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Hazard assessment of hydraulic fracturing chemicals using an indexing method

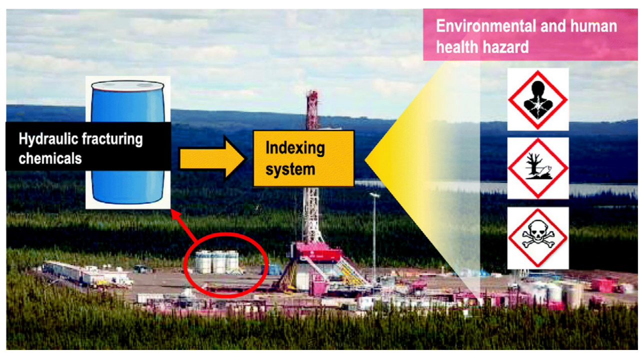
Guangji Hu, Tianyi Liu, James Hager, Kasun Hewage, Rehan Sadiq *

School of Engineering, The University of British Columbia, Okanagan Campus, Kelowna, BC V1V 1V7, Canada

HIGHLIGHTS

- Assessed hydraulic fracturing chemicals using an indexing method
- Identified iron control agents as the most critical additive category
- Identified hydraulic fracturing additives as medium-level hazards overall
- Identified friction reducers as the category of lowest data completeness
- Aquatic toxicity and carcinogenicity are the main hazards of ingredients.

GRAPHICAL ABSTRACT



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ABSTRACT

The rapid expansion of unconventional natural gas production has triggered considerable public concerns, particularly regarding environmental and human health (EHH) risks posed by various chemical additives used in hydraulic fracturing (HF) operations. There is a need to assess the potential EHH hazards of additives used in real-world HF operations. In this study, HF additive and fracturing fluid data was acquired, and EHH hazards were assessed using an indexing approach. The indexing system analyzed chemical toxicological data of different ingredients contained within additives and produced an aggregated EHH safety index for each additive, along with an indicator describing the completeness of the chemical toxicological data. The results show that commonly used additives are generally associated with medium-level EHH hazards. In each additive category, ingredients of high EHH concern were identified, and the high hazard designation was primarily attributed to ingredients' high aquatic toxicity and carcinogenic effects. Among all assessed additive categories, iron control agents were identified as the greatest EHH hazards. Lack of information, such as undisclosed ingredients and chemical toxicological data gaps, has resulted in different levels of assessment uncertainties. In particular, friction reducers show the highest data incompleteness with regards to EHH hazards. This study reveals the potential EHH hazards associated with chemicals used in current HF field operations and can provide decision makers with valuable information to facilitate sustainable and responsible unconventional gas production.

1. Introduction

Unconventional natural gas production has significantly expanded in North America, owing to combined use of horizontal drilling and hydraulic fracturing (HF) techniques. These technical advances have

* Corresponding author at: School of Engineering, The University of British Columbia, Okanagan, 3333 University Way, Kelowna, British Columbia V1V 1V7, Canada.
E-mail address: rehan.sadiq@ubc.ca (R. Sadiq).

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enabled exploitation of unconventional natural gas reservoirs, such as low-permeability organic-rich shale formations and "tight-gas" reservoirs, redrawing the domestic energy landscape in Canada (Rivard et al., 2014). In 2012, Canada was the third largest producer of natural gas in the world and exported $15.6 billion worth of natural gas. The unconventional gas industry was responsible for about 15% of total natural gas production. By 2025, Canadian natural gas production is projected to be at least 25% greater than current levels, and the increase will be primarily attributed to unconventional natural gas production (NEB, 2013).

In Canada, unconventional natural gas production has been distributed within several major shale plays, the most important plays include the Muskwa-Otter Park shale members of the Horn River Basin of Northern British Columbia (BC) and the adjacent Montney Basin, spanning the BC and Alberta border, as well as the Duvernay Formation in West-central Alberta (NRC, 2016). As a major natural gas producing province, BC is particularly well poised to benefit from the recent overhaul of the natural gas industry. As of 2014, over a thousand wells have been drilled for shale gas exploration or production in BC, and in most cases, completion processes have involved HF (FracFocus, 2014). The HF process involves the pumping of large volumes of fracturing fluid, consisting of a base fluid (primarily water), proppants (typically quartz sand), and various additives, under high pressure into a perforated wellbore to initiate and expand fractures within the adjacent geological formation (Vidic et al., 2013). The fractures increase the permeability of the formations, allowing for the previously trapped natural gas to flow through the formations into the wellbore (Ferrer and Thurman, 2015).

Despite the promising resource potentials and economic benefits, unconventional gas production has aroused considerable public concerns regarding environmental and human health (EHH) impacts caused by HF operations (Vengosh et al., 2014). The chemicals used in HF are of concern due to the potential of soil, groundwater, and surface water contamination (Boudet et al., 2014; Burton et al., 2016; Long, 2014; Vengosh et al., 2014). In HF, various additives are used in the fracturing fluids to meet different engineering requirements. The additives serve various functions, such as inhibiting the growth of microorganisms, facilitating the transportation of proppants into fractures, and preventing mineral scaling of the well (Stringfellow et al., 2014). An additive consists of several ingredients at different concentrations. The relationship between ingredients, additives, and fracturing fluids is outlined in Fig. 1. According to their functions, additives can be divided into several categories, including: gelling agents, friction reducers, crosslinkers, breakers, biocides, corrosion inhibitors, scale inhibitors, iron control chemicals, clay stabilizers, surfactants, and demulsifiers (Barati and Liang, 2014; Hurley et al., 2016; Stringfellow et al., 2014).

It has been reported that over 2500 additives, consisting of 750 different ingredients, have been used in HF operations in the United States (Soeder et al., 2014). A typical HF operation may use 3 to 12 additives based on the identified needs for the given well (Hurley et al., 2016). Some of these additives contain ingredients that are potential carcinogens, mutagens, reproductive toxicants, and substances with acute and long-term aquatic toxicities (Finkel and Hays, 2013; Kassotis et al., 2014; Rogers et al., 2015; Soeder et al., 2014; Stringfellow et al., 2014). Although there are various government regulations, industry codes-of-practice, and company standard operating procedures in place to prevent or minimize the likelihood of accidental releases of HF fluids, the risk of HF fluid contamination cannot be neglected. Any unintended release or disposal of the fluids could pose a health risk to the aquatic environment and the surrounding water users (Akob et al., 2016; Cozzarelli et al., 2017; Kassotis et al., 2016; Luek and Gonsior, 2017; Orem et al., 2017; Soeder et al., 2014). Additionally, since fracturing fluids usually contain a set of additives consisting of one or more ingredients, the composite hazard of additives is difficult to calculate, increasing the complexity and uncertainty in risk assessment.

