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Identifying chemicals of concern in hydraulic fracturing fluids used for oil production☆

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ABSTRACT

Chemical additives used for hydraulic fracturing and matrix acidizing of oil reservoirs were reviewed and priority chemicals of concern needing further environmental risk assessment, treatment demonstration, or evaluation of occupational hazards were identified. We evaluated chemical additives used for well stimulation in California, the third largest oil producing state in the USA, by the mass and frequency of use, as well as toxicity. The most frequently used chemical additives in oil development were gelling agents, cross-linkers, breakers, clay control agents, iron and scale control agents, corrosion inhibitors, biocides, and various impurities and product stabilizers used as part of commercial mixtures. Hydrochloric and hydrofluoric acids, used for matrix acidizing and other purposes, were reported infrequently. A large number and mass of solvents and surface active agents were used, including quaternary ammonia compounds (QACs) and nonionic surfactants. Acute toxicity was evaluated and many chemicals with low hazard to mammals were identified as potentially hazardous to aquatic environments. Based on an analysis of quantities used, toxicity, and lack of adequate hazard evaluation, QACs, biocides, and corrosion inhibitors were identified as priority chemicals of concern that deserve further investigation.

1. Introduction

Hydraulic fracturing and other types of well stimulation treatments, such as acid stimulation and acid fracturing, are being used extensively throughout the U.S. and globally to increase oil and gas production and extract resources that would otherwise be inaccessible (Clark et al., 2013; King, 2012; Long et al., 2015a). These well stimulation treatments, collectively referred to as unconventional oil and gas development, use a wide variety of chemical additives (King, 2012; Stringfellow et al., 2014; Elsner and Hoelzer, 2016) and can cause both direct and indirect impacts on the environment and human health (Long et al., 2015b; Long, 2014; Jain, 2015; Gregory and Mohan, 2015). Potential direct impacts may include a hydraulic fracture extending into protected groundwater, accidental spills of fluids containing hydraulic fracturing chemicals, or inappropriate disposal or reuse of produced water containing hydraulic fracturing chemicals (Burton et al., 2016; Vengosh et al., 2014). Indirect impacts are impacts not specific to the activity of well stimulation, but are impacts associated with all oil and gas production that also occur at production sites enabled by unconventional methods. Impacts that are independent of well stimulation, such as long-term emissions of volatile hydrocarbon air pollutants, fugitive methane emissions, groundwater contamination from produced water spills or casing failures, etc., will occur as part of all oil and gas development and can occur whether or not a well was completed using stimulation technology (Long et al., 2015b). Most of the direct impacts of unconventional oil and gas development can be attributed to chemical use during well stimulation (Long et al., 2015b).

In order to understand the direct impacts of unconventional oil

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and gas development, it is therefor necessary to understand and evaluate the types and amounts of chemicals used during well stimulation. Hydraulic fracturing practices and chemical-use varies by region of the USA and hydraulic fracturing is most frequently used for production of natural-gas from shale and similar source rock formations (Long et al., 2015a; U.S. EPA, 2015a; California Council on Science and Technology (CCST), 2014). Previous studies have evaluated and characterized chemical additives in fracturing fluids based on use nationally (Stringfellow et al., 2014; Elsner and Hoelzer, 2016; U.S. EPA, 2015a; SCAQMD, 2013; Long et al., 2015c; U.S. Environmental Protection Agency (U.S. EPA), 2013a) and these analyses of chemical use are therefore weighted toward chemical use for natural gas development.

In this review we examine the use of chemicals for hydraulic fracturing in the context of oil development. In California, hydraulic fracturing is exclusively used for oil production and it is estimated that approximately 20% of oil production in California is dependent on unconventional oil recovery, predominately acidizing and hydraulic fracturing in diatomite formations (Long et al., 2015a). California is the third largest producer of oil in the USA and hydraulic fracturing has occurred in both onshore and offshore oil fields (Long et al., 2015a; Houseworth and Stringfellow, 2015; US EIA, 2014). We evaluate chemical additives used for hydraulic fracturing and acidizing of oil reservoirs in California, with the objective of obtaining a better understanding of the types and amounts of chemicals used in oil production. In an effort to demystify the often confusing use of chemicals in well stimulation, we evaluate mass and frequency of use by both functionality and chemical classification. Our goal is to understand the significance of individual chemicals and chemical mixtures, the amounts at which they are being used, the purpose of their use, the class of chemical to which they belong, and other distinguishing characteristics. We use a rational approach, identifying the chemicals used most frequently and in the highest mass and cross reference these materials with toxicity analysis, to create a priority chemical list for further investigation and regulation.

