alkhudhiri et al., 2013). Management strategies for flowback and produced water adopted by hydraulic fracturing operations, include recycling or reuse for future hydraulic fracturing production, deep well injection, transport to and treatment for reuse in plants that specifically handle hydraulic fracturing wastewater (Warner et al., 2013; Harkness et al., 2015), however; limitations exist for each option (Lutz et al., 2013; Harkness et al., 2015). Recycling or reusing the flowback or produced water as a replacement for fresh water when composing hydraulic fracturing fluids can decrease the volume of fresh water required to put a well into production. However, the various chemical species that already exist in the recycled flowback or produced waters can potentially change the chemical species and concentrations in hydraulic fracturing fluids. The actual concentrations of chemicals in

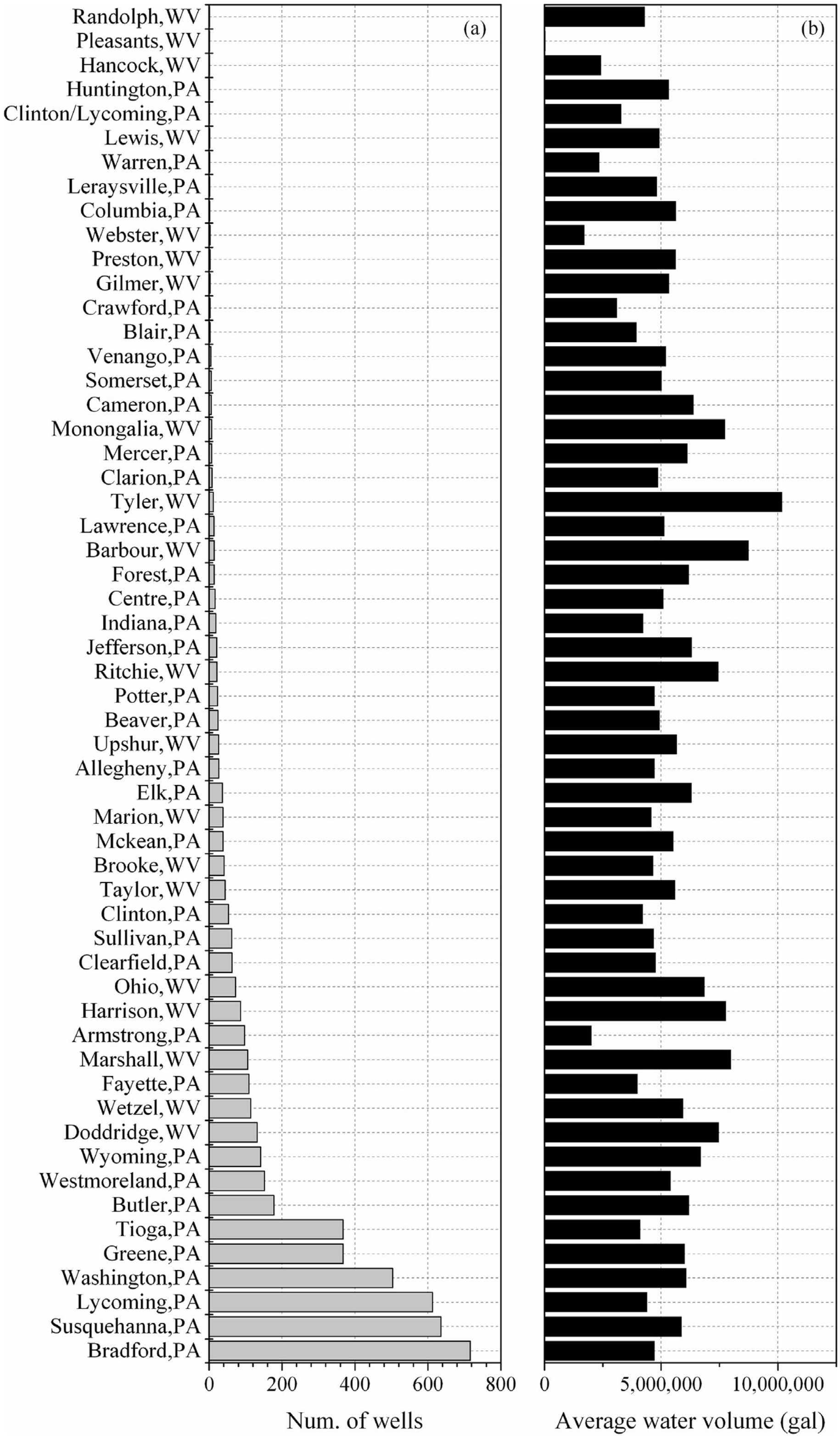

Fig. 2. a) Num. of wells and b) average water volume (gal) in each county in Pennsylvania (PA) and West Virginia (WV) in the Marcellus Shale Play. More detailed information regarding these chemicals is shown in Table S6 in the supplementary information.

hydraulic fracturing fluids may be higher or lower than the reported concentrations. For the wells where the operators reported the use of recycled produced water, only the chemical components listed in the disclosures were considered as the recycled water can contain other chemical constituents. Table S7 (in the supplementary information) lists the wells where recycled produced water was used to replace part of the fresh water. In these cases, there were 1112 out of 5071 wells or approximately 19.7% of the wells where recycled produced water was used.

