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A decision analysis framework for estimating the potential hazards for drinking water resources of chemicals used in hydraulic fracturing fluids

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Abstract

Despite growing concerns over the potential for hydraulic fracturing to impact drinking water resources, there are limited data available to identify chemicals used in hydraulic fracturing fluids that may pose public health concerns. In an effort to explore these potential hazards, a multi-criteria decision analysis (MCDA) framework was employed to analyze and rank selected subsets of these chemicals by integrating data on toxicity, frequency of use, and physicochemical properties that describe transport in water. Data used in this analysis were obtained from publicly available databases compiled by the United States Environmental Protection Agency (EPA) as part of a larger study on the potential impacts of hydraulic fracturing on drinking water. Starting with nationwide hydraulic fracturing chemical usage data from EPA's analysis of the FracFocus Chemical Disclosure Registry 1.0, MCDAs were performed on chemicals that had either noncancer toxicity values ($n = 37$) or cancer-specific toxicity values ($n = 10$). The noncancer MCDA was then repeated for subsets of chemicals reported in three representative states (Texas, $n = 31$; Pennsylvania, $n = 18$; and North Dakota, $n = 20$). Within each MCDA, chemicals received scores based on relative toxicity, relative frequency of use, and physicochemical properties (mobility in water, volatility, persistence). Results show a relative ranking of these chemicals based on hazard potential, and provide preliminary insight into chemicals that may be more likely than others to impact drinking water resources. Comparison of nationwide versus state-specific analyses indicates regional differences in the chemicals that may be of more concern to drinking water resources, although many chemicals were commonly used and received similar overall hazard rankings. Several chemicals highlighted by these MCDAs have been reported in groundwater near areas of hydraulic fracturing activity. This approach is intended as a preliminary analysis, and represents one possible method for integrating data to explore potential public health impacts.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2016.08.167>.

Abstract

Keywords

Hydraulic fracturing; Hazard evaluation; Exposure assessment

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1. Introduction

Recent advances in hydraulic fracturing and directional drilling techniques are enabling a significant increase in domestic energy production in the United States (US) (EIA, 2014). Hydraulic fracturing is a stimulation technique used to increase production of oil and gas from geological formations. Large volumes of fluid are injected into deep underground wells, using pressure high enough to fracture the hydrocarbon formation. The resulting fractures are held open by proppants (e.g. quartz or other solid materials) that are added to the fracturing fluid, allowing gas or oil to flow to the production well.

Most hydraulic fracturing fluids are water-based, and are composed 98% of water and proppant. Hydraulic fracturing fluids also contain <2% chemical additives, which are added for specific purposes: e.g., to improve the transport of proppant, increase the formation of fractures, and perform other functions that help optimize performance of the well (Barati and Liang, 2014; Stringfellow et al., 2014; US EPA, 2015a). It has been estimated that a median of 14 chemicals is used per well, with the number, type, and volume of chemicals varying from well to well depending upon site- and company-specific factors (US EPA, 2015a). Because hydraulic fracturing often involves millions of gallons of fluid, there may be tens of thousands of gallons of chemicals stored onsite and used for hydraulic fracturing activities (US EPA, 2011a).

There are potential subsurface and surface pathways by which the chemicals in hydraulic fracturing fluids may be introduced into drinking water resources (Vengosh et al., 2014). For instance, data suggests that surface spills and leaks have resulted in the unintentional release of hydraulic fracturing chemicals to surface water, groundwater, and soil (DiGiulio and

Jackson, 2016; Drollette et al., 2015; Llewellyn et al., 2015; US EPA, 2015e). Additionally, injected fluid has the potential to enter water resources due to well blowouts, failures of well integrity, or intersection of the fracture network with groundwater (DiGiulio and Jackson, 2016; Rozell and Reaven, 2012; US EPA, 2015d). To date, there are significant limitations associated with the publicly available data on these potential impacts, making it difficult to ascertain the frequency and severity of such events (Brantley et al., 2014; Jackson et al., 2013; Vidic et al., 2013). This lack of data creates a challenge for the hazard evaluation of hydraulic fracturing chemicals.