The use of additives with minimized EHH effects is encouraged for the responsible and sustainable development of the unconventional gas industry (Gordalla et al., 2013; Hurley et al., 2016; Kargbo et al., 2010). Nevertheless, the process of selecting environmentally friendly additives can be difficult without knowing the respective EHH implications. Methods which can effectively assess the additive hazard and produce comparable results are therefore required to facilitate decision making. Various methods have been developed for evaluating potential EHH risks of chemicals used in the oil and gas industry (Hepburn, 2012; Hurley et al., 2016; Jordan et al., 2010; Verslycke et al., 2014), but limited results have been published reflecting the HF chemical hazards in a

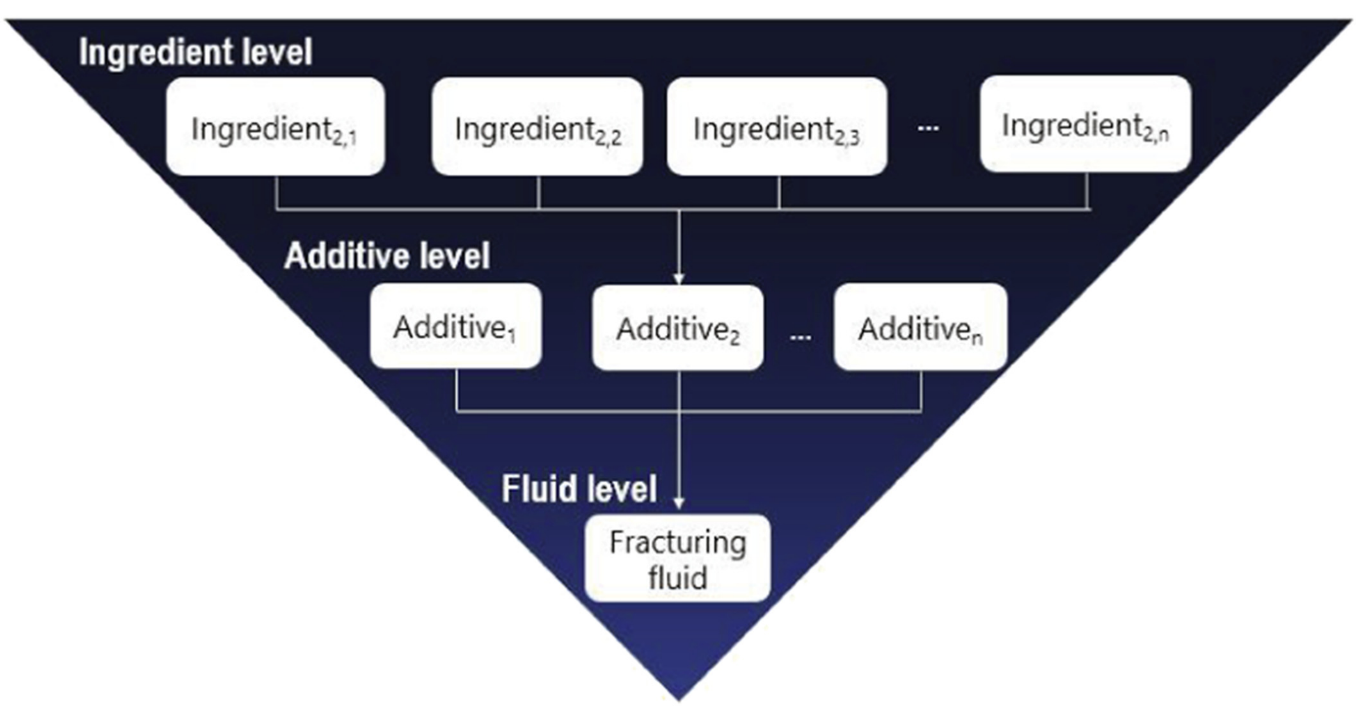

Fig. 1. Hydraulic fracturing chemical hierarchy.

real-world scenario (Ferrer and Thurman, 2015; Hurley et al., 2016; Maule et al., 2013; Stringfellow et al., 2014, 2017). A systematic assessment of chemical hazards in HF field operations is critical for diagnosing the potential risk of current chemical use status, and promoting improvements for minimizing chemical hazards in HF.

The objectives of this study were to identify chemicals commonly used in HF field operations in BC and evaluate their EHH hazard potentials at the ingredient, additive, and fluid levels. The results reflect the potential EHH hazards of HF chemicals used in real-world situations and provide a reference for mitigating EHH impacts posed by unconventional gas development.

2. Methodology

The assessment was carried out using the framework shown in Fig. 2. The additive data was acquired from a publicly accessible database, and the representative additives were selected for the assessment. The ingredients of the selected additives were identified and their toxicological data was searched. The toxicological data was processed using an indexing system. The ingredient hazard assessment results were then aggregated to generate a hazard assessment result for the respective additive.

2.1. Additive data acquisition

The data related to additives used in HF operations in BC from November 2011 to August 2014 was collected from the FracFocus Chemical Disclosure Registry database (FracFocus, 2014), which contains broad and general information regarding additives used in different wells throughout BC. The additives were grouped into several functional categories according to their engineered purposes. Within each category, the representative additives were selected for hazard assessment according to their use frequencies. Additives used <1% of total use of each additive category were not considered as a representative sample, and therefore were not included in the assessment. The use frequency of an additive was determined by counting the number of unique instances in which an additive's trade name, a specific well number, and operation date appeared in the database.

2.2. Hazard assessment method

Hydraulic fracturing chemical hazard was assessed at the ingredient, additive, and fracturing fluid levels using an indexing system. The indexing system was modified based on the Hydraulic Fracturing Fluid Greenness Assessment System (HyFFGAS) developed by Hurley et al. (2016). The modified system uses various authoritative chemical toxicity databases in addition to the Materials Safety Data Sheets (MSDSs) used by the HyFFGAS. Also, the modified system employs a data availability index (DAI) as a measurement of data completeness. The indexing system can aggregate non-commensurate multiparameter chemical toxicological data into a numeric value, allowing for the comparative index to be calculated for each ingredient, additive, or fracturing fluid. The resulting index values reflect the EHH safety of chemicals on a scale from 0 to 10, with 0 being the least safe and 10 being the most safe (Hurley et al., 2016). In the context of this study, the term “safe” is used to describe a situation where there is a low EHH hazard potential associated with an unintended release of a HF ingredient, additive, or fracturing fluid.