3.2. Types and frequency of organic species used in hydraulic fracturing fluids

Figs. 3 and 4 shows the frequency and number of wells in which different organic and inorganic compounds were used in the hydraulic fracturing fluids for the wells studied. The organic compounds were found in the 5070 wells with a frequency of 68,555 and the inorganic compounds were added in 5069 wells with a frequency of 25,242. The greater frequency compared to the number of wells studied is a result of the organic compounds showing up more than once in the chemical disclosure data as the chemical additive compositions may contain some of the same compounds. The organic compounds were divided into sub-groups including organics containing oxygen, which occurred in 5062 wells and had the highest frequency of 52,181. These compounds were followed by organics containing nitrogen, sulfur, or phosphorus, which were revealed to be in 4877 wells with a frequency of 17,575. Hydrocarbons were added in 4256 wells with a frequency of 8542. The following sections describe the different functional groups for the organics species and their properties that may be harmful to the environment.

3.2.1. Organics containing oxygen

3.2.1.1. Alkoxy and ethoxy. Alkoxy group (-OR) is an alkyl group bonded to oxygen (Brown, 2013), while ethoxy group is $-OC_2H_5$. Ethoxylation adds ethylene oxide functional groups onto alcohols or phenols, forming compounds such as ethylene, propylene, and polypropylene glycols. Ethylene oxide (CAS: 107-21-1, or ethylene glycol) was found in 2132 wells with the mean concentration of 75 ppm. Staples et al. (2001) suggested ethylene glycol is not persistent due to the rapid biodegradation under both of aerobic and anaerobic conditions after reviewing its fate and risk from previous studies. Most of the alkoxy groups observed in the reported organics is the ethoxy group (Fig. 5 and Table S8 in the supplementary information). More than half of the organics with ethoxy groups belong to alcohol ethoxylates (AEOs), which are produced through the ethoxylation of alcohols. More than 99% AEOs can be effectively removed in WWTPs (Morrall et al., 2006). Their biodegradation mechanisms are scission and then ω- or β-oxidation of the alkyl chain (Steber and Wierich, 1985), and the alkyl chain was reported to hinder anaerobic degradation (Mosche, 2004).

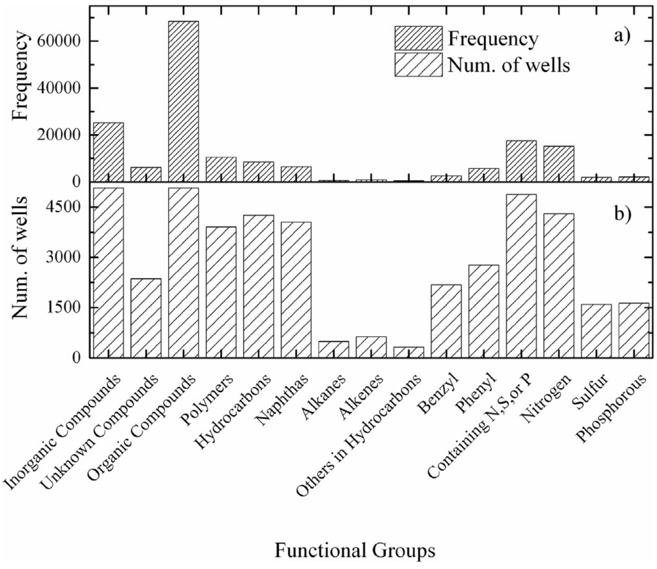

Fig. 3. a) The frequency of the compounds used in hydraulic fracturing fluids, which are categorized based on their functional groups, and b) the number of wells that reported the use of these compounds is shown.

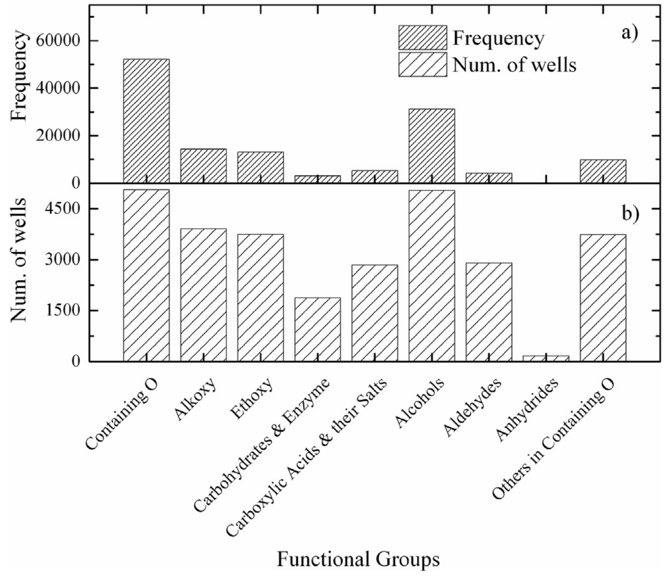

Fig. 4. a) The frequency of the compounds used in hydraulic fracturing fluids, which are categorized based on their functional groups, and b) the number of wells that reported the use of these compounds is shown. These compounds have functional groups that contain oxygen.