In an effort to better understand the potential hazards that may be posed by hydraulic fracturing activity, the US Environmental Protection Agency (EPA) has conducted a long-term study of the potential impacts of hydraulic fracturing on drinking water (US EPA, 2011a; US EPA, 2012b). As part of this larger study, EPA compiled a list of 1076 chemicals that have reported use in hydraulic fracturing fluids, and used selected sources to compile available information on the toxicity, frequency of use, and physicochemical properties of these chemicals. For toxicity, EPA identified high-quality, peer-reviewed toxicity values that can be used as benchmarks for human health risk assessment, including chronic oral reference values (RfVs) for noncancer effects, and oral slope factors (OSFs) for cancer. RfVs estimate the amount of chemical that can be ingested daily by the human population that is likely to be without appreciable risk of health effects over a lifetime (US EPA, 2011b), while OSFs are the upper bound on increased cancer risk from lifetime oral exposure to a chemical (US EPA, 2011b). For frequency of use, EPA extracted data from the FracFocus Chemical Disclosure Registry 1.0 ("FracFocus 1.0"), which is an industry-supported database where oil and gas production well operators can disclose information about the ingredients used in hydraulic fracturing fluids at individual wells. For physicochemical properties, EPA used software programs such as EPA's Estimation Program Interface (EPI) Suite™ to generate measured and/or estimated values that describe chemical solvency and interaction with various environmental media. These data were compiled into publicly available databases, which can be downloaded from EPA's website (US EPA, 2015b; US EPA, 2015c).

In the absence of exposure assessment information, it is difficult to determine which hydraulic fracturing-related chemicals may be of greater concern than others to drinking water resources. By integrating the types of data that are available on EPA's databases, however, it may be possible to gain preliminary insight into the relative hazards associated with these chemicals. Multi-criteria decision analysis (MCDA) is one possible approach that can be used to facilitate data integration. MCDA is a well-established decision support tool, which is used to integrate multiple lines of evidence to develop an overall ranking or classification (Hristozov et al., 2014; Huang et al., 2011; Linkov et al., 2011; Mitchell et al., 2013). Using MCDA, a problem is approached by dividing it into smaller criteria that need to be evaluated; the criteria are each analyzed individually, and then combined to provide an integrated evaluation. This approach is structured yet flexible, and offers a transparent means of combining information to provide weight of evidence and insight into a complex problem. MCDA has gained increasing popularity as an environmental decision-making tool over recent years (Huang et al., 2011).

Here, in order to illustrate how data integration could be used to explore potential hazards, we develop and employ an MCDA framework to analyze and rank selected subsets of chemicals that have information available in the databases of EPA's hydraulic fracturing study. Using the framework, chemicals are assigned scores based on toxicity, frequency of use, and physicochemical properties that describe transport in water. These scores are then combined to develop an overall ranking based on hazard potential. To better evaluate the different types of toxicity data that are available for these chemicals, we performed separate MCDAs for noncancer effects and for cancer, as outlined below in Section 2. We first perform this analysis using nationwide chemical usage data from EPA's analysis of FracFocus 1.0. Next, to investigate the extent of regional differences and examine the applicability of the MCDA model at the regional scale, we repeated the noncancer analysis using subsets of chemicals that were reported by FracFocus 1.0 in Texas, Pennsylvania, and North Dakota. These representative states differ with regards to geography and geology, and are significant regions of hydraulic fracturing activity; disclosures from Texas, Pennsylvania, and North Dakota comprised approximately 48%, 6.5%, and 5.9% of all disclosures to FracFocus 1.0, respectively (US EPA, 2015a). Lastly, to provide environmental context for these analyses, we compare chemical rankings from the MCDA to the results of several studies that have reported these chemicals in water resources near areas of hydraulic fracturing activity.