The potential hazard of HF chemicals was broadly categorized into two classes, namely environmental health hazard and human health hazard (Hurley et al., 2016). Each hazard class contains several hazard categories and each category contains two or more hazard criteria. The hazard categories (e.g., carcinogen, aquatic toxicity, and dermal toxicity) and criteria of each hazard category (e.g., Group 1 or 2 carcinogen) were defined on the basis of the Globally Harmonized System for Classification and Labeling of Chemicals (GHS), which is implemented by the United Nations to provide an international standard for describing chemical hazard (United Nations, 2013). The hazard categories and criteria were assigned numerical values, generating an indexing matrix for each hazard class to quantify the severity of a hazard (Appendix I).

The hazard assessment began at the ingredient level. The ingredients were first identified by their unique chemical abstracts service registration numbers (CASRN), and then the chemical toxicological data was

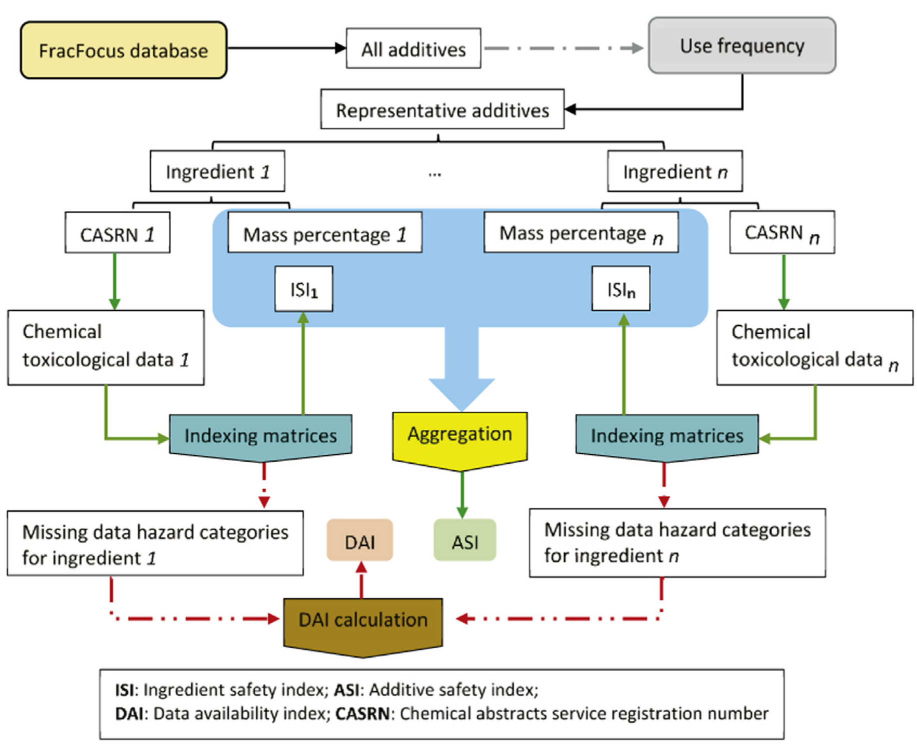

Fig. 2. Hazard assessment framework overview.

obtained from various chemical toxicity databases, such as: the European Chemical Agency (ECHA), Environment Canada and Climate Change (ECCC), TOXNET-Hazardous Substances Data Bank (TOXNET-HSDB), Organization for Economic Cooperation and Development Existing Chemical Database (OECD), and International Agency for Research on Cancer (IARC), National Toxicity Program (NTP), and relevant MSDSs (BASF, 2017; Dow, 2017; ECCC, 2017; ECHA, 2017; IARC, 2017; NTP, 2011; OECD, 2017; SA, 2017; Stepan, 2014, 2016; TOXNET, 2017). The chemical toxicological data of an ingredient was converted into numeric values by matching the data with the indexing matrices (Appendix I), producing an environmental health score and a human health score for the ingredient. The lack of CASRN and toxicological data for an ingredient will increase the uncertainty of assessment results. For the missing toxicological data in a hazard category, both the best (least hazardous) and worst (most hazardous) scenarios in the hazard category were considered (Hurley et al., 2016). Therefore, the missing toxicological data is treated as a range of scores, representing the most conservative (i.e., the highest possible hazard) and the most optimistic scenarios (i.e., the lowest possible hazard). The environmental health scores and human health scores, presented as a range due to missing toxicological data, were then aggregated using a mathematically weighted sum aggregation with equal mathematical weights of 0.5 to generate an ingredient safety index (ISI). The lowest environmental health score and human health score were aggregated to generate the minimum ISI for the ingredient, and the highest scores were aggregated to generate the maximum ISI. The ISI is on a scale ranging from 0 (the most hazardous and least safe) to 10 (the least hazardous and most safe). The same scale is maintained at the additive and fluid levels. An additive safety index (ASI) can be calculated by aggregating the ISIs of all ingredients within an additive. A weighted sum method was used for the aggregation, in which the normalized maximum mass percentage of an ingredient was used as a corresponding mathematical weight (*MW*) of the ingredient, as shown in Eq. (1):

$$\text{ASI} = \sum_{i=1}^{n} ISI_i \times MW_i \tag{1}$$

where ASI is the additive safety index, ISI_i is the ingredient safety index of ingredient *i*, and *MW* is the mathematical weight of ingredient *i*.

The fracturing fluid safety index (FSI) can be calculated by aggregating the ASIs of additives within the fracturing fluid using the same weighted sum method. The resulting FSI represents the aggregated hazard of all additives that make up the fluid. Due to the missing chemical toxicological data at the ingredient level, the ASIs/FSIs were also presented as a range defined by the minimum and maximum values, representing the lowest and highest possible EHH hazard for an additive/fracturing fluid, respectively. An average ASI can be calculated according to the minimum and maximum ASIs, representing an amalgamated EHH hazard assessment result. An overall ASI of each additive category was produced by aggregating the average ASIs of different additives weighted by their normalized use frequencies. As Table 1 shows, five EHH hazard levels were used to interpret the hazard implications of safety index values (i.e., ISI, ASI, and FSI) (Hurley et al., 2016).

