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Research article

An analysis of chemicals and other constituents found in produced water from hydraulically fractured wells in California and the challenges for wastewater management

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ABSTRACT

As high-volume hydraulic fracturing (HF) has grown substantially in the United States over the past decade, so has the volume of produced water (PW), i.e., briny water brought to the surface as a byproduct of oil and gas production. According to a recent study (Groundwater Protection Council, 2015), more than 21 billion barrels of PW were generated in 2012. In addition to being high in TDS, PW may contain hydrocarbons, PAH, alkylphenols, naturally occurring radioactive material (NORM), metals, and other organic and inorganic substances. PW from hydraulically fractured wells includes flowback water, i.e., injection fluids containing chemicals and additives used in the fracturing process such as friction reducers, scale inhibitors, and biocides – many of which are known to cause serious health effects. It is hence important to gain a better understanding of the chemical composition of PW and how it is managed. This case study of PW from hydraulically fractured wells in California provides a first aggregate chemical analysis since data collection began in accordance with California's 2013 oil and gas well stimulation law (SB4, Pavley). The results of analyzing one-time wastewater analyses of 630 wells hydraulically stimulated between April 1, 2014 and June 30, 2015 show that 95% of wells contained measurable and in some cases elevated concentrations of BTEX and PAH compounds. PW from nearly 500 wells contained lead, uranium, and/or other metals. The majority of hazardous chemicals known to be used in HF operations, including formaldehyde and acetone, are not reported in the published reports. The prevalent methods for dealing with PW in California – underground injection and open evaporation ponds – are inadequate for this waste stream due to risks from induced seismicity, well integrity failure, well upsets, accidents and spills. Beneficial reuse of PW, such as for crop irrigation, is as of yet insufficiently safety tested for consumers and agricultural workers as well as plant health. Technological advances in onsite direct PW reuse and recycling look promising but need to control energy requirements, productivity and costs. The case study concludes that (i) reporting of PW chemical composition should be expanded in frequency and cover a wider range of chemicals used in hydraulic fracturing fluids, and (ii) PW management practices should be oriented towards safer and more sustainable options such as reuse and recycling, but with adequate controls in place to ensure their safety and reliability.

1. Introduction

Significant unconventional oil and natural gas deposits and the advancement of technologies for stimulating production from these sources, including the use of high-volume hydraulic fracturing (HF), have led to an unprecedented expansion in U.S. oil and gas production over the past decade (EIA, 2014). Large-volume hydraulic fracturing (HF) is a well stimulation technique involving the pumping of large amounts of water mixed with a proppant (typically sand) and chemicals under high pressure into the shale formation to create, expand and prop open fractures to release trapped oil and gas to the well surface (EPA, 2015a). An issue arising concomitantly with oil and gas production, conventional and unconventional, is the generation of large amounts of produced water (PW) (Groundwater Protection Council, 2015), a byproduct that

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flows to the well surface together with the oil and gas and is typically high in TDS (including sodium, potassium, bromide, calcium, fluoride, nitrate, phosphate, chloride, sulfate, magnesium), oil and other hydrocarbons, naturally occurring radioactive materials (NORM), metals, and other substances originating from the formation and the well stimulation processes. Benko and Drewes (2008) found that the TDS content of PW in the Western United States ranges from 1,000 mg/L to 400,000 mg/L and the oil and grease content varies between 40 mg/L and 2000 mg/L (Benko and Drewes, 2008). In wells stimulated using HF, varying amounts of the injection fluid returns to the wellhead for a period after the stimulation. Referred to as flowback it contains chemicals and additives used to facilitate the HF process, but may also include compounds such as NORM and heavy metals washed out of the formation (Sovacool, 2014). Some of the controversy surrounding the use of HF has been galvanized by the lack of information available concerning the types and amounts of chemicals used for HF and the volumes and chemical composition of the wastewater produced (Centner and O'Connell, 2014; EPA, 2016a; Konschnik et al., 2013; Rawlins, 2013). Several studies of HF fluids found hundreds of chemicals and compounds, many of which are known carcinogens, toxic to developmental, neurological, and other processes, or otherwise harmful to human and ecological health (Colborn et al., 2011; EPA, 2015b; Stringfellow et al., 2014) (see Table 1).

The wastewater volumes produced by HF stimulated wells are substantial, ranging from 210,000 to 2,100,000 gallons during the flowback, and median flow rates of 200–800 gallons per day during production (Federal Register, 2016). California has a particularly high PW to oil ratio, generating on average 15 barrels (630 gallons) of wastewater for every barrel of oil; equivalent to an estimated 130 billion gallons of wastewater annually (Clean Water Action, 2015). The volumes and chemical composition of PW thus raise questions about the appropriate management strategies to control the risk of harm to human health and the environment.