AEOs are nonionic surfactants used for the replacement of alkylphenol ethoxylates (APEOs) (Traverso-Soto et al., 2014). APEOs are produced by sequential addition of ethylene oxide to alkylated phenols or alkylphenols (APs) (Cruceru et al., 2012). The observed APEOs in the hydraulic fracturing fluids include octoxynol 9 (CAS: 68412-54-4) occurring in 552 wells with an average concentration of 2.2 ppm, polyethylene glycol nonylphenyl ether (CAS: 9016-45-9) in 158 wells with an average concentration of 39 ppm. Other less commonly observed ethoxylated compounds include 4-nonylphenol branched ethoxylates (CAS: 127087-87-0) in 71 wells with an average concentration of 0.73 ppm and nonylphenol ethoxylates (CAS: N/A) in 145 wells with an average concentration of 7.0 ppm. Though these compounds have not been observed in all wells and may not be considered toxic, the degradation intermediates of APEOs, such as short-chain APEOs and APs (*i.e.* 4-*tert*-octylphenol, and 4-nonylphenol) are considered more toxic, persistent, and estrogenic than their parent compounds (Staples et al., 2004; Huang et al., 2013; Wu et al., 2013a; Vazquez and Lo Nostro, 2014).

Both AEOs and APEOs are derived from polyethylene glycols (PEGs) (Traverso-Soto et al., 2014). The degradation of PEGs through both advanced oxidation processes (AOP) (Chiou et al., 2004; Haseneder et al., 2007; Yuan et al., 2013) and biotechnology (Otal and Lebrato, 2002; Huang et al., 2005; Bernhard et al., 2008) have been well documented. PEGs observed in the hydraulic fracturing fluids included polyethylene glycol (CAS: 25322-68-3) in 1647 wells with a mean concentration of 132 ppm, and 2-butoxyethanol (CAS: 111-76-2) in 1300 wells with a mean concentration of 280 ppm. Polypropylene glycols (PPGs) are synthetic non-toxic polymers used in the formulation of copolymers along with PEGs (Zgola-Grzeskowiak et al., 2007). Polypropylene glycol (CAS: 25322-69-4) appeared in 78 wells with an average concentration of 7.9 ppm. Zgola-Grzeskowiak et al. (2006) reported around