Our objective is to demonstrate one possible framework for integrating available data on the chemicals used in hydraulic fracturing fluids, and to apply this framework in order to rank and compare within selected subsets of these chemicals. This analysis is not intended to define whether or not a chemical will present a human health hazard, or indicate that one chemical is safer than another. Rather, it serves as a model that can be used when exposure assessment data are not available, which places the toxicity of these chemicals into the context of factors that affect occurrence and environmental transport. By integrating these data, we can develop a qualitative metric to identify chemicals that may be more likely than others to impact drinking water resources. This should be considered a preliminary analysis, and should not be used in place of local data on chemical exposures.

2. Methods

The MCDA framework employed in this study is a three-part prioritization model, which incorporates data on toxicity, frequency of use, and physicochemical properties (Fig. 1). This framework is based on aspects of the method by Mitchell et al. (2013), who developed an MCDA approach for ranking chemical exposure potential by integrating data on physicochemical properties and life cycle analysis. The underlying philosophy of this approach is similar to chemical prioritization frameworks such as EPA's Design for the Environment Program Alternatives Assessment Criteria for Hazard Evaluation (US EPA, 2011), as well as the National Research Council's recent "A Framework to Guide Selection of Chemical Alternatives" document (National Research Council, 2014), which are tools designed to evaluate and differentiate among chemicals based on toxicity, physicochemical properties, industrial application, and other considerations.

In this study, we used an MCDA framework that we designed specifically to fit the scope of EPA's hydraulic fracturing study, using information that is publicly available. Chemicals used in hydraulic fracturing fluids were evaluated and assigned scores based on three criteria: a Toxicity Score, an Occurrence Score, and a Physicochemical Properties Score. The three scores were each standardized based on the highest and lowest respective score within the given subset of chemicals, and then summed to develop a Total Hazard Potential Score for each chemical. The Total Hazard Potential Scores reflect a relative ranking of each chemical within the given subset of chemicals. This approach— summing individual scores from multiple criteria to develop a total score—is a basic protocol that is often employed in MCDA methodologies (Huang et al., 2011), and is similar to the method used by Mitchell et al. (2013) for ranking of chemicals of concern.

To explore the different types of toxicity values that EPA identified for these chemicals, two different versions of the MCDA are performed: 1) a noncancer MCDA, in which the Toxicity Score is calculated using RfVs; and 2) a cancer MCDA, in which the Toxicity Score is calculated using OSFs. We did not attempt to combine noncancer and cancer analyses into a single MCDA, because very few chemicals had both noncancer and cancer values available from the databases of EPA's hydraulic fracturing study. Cancer MCDAs were not performed for the state-specific analyses (Texas, Pennsylvania, and North Dakota), as few chemicals had sufficient data available for inclusion.

In total, five iterations of the MCDA were performed as part of this study: 1) noncancer MCDA, using nationwide data; 2) cancer MCDA, using nationwide data; and 3–5) noncancer MCDAs, using state-specific data from Texas, Pennsylvania, and North Dakota, respectively. The methodology used to calculate these scores is described in detail in the following text, and an example of MCDA score calculation can be found in the Supporting Information.

2.1. Toxicity Score (noncancer MCDA)

For the noncancer MCDA, Toxicity Scores were calculated based upon chronic oral RfVs from US federal sources, which were compiled by EPA as part of the larger hydraulic fracturing study and are available on a draft database (<http://cfpub.epa.gov/ncea/hfstudy/recordisplay.cfm?deid=308341>) (US EPA, 2015c). We elected to focus our analysis on chronic oral RfVs because they are lower than acute or shorter duration toxicity values, and are therefore more health protective. Chronic toxicity values also account for the potential that chemical exposure may be continuous, in low concentration, and over a longer duration. We selected RfVs from US federal sources for this analysis, because these values tend to undergo more extensive peer review relative to other sources of toxicity values. EPA's draft database also contains RfVs for less-than-chronic durations (acute and intermediate) and for inhalation, as well as RfVs from state and intergovernmental sources, which were not considered here.