To measure the data completeness of the ASI and FSI results, a data availability index (DAI) was calculated according to Eq. (2) (Intrinsik, 2013). The DAI reflects the extent to which chemical toxicological data exists for the various ingredients within an additive (Intrinsik, 2013). A high DAI signals that a substantial amount of chemical toxicological data is available to support the assessment result; whereas, a low DAI indicates less supporting data and greater uncertainty. Five levels of data completeness were also used to interpret DAI values (Table 2). The DAIs of different additives in the same functional category were also aggregated by their normalized use frequencies to generate an overall DAI for the additive category.

$$\text{DAI} = 100 - \frac{\text{Total number of data missing hazard categories} \times 100}{\text{Total number of ingredients} \times \text{total number of hazard categories}} \tag{2}$$

3. Results and discussion

3.1. Additive data

From November 2011 to August 2014, a total of 1245 different HF operations were carried out in BC. This number is based on the combinations of operation dates and the well numbers. These HF operations were conducted in a total of 974 different wells. According to the FracFocus database, a total of 574 different ingredients have been used in base fluids, proppants, and additives in BC. Of these, 530 ingredients are contained in 376 different additives. As a comparison, the US EPA has reported that 692 unique ingredients have been used in HF in the US from 2011 to 2013, and 598 of them were present in additives and fracturing fluids (EPA, 2015). In California, over 300 ingredients have been used in 1623 HF treatments between 2011 and 2014 (Stringfellow et al., 2017). A total of 105 representative additives were selected from 13 functional categories for the hazard assessment. These selected additives only account for 28% of the total additives recorded in the database; however, they account for >80% of the total use of each additive category. This high percentage indicates that the selected additives offer a good representation of the additives generally used in HF operations. The chemical use data also indicates that many additives were used infrequently in BC, similar to the HF chemical use situation reported in California (Stringfellow et al., 2017). The EHH hazards of selected additives were evaluated and interpreted based on their use frequencies, hazardous component ingredients, and the data completeness levels.

3.2. Hazard assessment results

Both the general hazard assessment results of different additive categories and the specific hazard profiles of individual additives within each category were reported. The general hazard assessment results draw the baseline performance of HF chemical use in BC regarding the EHH hazard implications, and the specific hazard profiles of individual additives provide more detailed information related to the component ingredients of greatest EHH hazard concern.

3.2.1. Additive category assessment results

The distributions of the ASIs, use frequencies, and DAIs of all selected additives are shown in Fig. 3. The ASIs were calculated under two scenarios due to missing ingredient information and chemical toxicological

Table 1
Hazard levels corresponding to safety index ranges.
Hurley et al. (2016).

Safety index	Hazard level
10	No hazard
<10 but ≥8	Low
<8 but ≥5	Medium
<5 but ≥3	High
<3	Severe

Table 2
Data completeness levels corresponding to data availability index (DAI) ranges.
Intrinsik (2013).

DAI	Data completeness
≥75	High
<75 but ≥50	Medium
<50 but ≥25	Low
<25	Very low

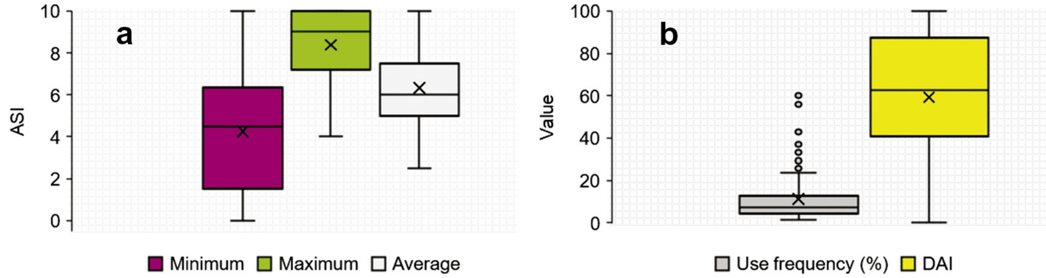

Fig. 3. Distribution of (a) additive safety indices (ASIs) and (b) use frequency and data availability indices (DAIs) of all selected additives.

data. The minimum ASI represents the most conservative scenario, reflective of the highest possible EHH hazard of the additives, while the maximum ASI represents the lowest possible EHH hazard. As shown in Fig. 3a, the distribution of the minimum ASIs shows that half of the additives are associated with high ($3 \le ASI < 5$) to severe ($ASI < 3$) EHH hazard. The median value (i.e., 4.5) of the minimum ASIs is lower than 5, reflecting a high hazard level. Under the most optimistic scenario, most of the maximum ASIs fall within low ($8 \le ASI < 10$) EHH hazard level. However, even under the most optimistic scenario, the bottom quartile of the maximum ASIs of some additives fall within the range from 4 to 7.2, and thus they are associated with medium ($5 \le ASI < 8$) to high-level EHH hazards. The interquartile range (i.e., 5 to 7.5) and median value (i.e., 6) of the average ASIs show that the additives typically have a medium-level EHH hazard. The distribution of ASIs suggests that there are opportunities for EHH hazard mitigation related to additive use in HF operations in BC.

As Fig. 3b shows, most of the additives have been used <15% of the total usage within each additive category. A few additives, shown as the outliers and those between the third quartile and the maximum value, have been predominantly used within their additive category. The general narrow distributions of use frequency suggest that most of the additives, except the outlier additives, have similar importance with respect to their use status. Additionally, the distribution of DAIs shows that the hazard assessment results are typically associated with medium ($50 \le DAI < 75$) to high ($75 \le DAI < 100$) level data completeness. Therefore, the hazard assessment results can provide relatively credible information for establishing a chemical hazard baseline in HF operations in BC.

The distributions of ASIs of different additive categories are shown in Fig. 4. Under the most optimistic scenario (Fig. 4a), nine additive categories out of thirteen typically show a low EHH hazard potential. However, the median values of the maximum ASIs of activators, biocides,