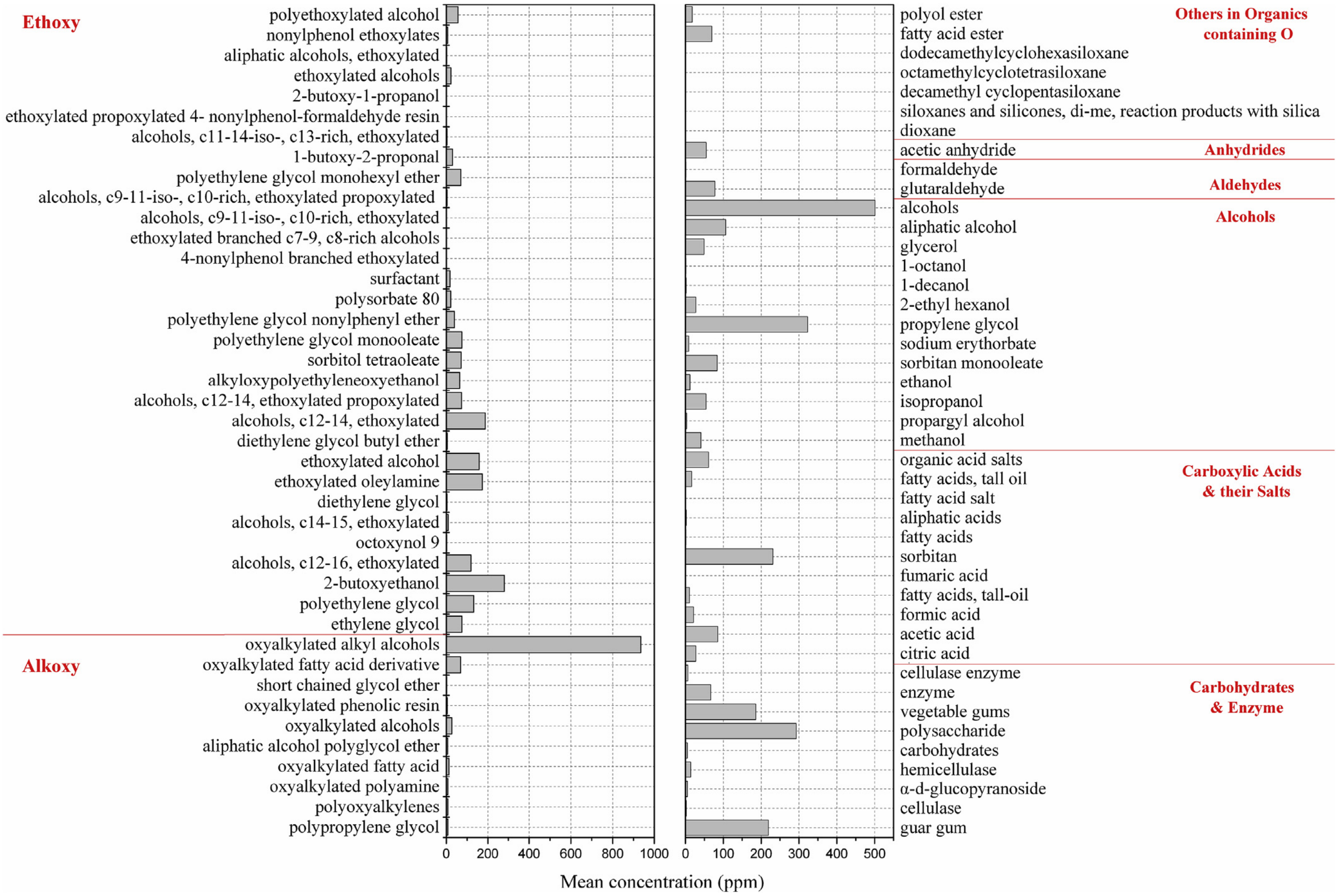

Fig. 5. Mean concentrations of organic compounds containing oxygen reported in hydraulic fracturing fluids for wells put into production in the Marcellus Shale Plays. More information regarding these chemicals is shown in Table S8 in the supplementary information.

99% of both PEGs and PPGs were removed under the River Water Die-Away Test through different biodegradation pathways. Hu et al. (2007) isolated three strains (*Sphingobium* sp. strain EK-1, *Sphingopyxis macrogoltabida* strain EY-1, and *Pseudomonas* sp. Strain PE-2), which can use both PEGs and PPGs as their sole carbon source.

3.2.1.2. Carbohydrates & enzymes. The Carbohydrates & Enzymes group includes carbohydrates, polysaccharides, or enzymes, which can be directly used as carbon sources by various microorganisms. Gums are natural, biosynthesized, or modified polysaccharides (Whistler, 2012). Vegetable gums (CAS: N/A) were observed in 93 wells with a mean concentration of 186 ppm. Guar gum (CAS: 9000-30-0), which appeared in 1642 wells with a mean concentration of 219 ppm, are polysaccharide gums extracted from trees and plants (Timar-Balazsy and Eastop, 2012). Guar gum is an environmentally friendly natural polysaccharide that can be readily degraded by microorganisms (Gastone et al., 2014). Lester et al. (2014) reported 90% removal of the guar gum was achieved by activated sludge after 10 h when the total dissolved solids (TDS) was 1500 mg/l. The removal efficiency decreased by 40% when TDS increased to 45,000 mg/l after 31 h of treatment time. Cellulase is a complex enzyme system for degrading cellulose, which is an abundant and water-insoluble biopolymer (Polaina and MacCabe, 2007). Cellulase (CAS: 9012-54-8) was found in 623 wells with a mean concentration of 1.96 ppm, while cellulase enzyme (CAS: N/A) appeared in 36 wells with a mean concentration of 6.2 ppm.

3.2.1.3. Carboxylic acids & their salts. Carboxylic acids are organic compounds with the carboxyl group (−COOH). Citric acid (CAS: 77-92-9) was reported to be used in 1629 wells with a mean concentration of 27.4 ppm. This compound is a chelating agent in the food industry and a reducing agent in photolytic and photocatalytic systems (Quici et al., 2007). Chen et al. (2013) reported 99.4% of the total organic carbon (TOC) was eliminated in a chloride photoelectrochemical process developed for mineralizing citric acid (5 mM or 961 ppm). Acetic acid (CAS: 64-19-7), found in 718 wells with the mean concentration of 85.0 ppm, is recalcitrant to oxidation due to the methyl group in α-position of the carboxyl group (Findik and Gunduz, 2007). Cihanoglu et al. (2015) found under the optimal conditions in heterogeneous Fenton-like oxidation, only 50.5% of acetic acid with the initial concentration of 100 mg/l was removed. Formic acid (CAS: 64-18-6), reported to be in 254 wells with a mean concentration of 21.2 ppm, is toxic to microorganisms and humans. Cruz Viggi et al. (2010) used non-acclimated activated sludge from a WWTP to treat formic acid, and found the removal rate gradually decreased to zero and biodegradation activity was greatly inhibited. AOPs are considered promising technologies for treating biologically persistent organics (Oller et al., 2011) and have been studied as a means for removing formic acid (Xiong et al., 2003; Mariani et al., 2013; Apiwong-ngarm et al., 2014).

3.2.1.4. Alcohols. Alcohols are organic compounds with one or more hydroxyl groups (−OH) bonded to a saturated carbon.

Methanol (CAS: 67-56-1), propargyl alcohol (CAS: 107-19-7), isopropanol (CAS: 67-63-0), and ethanol (CAS: 64-17-5) were the most commonly reported alcohols appearing in more than 1000 wells as shown in Table S8. Propylene glycol (CAS: 57-55-6), aliphatic alcohol, and other alcohols were found with mean concentrations higher than 100 ppm. Almost all of the added alcohols are considered to be toxic chemicals. Methanol, ethylene glycol, diethylene glycol (CAS: 111-46-6), and propylene glycol can result in alcohol-related intoxication, such as metabolic acidosis (Krautt and Kurtztt, 2008). Long-term inhalation of propargyl alcohol has been shown to increase the occurrence of respiratory/transitional epithelial adenoma in mice and rats (Thakur et al., 2013). 2-ethylhexanol (CAS: 104-76-7), found in 142 wells with a mean concentration of 27 ppm, is a volatile organic compound (VOCs) (Nalli et al., 2006), which can vaporize under normal atmospheric conditions. Short-term oral exposure to 2-ethylhexanol can induce liver peroxisome proliferation (WHO, 1993).