The following chronic oral RfVs were considered in this analysis:

- Chronic oral reference doses (RfDs) from EPA's Integrated Risk Information System (IRIS) database, EPA's Provisional Peer-reviewed Toxicity Value

(PPRTV) database, and EPA's Human Health Benchmarks for Pesticides (HHBP) database. A chronic oral RfD is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure for a chronic duration (up to a lifetime) to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime (US EPA, 2011b). This estimate is expressed in terms of mg/kg-day.

- Chronic oral minimal risk levels (MRLs) from the Agency for Toxic Substances and Disease Registry (ATSDR). An MRL is an estimate of daily human exposure to a hazardous substance at or below which the substance is unlikely to pose a measurable risk of harmful (adverse), noncancerous effects. Chronic oral MRLs are calculated based on oral exposure over a duration of 365 days or longer (ATSDR, 2009). This estimate is expressed in terms of mg/kg-day.

In total, chronic oral RfVs from US federal sources were available for 73 of the total 1076 chemicals with reported use in hydraulic fracturing fluids. Some chemicals had chronic oral RfVs available from more than one of these sources. For these chemicals, we applied the EPA Office of Solid Waste and Emergency Response (OSWER) Directive 9285.7-53 tiered hierarchy of toxicity values to determine which RfV should be used for input into the MCDA (US EPA, 2003). In this hierarchy, IRIS values are used before any other source, followed by PPRTVs, and then other available values. This hierarchy prioritizes toxicity values that are peer-reviewed, available to the public, and transparent about the methods used to develop the values. IRIS values have first priority because they normally represent EPA's scientific position regarding the toxicity of the chemicals based on data available at the time of the review (US EPA, 2003). For the purposes of this analysis, we made one modification to this approach: when considering pesticides, we used HHBP values first, followed by IRIS values, then PPRTVs, and then other values. HHBP values were prioritized because they represent the most up-to-date information on the toxicity of currently registered pesticides.

After a single RfV was determined for each chemical, Toxicity Scores for the noncancer MCDA were assigned based on a relative ranking. Within the suite of chemicals that were considered in the noncancer MCDA, RfVs were ranked based on quartiles, and each chemical was assigned a Toxicity Score of 1 to 4 (see Table 1). Chemicals in the lowest quartile received the highest Toxicity Score, as these chemicals have lower RfVs than other chemicals (i.e. may have lower thresholds for toxicity).

2.2. Toxicity Score (cancer MCDA)

For the cancer MCDA, Toxicity Scores were based upon OSFs from US federal sources, which were compiled by EPA and are available on the draft database (<http://cfpub.epa.gov/ncea/hfstudy/recordisplay.cfm?deid=308341>) (US EPA, 2015c). An OSF is defined as an upper-bound, approximating a 95% confidence limit, on the increased cancer risk from a lifetime oral exposure to an agent. This estimate, usually expressed in terms of the proportion (of a population) affected per mg/kg-day, is generally reserved for use in the low-dose region of the dose-response relationship, that is, for exposures corresponding to risks <1 in 100 (US EPA, 2011b). For this analysis, we considered OSFs from the IRIS, PPRTV,

and HHBP databases. EPA's draft database also contains OSFs from the California Environmental Protection Agency Toxicity Criteria Database, which were not considered here.

In total, OSFs from US federal sources were available for 15 of the total 1076 chemicals with reported use in hydraulic fracturing fluids. Some chemicals had OSFs available from more than one of these sources. As described in Section 2.1, we applied a tiered hierarchy to determine which OSF should be used in our analysis for these chemicals.