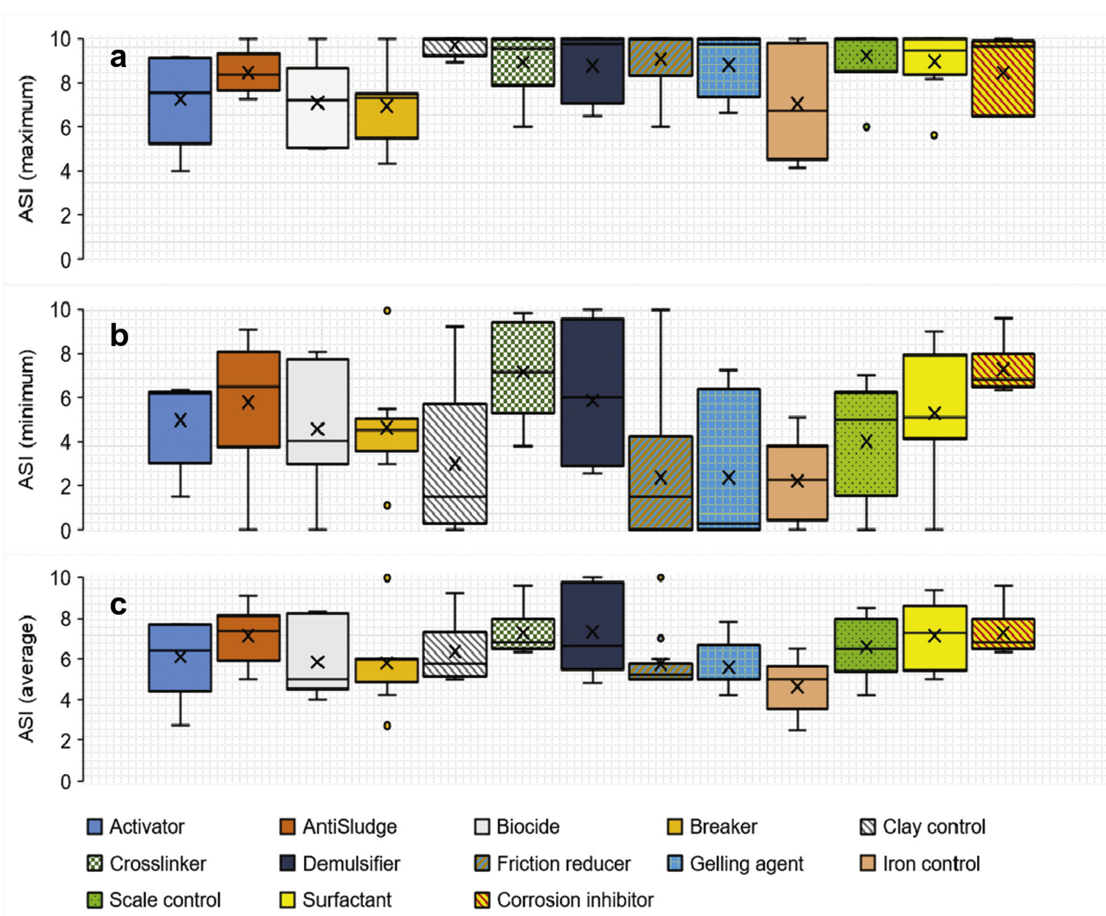

Fig. 4. Comparison of distributions of the (a) maximum, (b) minimum, and (c) average additive safety indices (ASIs) of different additive categories.

breakers, and iron control agents suggest that these additive categories still have a medium-level EHH hazard. Under the most conservative scenario (Fig. 4b), the median values of the minimum ASIs of all additive categories are lower than the low-level hazard threshold value (i.e., 8). Particularly, biocides, clay control agents, friction reducers, gelling agents, and iron control agents are associated with severe EHH hazards under the most conservative scenario. Due to the conservative nature of hazard assessment, the identified additive categories with severe EHH hazards require special attention during the selection of additives for producing fracturing fluids. Additive categories such as crosslinkers and corrosion inhibitors show a relatively lower EHH hazard as compared to other categories.

As shown in Fig. 4c, the average ASIs represent amalgamated EHH hazards of the different additive categories. All additive categories, except iron control agents, have median values of ASIs reflective of medium-level EHH hazards. Half of the iron control agents are associated with high and even severe EHH hazard, indicating that iron control agents are a critical additive category with respect to EHH hazard potential. By quantifying the EHH hazard of different additive categories, HF practitioners can identify the categories which should be most scrutinized to produce fracturing fluids with higher EHH safety. Also, chemical suppliers can allocate more resources to the identified high-hazard additive categories to change the additive formula to promote more effective EHH hazard mitigation.

The distribution of DAIs and use frequencies of different additive categories are compared in Fig. 5. As shown in Fig. 5a, the DAIs of activators, anti-sludge agents, biocides, and breakers generally fall within the range of the high data completeness level. In comparison, the hazard assessment results of clay control agents, friction reducers, gelling agents, and scale control agents suffer from low data completeness, indicating that more ingredient information should be disclosed and chemical toxicological data gaps should be filled for these additive categories to increase the confidence of the assessment results. The hazard assessment results of the remaining additive categories generally have a medium-level data completeness, revealing that opportunities exist to increase the transparency of chemical use in HF operations.

As shown in Fig. 5b, the individual additives within most of the additive categories have been used <15% of the total use. The relatively low use frequencies of additives suggest that the majority of additives have similar chances to be used in HF operations. Nevertheless, there are a few individual activators, anti-sludge agents, crosslinkers, and scale control agents that have been used more frequently compared to other additives with similar downhole functions. Particularly, outliers were found in breakers, demulsifiers, friction reducers, iron control agents, and corrosion inhibitors. The outliers represent the additives which have been predominantly used as compared to their respective alternatives, highlighting additives which require greater attention. The EHH hazard nature and the availability of chemical toxicological data of the ingredients contained in the outlier additives can greatly affect the EHH hazard and DAI performance of the related additive categories.

To investigate the influence of individual additives on the EHH hazard assessment results and the associated data completeness levels of their respective categories, the overall ASI and DAI were calculated for each additive category by aggregating the ASIs and DAIs of individual additives according to their use frequencies, respectively. The overall ASIs and DAIs of 13 additive categories, along with their functions, are summarized in Table 3. The additive categories are generally associated with medium-level EHH hazards, with overall ASIs ranging from 5.3 to 7.3 with different data completeness levels. Iron control agents have the lowest overall ASI of 4.7, making it the only category that belongs to the high EHH hazard designation. The reason for the high-level hazard for iron control agents is that this additive category has the largest number of carcinogens and mutagens. Other additive categories, such as the biocide and friction reducer categories, also require attention due to the relatively low overall ASIs and high use frequencies. Biocide is the category associated with the highest number of Categories 1 and 2 aquatic toxicants, due to their designed purpose, resulting in a relatively low overall ASI. This finding aligns with the fact that biocides are subject to more regulation than other chemicals used in HF due to their high toxicity (Camarillo et al., 2016). There is also a concern with biocides related to flowback and produced water treatment, since the designed toxic effect may interfere with biological processes (Kahrilas et al., 2015).