The alcohols frequently reported in the hydraulic fracturing fluids at high concentrations are known to be readily removable. Biodegradation is considered to be the most inexpensive wastewater treatment technology that can remove methanol (Vallero et al., 2003; Paulo et al., 2004), ethanol (Welz et al., 2011), and propylene glycol (Delorit and Racz, 2014; Lissner et al., 2015). Biodegradation is also feasible for removing isopropanol and diethylene glycol. Geng et al. (2015) found that *P. denitrificans* GH3 had the ability to utilize 90.3% of the isopropanol provided as the sole carbon source within 7 days. Sriprapat et al. (2011) used the plant *E. cordifolius* to treat diethylene glycol contaminated water, and found that 95% of COD was reduced and no diethylene glycol remained after 12 days.

3.2.1.5. Aldehydes and anhydrides. Aldehydes are organic chemicals with a (—CHO) functional group, while anhydrides are organics with two acyl groups bonded to the same oxygen atom (R-O-R). Glutaraldehyde (CAS: 111-30-8) was reported in 1843 wells with a mean concentration of 77.5 ppm. It is commonly used as a biocide to inhibit the growth of microorganisms, and exhibits acute toxicity toward aquatic organisms (Leung, 2001b). Although displaying a low acute dermal and inhalation toxicity to humans, it is very toxic through acute oral intake and extremely irritating to the eyes and skin (U.S. EPA, 2007). Formaldehyde (CAS: 50-00-0), reported in 556 wells with a mean concentration of 1.2 ppm, is a volatile organic compound. It is widely used as a disinfectant and was classified as “carcinogenic to humans” (Group 1) by the International Agency for Research on Cancer (IARC) (WHO, 2006). Acetic anhydride (CAS: 108-24-7), found in 166 wells with a mean concentration of 54.7 ppm, is highly corrosive and severely irritating.

Glutaraldehyde is easily degraded in wastewater through either AOPs or biotechnology. Leung (2001b) reviewed the fate and toxicity of glutaraldehyde, and found it can be easily biodegraded in water under either aerobic or anaerobic condition. Leung (2001a) also showed that glutaraldehyde tended to stay in the aquatic phase of the water-sediment system, and had a pseudo-first-order half -life of 10.6 h and 7.7 h under aerobic and anaerobic conditions, respectively. Kist et al. (2013) found 72.0–75.0% of the glutaraldehyde in solution was removed through the combination of O_3/UV.

The degradation of formaldehyde has been well studied. Methylotrophic yeast *Hansenula polymorpha* can utilize formaldehyde up to 1750 mg/l in wastewater, while formaldehyde in this concentration is toxic to most microorganisms (Kaszycki et al., 2001). *Aspergillus nomius* SGFA1 and *Penicilium chrysogenum* SGFA3, isolated from untreated sewage sediments in formaldehyde-contaminated areas, degraded 3000 and 9000 mg/l of formaldehyde completely within 7 days, respectively (Yu et al., 2014). 96.1% of formaldehyde with an initial concentration of 1000 mg/l was removed after 2 h by the photocatalyst of ZnO nanoparticles, which were immobilized on glass plates (Soltani et al., 2015).

3.2.2. Polymers

Polyacrylamides are produced through the free radical polymerization of acrylamide. As seen from Fig. 6 and Table S9 in the supplementary information, polyacrylamides and acrylamide frequently appeared as components in polymers. Long chain polyacrylamide (CAS: N/A) were found in 98 wells with a mean concentration greater than 1000 ppm. Polyacrylamides are generally considered as non-toxic polymers. They can be removed through thermal, photo-, biological, chemical, and mechanical degradation, but the acrylamide monomer, as a primary degradation intermediate, is carcinogenic and worth noting (Caulfield et al., 2002; Lu et al., 2012). In one study, aerobic granules utilized polyacrylamides as sole carbon and nitrogen sources with a degradation rate of 2.2 mg/g MLSS • h, exhibited no acrylamide monomer during the breakdown process (Liu et al., 2012). Conventional polymers can persist for a long time after disposal, and include polyethylene, polypropylene and water-soluble polymers (Gross and Kalra, 2002). These persistent polymers also appeared in the hydraulic fracturing fluids. Cationic water-soluble polymers (CAS: N/A) have been used in hydraulic fracturing fluids for the treatment of 162 wells with a mean concentration of 829 ppm. Biodegradable polymers are environmentally friendly materials, which can be mineralized into CO_2 and H_2O by microorganisms in the natural environments (Beach et al., 1995; Guo et al., 2012). Using biodegradable polymers to replace conventional polymers in the hydraulic fracturing fluids would be environmentally beneficial.

