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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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ABSTRACT

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