Among all additive categories, friction reducers, biocides, surfactants, demulsifiers, and iron control agents, have been used the most frequently. This high use frequency is attributed to the fact that roughly 60% of HF operations in BC involve slickwater treatment (Johnson and

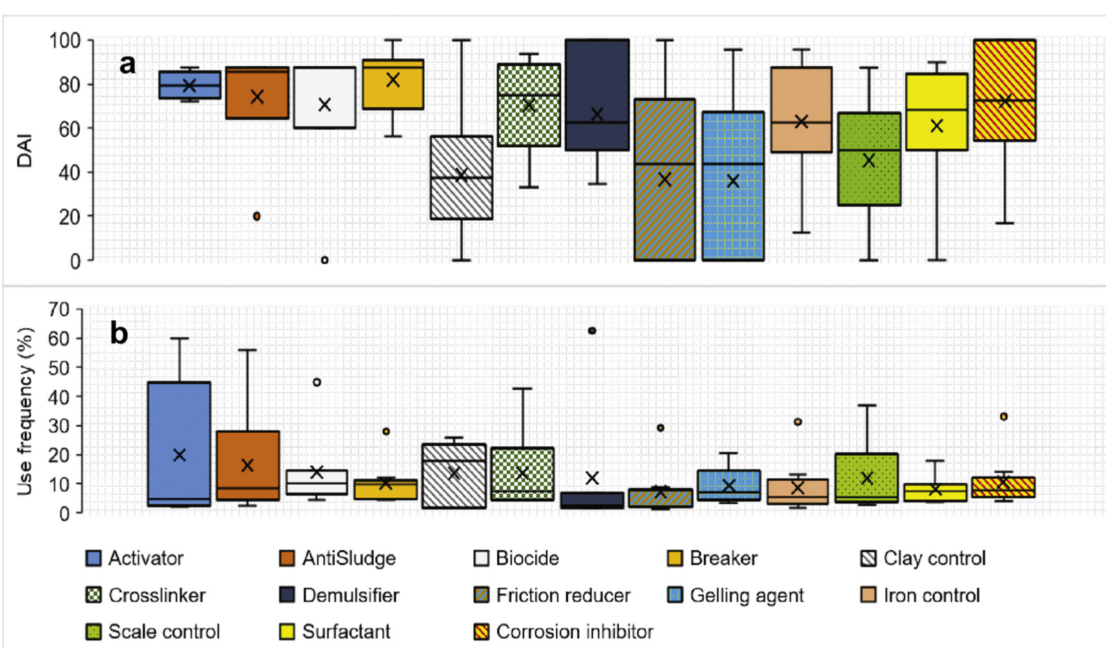

Fig. 5. Comparison of distributions of (a) data availability indices (DAIs) and (b) use frequencies of different additive categories.

Table 3
Summary of overall hazard assessment for each additive category.

Additive	Additive function	Overall ASI	Hazard level	Overall DAI	Data completeness	Uses (times)
Activator	Soften polymer coating (e.g., resin) of proppant, facilitating the bonding of proppants (Zoveidavianpoor and Gharibi, 2015)	7.0	Medium	82.0	High	83
Gelling agent	Increase fracturing fluid viscosity for improved proppant suspension and transport (Hurley et al., 2016)	5.3	Medium	33.9	Low	227
Crosslinker	Bind the gelling agents to increase fracturing fluid viscosity and elasticity (Esmaeilirad et al., 2016)	7.7	Medium	56.8	Medium	140
Breaker	Break the crosslinked gelling agents and reduce the viscosity of fluids to facilitate the flowback of fluids (Harris et al., 1997)	5.8	Medium	83.0	High	379
Anti-sludge agents	Prevent the formation of acid sludge generated from the acidification for well case cleaning (Stringfellow et al., 2014)	6.3	Medium	48.7	Low	87
Biocide	Reduce microbial populations to mitigate the risk of reservoir souring and microbially-induced corrosion (Kahrilas et al., 2015)	5.3	Medium	81.7	High	538
Clay stabilizer	Reduce clay swelling and prevent well clogging (Berry et al., 2008)	5.7	Medium	25.3	Low	258
Corrosion inhibitor	Form a physically adsorbed film at the metal/metal-oxide surface of the well system to prevent corrosion by acids, salts, and corrosive gas (Rostami and Nasr-El-Din, 2009)	7.2	Medium	68.5	Medium	254
Scale inhibitor	Reduce the likelihood of mineral scale formation and deposition (Crabtree et al., 1999)	7.0	Medium	54.5	Medium	265
Friction reducer	Reduce the surface tension between the geologic formation and fracturing fluid to increase flow rates (SPE, 2016)	5.3	Medium	22.4	Very low	1417
Iron control agent	Prevent precipitation of metal oxides, such as iron (III) oxide, which can block fractures (Stringfellow et al., 2014)	4.7	High	66.7	Medium	432
Surfactant	Decrease fluid surface tension, promoting fracturing fluid injection (Hurley et al., 2016; Wang et al., 2012)	7.3	Medium	62.3	Medium	531
Demulsifier	Break the emulsions stabilized by the surfactants, promoting fracturing fluid recovery (Flink, 2013)	5.6	Medium	46.9	Low	487

Note: ASI = additive safety index; DAI = data availability index.

Johnson, 2012), and these additives are the essential components of slickwater fracturing fluid to ensure high fluid efficiency and high pump rates (SPE, 2016). Moreover, the overall DAIs of different additive categories show low to medium-level data completeness due to missing data, specifically because of undisclosed ingredient information and chemical toxicological data gaps of high use frequencies additives. This finding is consistent with the results from a HF chemical investigation in California during the same period (Stringfellow et al., 2014, 2017). To understand the main EHH hazard concerns of each additive category, the individual additives within each category and their component ingredients are investigated.

3.2.2. Additive hazard profiles

The individual additives in this study are presented in non-implicative codes due to the proprietary nature of additive suppliers. The codes were assigned to individual additives based on their use frequencies within the respective categories. For example, the most frequently used gelling agent was coded as GA1. Similarly, GA2 represents the gelling agent that has the second-highest use frequency. The detailed ingredient compositions, use frequencies, and chemical toxicological data of the selected additives are included in Appendix II. The visualized comparison and hazard description of the selected additives are included in Appendix III. Hydraulic fracturing chemical suppliers and operators can find useful information from Appendix II and III to aid in identifying the individual additives and ingredients associated with high EHH hazard and chemical toxicological gaps, thus enabling the development of additive formulas with lower EHH hazard. The percentages of additives containing ingredients with different hazards are summarized in Table 4. Due to the high percentage (43%) of additives containing ingredients that are of high aquatic toxicity, aquatic toxicity could be considered as a primary EHH concern. This is an important finding, as many reported studies have mainly focused on the adverse human health effects (e.g., carcinogenicity, and reproductive and developmental toxicity) of HF chemicals (Chen and Carter, 2017; Elliott et al., 2017; Luek and Gonsior, 2017; Rogers et al., 2015). Biodegradability and carcinogenicity are also critical EHH hazard categories that raise the EHH hazard concerns of additives. In comparison, human oral toxicity is of less concern, due to the low percentage (2%) of additives containing ingredients of high oral toxicity. It is important to note that additives can contain ingredients of more than one hazard category. For example, demulsifier DE 1 contains two ingredients of concern (Table 5), namely ethoxylated alcohols and methyl isobutyl ketone, which are a Category 1 aquatic toxicant and Group 2B carcinogen, respectively. The mixed EHH hazard categories of ingredients could increase the complexity and uncertainty in hazard evaluation of additives. However, non-commensurate ingredient EHH hazard categories can be

Table 4
Percentages of additives containing ingredients of various hazards.