3.2.3. Hydrocarbons

Fig. 7 and Table S10 (supplementary information) show the different hydrocarbons and their mean concentrations reported in the hydraulic fracturing chemical additives. Hydrocarbons are organics composed of only carbon and hydrogen. Alkanes are saturated hydrocarbons while alkenes are categorized as unsaturated hydrocarbons (Brown, 2013). Naphtha is the liquid fraction of hydrocarbons from petroleum, which can be grouped into aliphatic and aromatic naphtha (Speight, 2006). Light naphtha boils from 30 to 90 °C with 5–6 carbons while heavy naphtha boils from 90 to 220 °C with 6–12 carbons (Speight and Arjoon, 2012). Hydrocarbons are an ideal food source for various microorganisms, and hydrocarbon-degrading bacteria have been widely reported (Rajasekar et al., 2005). Biodegradation of oil occurs mainly through degradation of aliphatic or light aromatic fractions, while the high molecular weight aromatics are recalcitrant in the environment (Leahy and Colwell, 1990). Heavy aromatic naphtha (CAS: 64742-94-5) was used in the hydraulic fracturing fluids of 126 wells with a mean concentration of 2.6 ppm. Naphthalene (CAS: 91-20-3), added in 144 wells with a mean concentration of 0.59 ppm, is one of the typical polycyclic aromatic hydrocarbons (PAHs) found in hydraulic fracturing fluids. It was classified as a possible carcinogen (Group 2B) by IARC, due to the fact that there is insufficient or inadequate evidence of its potential carcinogenic effects on animals and humans (WHO, 2002). PAHs are highly toxic and persistent in the natural environments (Wu et al., 2013b; Jing et al., 2014). Microbial degradation of naphthalene under both aerobic and anaerobic conditions has been well studied and documented (Xu et al., 2014; Estelmann et al., 2015; Kummel et al., 2015).

3.2.4. Benzyl and phenyl

Chemicals in the benzyl and phenyl groups contain $C_6H_5CH_2$— and C_6H_5-, respectively. As seen in Fig. 8 and Table S11 in the supplementary information most of the organics with one or more

Fig. 6. Mean concentrations of polymers reported in hydraulic fracturing fluids for wells put into production in the Marcellus Shale Plays. More information regarding these chemicals is shown in Table S9 in the supplementary information.

benzene rings were placed in the benzyl category. Three isomers of xylene, benzene, toluene, ethylbenzene, and xylene, together notoriously known as BTEX, are the most persistent gasoline compounds (Osterreicher-Cunha et al., 2009; Huang and Li, 2014). Xylene (CAS: 1330-20-7) was found in the hydraulic fracturing fluids for the treatment of 47 wells with a mean concentration of 1.6 ppm. Trimethylbenzene (TMB) includes 1,2,3-trimethylbenzene (123-TMB, CAS: 526-73-8), 1,3,5-trimethylbenzene (135-TMB, CAS: 108-67-8), and 1,2,4-trimethylbenzene (124-TMB, CAS: 95-63-6). 124-TMB and 135-TMB appeared in the hydraulic fracturing fluids with a mean concentration of 0.15 and 0.09 ppm, respectively. TMB and BTEX can be easily degraded under aerobic conditions, but both are recalcitrant under anaerobic conditions (Chen et al., 2009).

Benzalkonium chloride (CAS: 68424-85-1), found in 1046 wells with a mean concentration of 19.5 ppm, is used as a disinfectant (Bassarab et al., 2011) and is a quaternary ammonium compound (QAC). QACs contain a nitrogen atom with four functional groups attached and a positive charge (McMurry, 2010). Benzalkonium chloride is considered persistent because it tends to be adsorbed onto the sludge in WWTPs and is not biodegradable under anaerobic condition (Tezel and Pavlostathis, 2009). Zhang et al. (2011) found the degradation of benzalkonium chloride (mostly

Fig. 7. Mean concentrations of hydrocarbons reported in the hydraulic fracturing fluids for wells put into production in the Marcellus Shale Play. Further information regarding these chemicals is presented in Table S10 in the supplementary information.