Using new data collected by the state's Division of Oil, Gas and Geothermal Resources (DOGGR) in accordance with Senate Bill 4 (Pavley, 2013), the present study examined 851 oil wells in California to gain a better understanding of the potential hazards posed by PW and assess the adequacy of current PW management strategies. California serves as a suitable case study because SB4 is widely seen as a pilot law to address information gaps in the oil and gas industry and thus offers a starting point to evaluate the adequacy of the new information with regard to PW management.

2. Materials and methods

The data for this case study were compiled from individual well reports submitted by operators to DOGGR, the California state agency tasked under SB4 with publishing the information relating to well stimulation activities (CA Division of Oil, Gas and Geothermal Resources, 2015). The publicly available repository referenced 851 well reports at the time of access (June 30, 2015). The inventory is not comprehensive, however, because some wells had missing or incomplete reports and because of the decades-long history of HF in California, not all hydraulically fractured wells are represented. For the purpose of this study, only HF wells are included (i.e., wells stimulated using acid fracturing, matrix acidizing, etc. are excluded). SB4 regulations require operators to submit only one report per well after stimulation finished. Thus, the data represent a cross-sectional sample of the produced water composition of hydraulically fractured wells.

Of the 851 initial wells available in DOGGR's repository, 20 wells were not stimulated using HF, 116 well reports were listed as "pending," 56 reports stated that the sample was unsuitable for analysis, and 6 reports contained faulty links. An additional group of 24 wells were linked to the same single report. Inquiries to the listed contact person remained unanswered and, therefore, only one of the 24 wells was included in the study. These data limitations reduce the count of wells included in the study to 630. These wells were stimulated between January 2, 2014 and May 27, 2015. A small number of well reports contained only geochemical information and individual well reports did not always contain data for all constituents represented in the full database. The number of wells that measured the constituent (N) and the number of wells that contained measurable concentrations (N_a) are both noted in the Supplementary Material (Tables A.1–A.5). For many constituents, more than 25% of wells had readings below detection limits. The summary statistics are computed with only nonzero values, with the number of wells included (N_a) noted throughout.

For some well reports the chemical data is not rigorously supported. Specifically, many analyses used EPA methods 8260B and

Table 1
Summary of the types and examples of chemicals commonly used in HF, adapted from FracFocus, https://fracfocus.org/chemical-use/what-chemicals-are-used.

Type	Function	Selected Examples
Acids	Improve injection or penetration; dissolve minerals to reduce clogging	Hydrochloric acid
Biocides	Prevent bacterial growth, which can erode pipes and interfere with fracking process	Glutaraldehyde; Quaternary ammonium compounds; Tetrakis hydroxymethyl phosphonium sulfate
Breakers	Break down gellants; added at end of sequence to enhance flowback	Ammonium persulfate; Sodium, calcium chloride; Magnesium oxide; Magnesium peroxide
Clay stabilizers	Prevent clay plugs of fractures	Choline chloride; Sodium chloride; Tetramethyl ammonium chloride
Corrosion inhibitors	Reduce rusting	Isopropanol; Methanol; Formic acid; Acetaldehyde
Crosslinker	Maintain fluid viscosity; may include carrier fluids	Potassium metaborate; Triethyanolamine zirconate; Petroleum distillate; Boric acid; Zirconium complex; Sodium tetraborate
Friction reducers	Make water slick to increase rate and efficiency of fluid movement	Polyacrylamide; Methanol; Ethylene glycol; Petroleum distillate
Gellants (gelling agent)	Increase viscosity and suspend sand during proppant transport, as a product stabilizer	Guar gum; Polysaccharide blend; Ethylene glycol; Hydrotreated light petroleum distillate
Iron control	Prevent precipitation of metal oxides	Citric acid; Acetic acid; Thioglycolic acid; Sodium erythorbate
Non-emulsifier	Prevent formation of emulsions, and as a product stabilizer	Lauryl sulfate; Isopropanol; Ethylene glycol
pH control	Maximize effectiveness of other additives	Sodium hydroxide; Potassium hydroxide; Acetic acid; Sodium carbonate
Proppants	Hold fissures open for gas & oil escape	Silica (quartz; sand)
Scale control	Prevent mineral buildup and clogs	Copolymer of acrylamide and sodium acrylate; Sodium polycarboxylate; Phosphonic acid salt
Surfactants	Decrease surface tension and improve fluid passage	Lauryl sulfate; Ethanol; Naphthalene; Methanol; Isopropyl alcohol; 2-butoxyethanol