	Hazard category	Hazard criteria	Percentage (%) of additives
Environmental health hazards	Biodegradability	Not readily/rapidly or inherently biodegradable[a]	30
	Bioaccumulation potential	High[b]	14
	Aquatic toxicity	Categories 1 and 2 acute or chronic aquatic toxicity[c]	43
Human health hazards	Carcinogenicity	Group 1 or 2 carcinogen[d]	16
	Germ cell mutagenicity	Group 1 or 2 germ cell mutagen[d]	10
	Reproductive toxicity	Group 1 or 2 reproductive toxicity[d]	14
	Dermal toxicity	Category 1 or 2 dermal toxicity[e]	13
	Oral toxicity	Category 1 or 2 oral toxicity[f]	2

[a] Ingredients fail to pass the OECD Test 301 or Test 302.
[b] Ingredients with bioconcentration factor (BCF) ≥ 500 or log Kow ≥ 4.0.
[c] Ingredients with acute or chronic LC_{50}, EC_{50}, or IC_{50} values of 0 to 10 mg/L for fish, algae, or daphnia.
[d] Ingredients are known, presumed, or suspected carcinogens, mutagens, or reproductive toxicants.
[e] Ingredients with dermal toxicity of 0 to 200 mg/kg body weight.
[f] Ingredients with oral toxicity of 0 to 50 mg/kg body weight.

Table 5
Summary of additives and their component ingredients of significant hazard.

Additive category	Additive	Use frequency (%)	ASI (hazard level)	DAI (data completeness)	Ingredient(s) of concern	CASRN	ISI (hazard level)	EHH hazard(s)	References
Activator (AC)	AC3	4.8	3.0 (high)	75.0 (high)	Copper sulfate	7758-98-7	3.0 (high)	Category 1 aquatic toxicity; not rapidly/inherently biodegradable	ECCC, 2017; ECHA, 2017
Anti-sludge agent (AS)	AS2	18.5	7.8 (medium)	87.5 (high)	Benzene, C10–16-alkyl derives	68648-87-3	4.5 (high)	Category 1 aquatic toxicity; not rapidly biodegradable; high bio-accumulation potential	ECCC, 2017; ECHA, 2017
Biocide (BD)	BD6	6.5	8.3 (low)	60.0 (medium)	Dibromoacetonitrile	3252-43-5	1.3 (severe)	Group 2B carcinogen; Category 1 aquatic toxicity	ECHA, 2017; IARC, 2017
	BD3	10.7	6.3 (medium)	87.5 (high)	Bronopol	52-51-7	4.0 (high)	Category 1 aquatic toxicity; not rapidly biodegradable	ECHA, 2017; SA, 2017
Breaker (BR)	BR6	6.9	3.3 (high)	62.5 (medium)	Distillates (petroleum), straight-run middle	64741-44-2	2.5 (severe)	Category 1 aquatic toxicity; Group 2 reproductive toxicity; high bioaccumulation potential	ECCC, 2017; ECHA, 2017
Corrosion inhibitor (CI)	CI3	9.8	6.5 (medium)	100 (high)	Formaldehyde	50-00-0	5.0 (medium)	Group 1B carcinogen; Group 2 Mutagen	ECHA, 2017; IARC, 2017
Crosslinker (CL)	CL6	4.5	5.8 (medium)	87.5 (high)	Borate salt	1319-33-1	5.8 (medium)	Group 1 Reproductive toxicity; not rapidly/inherently biodegradable	ECHA, 2017
Clay stabilizer (CS)	CS7	1.7	5.9 (medium)	56.3 (medium)	Cocamido propyl betaine	61789-40-0	6.0 (medium)	Category 1 aquatic toxicity	ECHA, 2017
Demulsifier (DE)	DE1	33.2	4.8 (high)	34.4 (low)	Ethoxylated alcohols	78330-19-5	4.3 (high)	Category 1 aquatic toxicity	ECHA, 2017
					Methyl isobutyl ketone	108-10-1	5.8 (medium)	Group 2B carcinogen	IARC, 2017
Friction reducer (FR)	FR2	8.8	5.4 (medium)	50.0 (medium)	Distillates (petroleum), hydrotreated light	64742-47-8	6 (medium)	Category 2 aquatic toxicity; high bioaccumulation potential; not rapidly biodegradable	ECCC, 2017; Comet, 2015; SA, 2017
Gelling agent (GA)	GA7	4.4	7.0 (medium)	65.6 (medium)	Trimethyloctadecyl ammonium chloride	112-03-8	5.5 (medium)	Category 1 aquatic toxicity; not rapidly biodegradable	ECHA, 2017; Stepan, 2014
Iron control agents (IC)	IC1	31.3	5.3 (medium)	100 (high)	2-Mercaptoethanol	60-24-2	4.0 (high)	Category 1 aquatic toxicity; not rapidly biodegradable	ECHA, 2017; SA, 2017
	IC3	10.9	3.0 (high)	50.0 (medium)	Trisodium nitrilotriacetate monohydrate	18662-53-8	3.0 (high)	Group 2B carcinogen; Group 2 mutagen	ECHA, 2017; SA, 2017
Surfactant (SR)	SR8	3.8	5.1 (medium)	75.0 (high)	Coconut oil diethanolamine	68603-42-9	2.0 (severe)	Group 2B carcinogen; Group 2 reproductive toxicity; Category 2 aquatic toxicity; High bioaccumulation potential	ECHA, 2017; IARC, 2017; Stepan, 2016; BASF, 2017

Note: ASI = additive safety index; DAI = data availability index; CASRN = chemical abstract service registration number; ISI = ingredient safety index; EHH = environmental and human health.

converted into numerical scores and then aggregated to a final index for informed additive selection decision making.