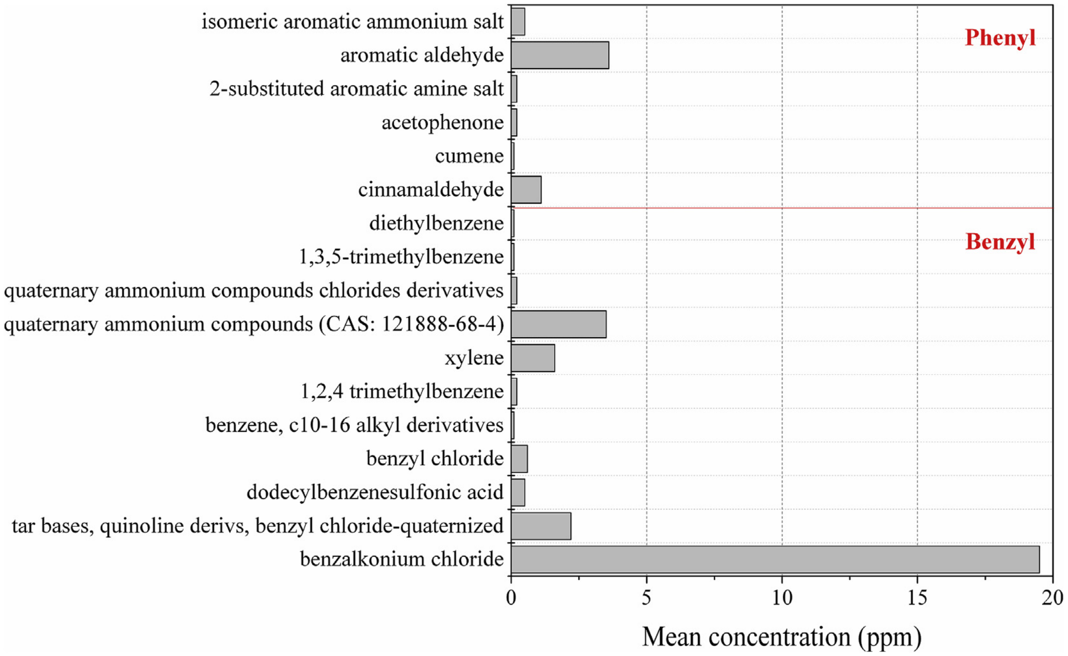

Fig. 8. Mean concentrations of organic compounds with benzyl and phenyl functional groups reported in the hydraulic fracturing fluids for wells put into production in the Marcellus Shale Play. More information regarding these chemicals is presented in Table S11 in the supplementary information.

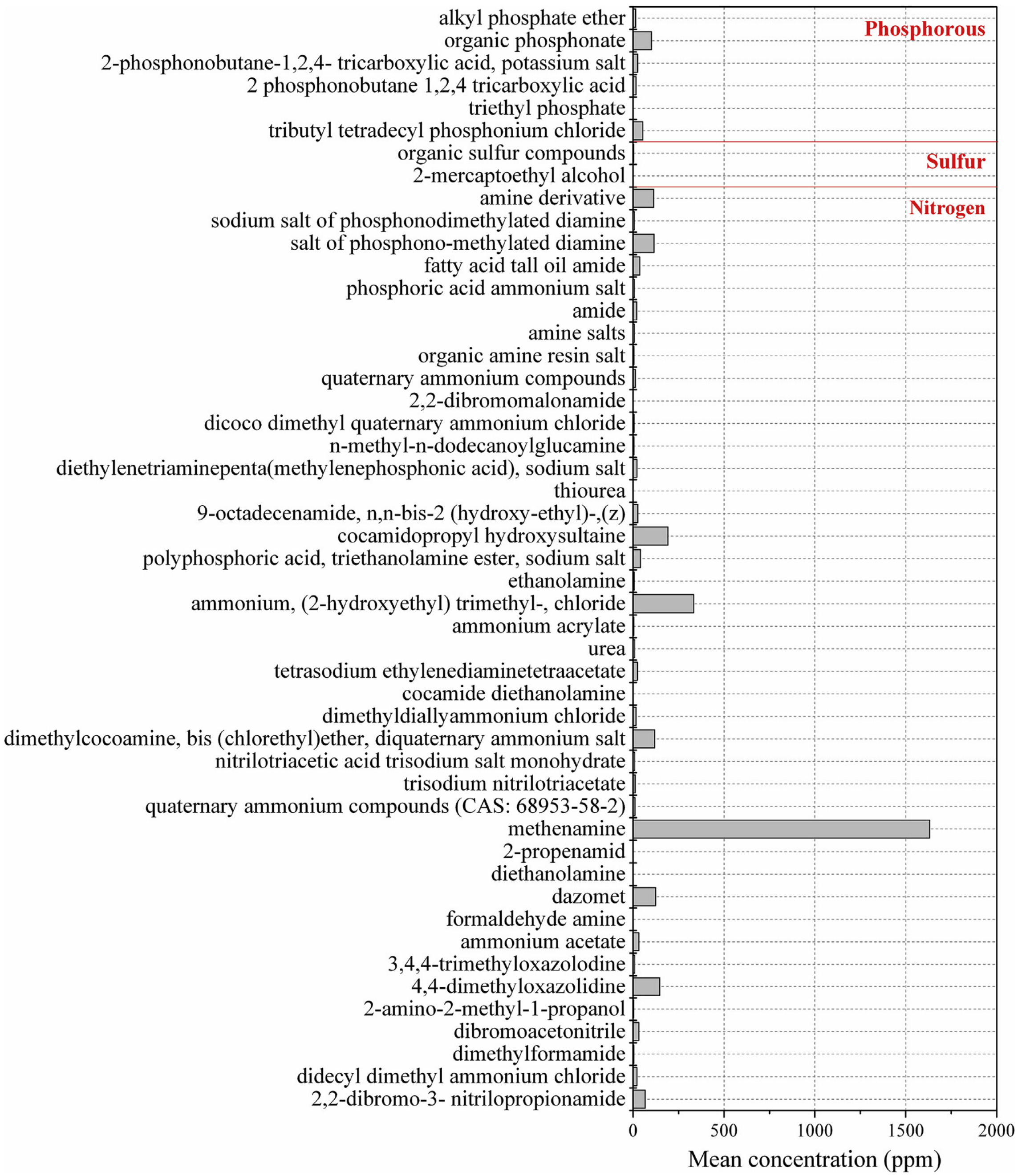

Fig. 9. Mean concentrations of organic compounds containing nitrogen, sulfur, or phosphorus reported in the hydraulic fracturing fluids for wells put into production in the Marcellus Shale Play. More information regarding these chemicals is presented in Table S12 in the supplementary information.

adsorbed on the sludge) under aerobic conditions, with the initial concentrations ranging from 5 to 20 mg l^{-1}, started when the aqueous chemical oxygen demand (COD) was completely consumed. AOPs are feasible technologies for degrading disinfectants or biocides, and can be further used to treat high concentration wastewater without the concern of inhibiting microbial degradation. Suchithra et al. (2015) found benzalkonium chloride (100 mg/l) was completely mineralized within 2 h by using hybridization of activated carbon onto TiO_2.