2. Materials and methods

Data on chemicals, concentrations, and water volumes used in hydraulic fracturing were obtained from the FracFocus database (versions 1 and 2) for hydraulic fracturing operations conducted in California between January 30, 2011 and May 19, 2014 (FracFocus, 2013a). The FracFocus database was started in 2011 and contains voluntarily disclosed data on hydraulic fracturing treatments. Entries in the FracFocus database were edited to standardize chemical names and to validate the assigned Chemical Abstracts Services Registry Number (CASRN). Masses of chemicals per treatment were only calculated for complete records where both volume and concentrations data were provided and where the sum of reported mass percentages was between 95% and 105%.

Data on acidizing treatments, including matrix acidizing, were compiled from data collected by the South Coast Air Quality Management District (SCAQMD) for treatments conducted between June 2013 and June 2014 (SCAQMD, 2013). The SCAQMD includes the counties of San Bernardino, Orange, Riverside, and Los Angeles, including the City of Los Angeles. The SCAQMD does not include the San Joaquin Valley nor Kern County, where the majority of hydraulic fracturing takes place in California (Long et al., 2015a, 2015c). Operators and chemical suppliers working in the SCAQMD must disclose chemical and materials used for drilling, hydraulic fracturing, and acidizing in that district. The SCAQMD data started being collected in 2013 (SCAQMD, 2013).

Toxicity data were collected from chemical databases and references (U.S. Environmental Protection Agency (U.S. EPA), 2013a; Service, 2014; National Library of Medicine, 2013a; U.S. Environmental Protection Agency (U.S. EPA), 2014; European Chemicals Agency (ECHA), 2000; Lewis and Sax, 1996; U.S. Environmental Protection Agency (U.S. EPA), 2013b; National Library of Medicine, 2013b; Organization for Economic Cooperation and Development (OECD), 2007). Rat and mouse oral toxicity data were collected to represent mammalian toxicity. Environmental toxicity data were collected for water flea (*Daphnia magna*), fathead minnow (*Pimephales promelas*), and trout (Rainbow Trout, *Oncorhynchus mykiss* and Brook Trout, *Salvelinus fontinalis*). Data on median lethal dose (LD50) were compiled for mammals, while data on median lethal concentration (LC50) and median effective concentration (EC50) were compiled for aquatic species. Toxicity ratings for chemical additives were assigned using the United Nations Globally Harmonized System (GHS) of Classification and Labelling of Chemicals (United Nations, 2013). In the GHS system, lower numbers indicate higher toxicity, with a designation of "1" indicating the most toxic category. Chemicals for which the LD50 or EC50 exceeded the least toxic GHS category were classified as non-toxic.

3. Results and discussion

3.1. Chemicals used in hydraulic fracturing and matrix acidizing

Using data collected from FracFocus, we identified 1623 individual hydraulic fracturing operations conducted in California between January 30, 2011 and May 19, 2014. During this time period, there were an estimated 5000 to 7000 hydraulic fracturing treatments in California (Long et al., 2015a), suggesting that the voluntary dataset represents one-third to one-fifth of the total hydraulic fracturing treatments. From these 1623 treatments, we identified 338 unique additives based on name and CASRN combinations, of which 228 were reported with a CASRN and 110 were identified by chemical or common name only or had proprietary designations. The additives included chemicals, mineral proppants and carriers, and base fluids consisting of water, salt, and brine solutions. There were 326 unique additive names in the database. Some additives—e.g. hemicellulose enzyme—had multiple CASRN and/or were identified by CASRN in some entries and proprietary designations in other entries. Of the 45,058 entries for additives, 3071 entries did not report CASRN under various claims for proprietary information (e.g. trade secret, confidential business information).

Matrix acidizing treatments applied in California involve the use of strong acids, including hydrochloric and hydrofluoric acid (Long et al., 2015a; Abdullah et al., 2016). Information concerning chemical use during matrix acidizing is not generally available, but the SCAQMD requires operators to report chemical use during acid treatments, which includes both routine well maintenance and matrix acidizing treatments. We analyzed the use of chemicals in conjunction with all acid treatments in the SCAQMD reporting area, which is limited to parts of Southern California (see methods). In the SCAQMD, we only examined chemicals reported with a valid CASRN. There were 78 chemicals identified as being used during acid treatments, of which 24 were not reported to the FracFocus disclosure registry (Table S1). Although this data is restricted to one region, the SCAQMD data was, to our knowledge, the only public source of high quality data on acid treatments available during this study.

The results of this analysis indicate that well over 300 chemicals have been used for hydraulic fracturing in California and that, based on reporting in only one region of California, an additional two dozen chemical additives are also used during matrix acidizing treatments (Table S1). Since common names were sometimes used for chemical additives on the disclosures (e.g., surfactant mixture,