Additives containing ingredients of significant hazard concern within each additive category are summarized in Table 5. The ingredients are identified of significant concern due to their hazardous properties (e.g., Category 1 aquatic toxicity, high bioaccumulation potential, and confirmed or suspected carcinogenicity, mutagenicity, and reproductive toxicity). Many of the ingredients are associated with high to severe EHH hazard levels according to the ISIs. Particularly, high aquatic toxicity and carcinogenicity are the primary EHH hazard concerns for these ingredients. Some of the ingredients, such as dibromoacetonitrile in BD6, distillates (petroleum) straight-run middle in BR6, and coconut oil diethanolamine in SR8, were identified with both extremely high aquatic toxicity and adverse human health effects, resulting in a severe EHH hazard level. Additionally, the ingredients of concern are primarily organic compounds. It has been reported that organic compounds have been used more frequently than inorganic substances in HF fluids (Chen and Carter, 2017), and thus it is reasonable to find more organic compounds of high EHH hazard. However, the inorganic ingredients also require attention since they might cause chronic adverse effects on environmental health due to their inherent persistent nature. From a hazard mitigation perspective, the additives containing ingredients of significant EHH hazard should be avoided in HF operations. More critically, additives such as AS2, DE1, FR2, and IC1 should be given priority in hazard mitigation, not only because they contain ingredients of high EHH hazard but also because they are the most commonly used additives within their respective additive categories.

The EHH hazard of additives was determined by the hazard of their component ingredients. As shown in Fig. 6, both the mean (5.7) and median (5.0) values of the average ISIs indicate a medium-level EHH hazard for the ingredients. The medium-level hazard was primarily due to relatively low environmental health score. The lowest value, lower quartile, and mean value of environmental health scores are lower

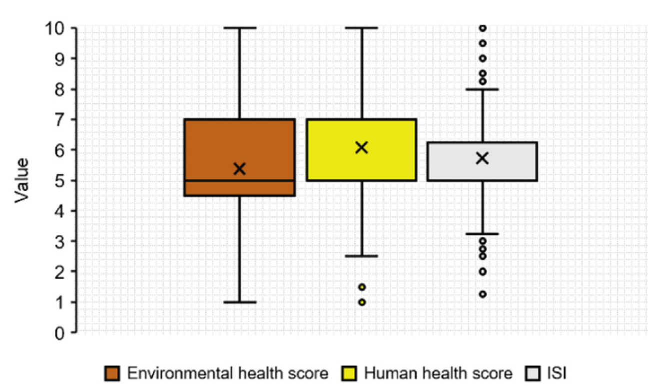

Fig. 6. Comparison of average environmental health scores, human health scores, and ingredient safety indices (ISIs) of different ingredients.

than the respective values of human health scores of the assessed ingredients. The relatively lower environmental health scores, combined with the finding which shows a large percentage of additives containing ingredients of environmental health hazard (Table 4), indicate that environmental health hazards are more critical than human health hazards for ingredients used in HF operations.

3.2.3. Fracturing fluids

Five fracturing fluids were randomly selected from the FracFocus database, and their FSIs were assessed. As Fig. 7 shows, fracturing fluids #28661 and #27551 have FSIs ranging from 4.2 to 9.0, with a medium-level of data completeness. The remaining three fluids show FSIs ranging from 3.3 to 9.3 with a relatively low level of data completeness. Due to the missing data, the EHH hazards of fracturing fluids are distributed from low to high. Among the five fracturing fluids, four of them contain ingredients with Category 1 aquatic toxicity, and four of them contain identified/suspected human carcinogens. Also, all five fracturing fluids contain non-inherently biodegradable ingredients. The average FSI lies between 6.3 and 7.5, showing that the fracturing fluids are associated with a medium-level EHH hazard. This result is consistent with the results from ingredient and additive assessments, which shows that the EHH hazard at the ingredient level can be successfully aggregated to the fracturing fluid level using the indexing system. Since ingredients are the fundamental elements of additives and fracturing fluids, reducing the use of ingredients of high EHH hazard could be an effective way to mitigate potential impacts posed by additives and fracturing fluids.

4. Conclusion

The EHH hazards of commonly used HF additives in BC were systematically assessed using an indexing system. The assessment results show that the commonly used additives are associated with medium to high levels of EHH hazard. Among the various additives, iron control agents show a high-level EHH hazard. Other commonly used additives, such as friction reducers, biocides, gelling agents, demulsifiers, clay control agents, and breakers, have an overall ASI < 6 (i.e., medium-level hazard), suggesting these additive categories are the primary areas for EHH hazard mitigation. Friction reducers show a very low level of data completeness during the assessment (i.e., an overall DAI < 25), and clay control agents, gelling agents, demulsifiers, anti-sludge agents also demonstrate a low level of data completeness (i.e., overall DAIs < 50), indicating more chemical information and toxicological data should be provided for these additive categories. More critically, a large percentage of additives containing ingredients of high aquatic toxicity and carcinogenic effects have been identified. Some of the most commonly used additives within their respective categories contain ingredients of combined high environmental health and human health hazards, resulting in high potential to pose serious threats to EHH if spills or contaminations occur. It was also found that environmental health hazards posed by HF additives are generally more critical than the human health hazards. The hazard assessment completed for five randomly selected fracturing fluids also indicates a medium-level EHH hazard based on the current use of fracturing fluids. Hydraulic fracturing operators should be encouraged to disclose more detailed chemical information to support a clearer understanding of the potential EHH hazards of chemical use in HF. Also, data gaps related to the toxicity of ingredients should be filled for more accurate and informed EHH hazard assessments. This study identifies the EHH hazards of representative additives used in Canadian unconventional gas production processes, and brings to light potential improvements that can contribute to promoting more sustainable and responsible unconventional energy production.

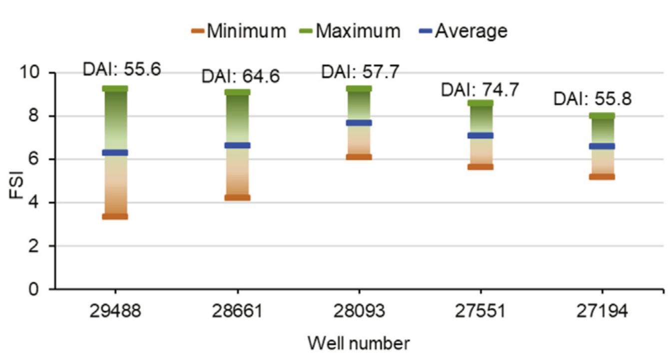

Fig. 7. Fracturing fluid safety indices (FSIs) and data availability indices (DAIs) of five randomly selected fracturing fluids.

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Appendix A. Supplementary data

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