3.2.5. Organics containing nitrogen, sulfur, or phosphorus

Organics containing nitrogen can possibly serve as carbon and nitrogen sources to microorganisms. Choline chloride (CAS: 67-48-1), added in the fluids of 70 wells with a mean concentration of 333 ppm, is a quaternary ammonium salt (see Fig. 9). Choline is a dietary constituent and readily biodegradable (United Nations Environment Programme). 4,4-dimethyloxazolidine (CAS: 51200-87-4), a chemical component in 438 wells with a mean concentration of 146 ppm, is a severe eye irritant with relatively low acute toxicity (U.S. EPA, 1996). Dazomet (CAS: 533-74-4) appeared in the formulation for 250 wells with a mean concentration of 123.90 ppm and is a biocide that forms methyl isothiocyanate (CAS: 556-61-6) when degraded (Sismanoglu et al., 2004; U.S. EPA, 2008). Dazomet is considered moderately toxic through oral intake, while methyl isothiocyanate is highly toxic to fish (lowest $LC_{50} = 51.2$ ppb) and aquatic invertebrates (lowest $LC_{50} = 55$ ppb)

(U.S. EPA, 2008). Acrylamide (CAS: 79-06-1), added to the fluids of 197 wells with a mean concentration of 1.04 ppm, is a human neurotoxin and was classified as potentially carcinogenic to humans (Group 2A) by IARC (WHO, 1986). Many isolated bacterial strains have the ability to use acrylamide as the sole carbon and nitrogen source (Jebasingh et al., 2013; Chandrashekar et al., 2014; Lakshmikandan et al., 2014).

Hexamethylenetetramine (HMT, CAS: 100-97-0), also called hexamine or urotropine, was added in the recipe for treatment of 152 wells with a mean concentration of 1632 ppm. While HMT is chemically and biologically stable due to its cyclic symmetric structure (Hutnan et al., 2005; Middelhoven and van Doesburg, 2007), two bacterial strains isolated from soil can utilize HMT as sole carbon and nitrogen source at a low rate (Middelhoven and van Doesburg, 2007). Acidic conditions are favorable for HMT degradation forming into formaldehyde and ammonia (Hutnan et al., 2005; Taghdiri et al., 2013). Hutnan et al. (2005) used an anaerobic baffled reactor to spatially separate the phases of hydrolysis, acidogenesis, acetogenesis and methanogenesis, resulting in a pH gradient along the reactor. 96% of HMT were removed at organic loading rates of 4 kg/m^3•d and retention time of 84 h, due to the higher hydrolysis activity under acidic conditions. Taghdiri et al. (2013) used silicotungstic acid as the catalysis, and found that more than 70% of HMT (based on TOC) was removed by H_2O_2/Fe^{2+} under the initial pH values of 1.75–2.25. Tributyl tetradecyl phosphonium chloride (CAS: 81741-28-8) was a chemical component for fracturing 701 wells with a mean concentration of 52.5 ppm, while triethyl phosphate (CAS: 78-40-0) appeared in 230 wells with 0.76 ppm. Both of these compounds were used as biocides, and little literature exists about their toxicity and degradation.

4. Conclusions

From September 2008 to August 2014, 4342 and 729 wells were fractured in Pennsylvania and West Virginia. Although the number of wells increased along with time, the growth rates have decreased since 2012. The decreasing development of shale gas may be due to the cost of production, demand for natural gas and the environmental concerns associated with hydraulic fracturing (Kerr, 2010; Sovacool, 2014). Among the 5071 wells investigated in this study, the Total Water Volume (gal) was 5,383,743 ± 2,789,077 (mean ± s.d.) with the median value of 4,911,362 and the True Vertical Depth (ft.) was 7061 ± 1069 with the median of 7054. The 5071 wells were fractured by 63 operators located throughout 56 counties in West Virginia and Pennsylvania. Of the 5.071 well, 1112 wells reported the use of recycled produced water, which can create uncertainty in the chemical composition of the water. In the disclosures of the 5071 wells there were 517 chemicals used to make up the different hydraulic fracturing fluids. Of the 517 chemicals, 96 were inorganic compounds, 358 were organic compounds, and 63 could not be identified. Organics were used in the hydraulic fracturing treatment of 5070 wells with a frequency of 68,555, while organics containing oxygen existed in 5062 wells with a frequency of 52,181.

Many toxic chemicals have been reported as ingredients in the hydraulic fracturing fluids, some of which are considered carcinogenic or potentially carcinogenic to humans and wildlife. Additionally, the degradation of some of these chemicals can potentially produce more toxic and persistent byproducts. Although most of the chemicals used in the hydraulic fracturing fluids can be removed, when adopting the appropriate treatments, some chemicals are persistent. The persistent organics that exist in hydraulic fracturing fluids increases the technological requirements of treatment processes and the cost of operations. Therefore, narrowing the number of individual chemicals used for the same purpose would enable more efficient and economic operations in treating hydraulic fracturing fluids.

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Appendix A. Supplementary data

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