After a single OSF was determined for each chemical, Toxicity Scores for the cancer MCDA were assigned based on a relative ranking. Within the suite of chemicals that were considered in the cancer MCDA, OSFs were ranked based on quartiles, and each chemical was assigned a Toxicity Score of 1 to 4 (see Table 1). Chemicals in the highest quartile received the highest Toxicity Score, as these chemicals have higher OSFs than other chemicals (i.e. are associated with a higher increased risk of cancer per unit dose).

2.3. Occurrence score

For both the noncancer and cancer MCDAs, an Occurrence Score was calculated based on the frequency at which each chemical was reportedly used in hydraulic fracturing fluids. This was determined based on chemical disclosure data from EPA's analysis of FracFocus 1.0 (US EPA, 2015a). For the analysis of FracFocus 1.0, EPA accessed data from disclosures in 20 states that were reported to FracFocus 1.0 between January 1, 2011 and February 28, 2013. As used in this report, "disclosure" refers to all data submitted for a specific oil or gas production well for a specific fracture date. This analysis identified usage data for 692 chemicals reported in hydraulic fracturing fluids, which is a subset of the total 1076 chemicals identified in EPA's larger hydraulic fracturing study. The chemical usage data from this analysis is compiled in a database that is publicly available on EPA's website (<http://www.epa.gov/hfstudy/epa-project-database-developed-fracfoc-1-disclosures>) (US EPA, 2015b).

We queried EPA's FracFocus 1.0 project database to determine the frequency with which each chemical was reported in these disclosures at the national level (for the nationwide analysis) and state level (for the state-specific analyses), including both oil and gas wells and without regard to the concentration of chemical that was used. Based on the results of this query, we determined the total number of disclosures in which each chemical was reported, and used this value for input in the MCDA. The results of the query, and detailed information on how to perform the query, are provided as Supporting Information.

The query also identified summary statistics on the concentrations of each chemical used in hydraulic fracturing fluids, which were based on data provided by industry in FracFocus 1.0 disclosures: maximum concentration (percent by mass) of chemical within an additive, as well as the mass percentage of each chemical within the total hydraulic fracturing fluid. We elected not to use this data in the MCDA, however, as it may be associated with significant uncertainty. For instance, EPA found that the maximum chemical concentrations often added up to >100% of the additive by mass (US EPA, 2015a). No information is provided regarding how operators calculated percent by mass within the total hydraulic fracturing

fluid. Given this uncertainty, we chose to simply focus on the frequency of use, but provide this concentration data in the Supporting Information files.

After frequency of use was determined for each chemical, Occurrence Scores were assigned based on a relative ranking. Within the suite of chemicals that were considered in each MCDA, frequency of use was ranked based on quartiles, and each chemical was assigned an Occurrence Score of 1 to 4 (see Table 1). Chemicals reported in a greater number of FracFocus 1.0 disclosures received higher Occurrence Scores.

2.4. Physicochemical Properties Score

For both the noncancer and cancer MCDAs, a Physicochemical Properties Score was calculated based upon inherent physicochemical properties which affect the likelihood that a chemical will be transported in water. These values were generated using EPI Suite software, and are available on EPA's draft database (<http://cfpub.epa.gov/ncea/hfstudy/recordisplay.cfm?deid=308341>) (US EPA, 2015c). EPI Suite models have been validated for their performance in estimating these physicochemical properties, and have undergone peer review by EPA's independent Science Advisory Board (US EPA, 2012a). In total, these EPI Suite estimates were available for 453 of the total 1076 chemicals that have reported use in hydraulic fracturing fluids.

We considered physicochemical property values related to three subcriteria: mobility, volatility, and persistence in water. To classify these values and assign a score to each chemical, we compared numerical values from EPI Suite against threshold values (Table 1). These threshold values are based upon previously published values employed by existing exposure assessment models, including EPA's Design for the Environment Program Alternatives Assessment Criteria for Hazard Evaluation (US EPA, 2011), EPA's Pollution Prevention (P2) Framework (US EPA, 2012), and Mitchell et al. (2013). Three subcriteria scores (Mobility Score, Volatility Score, and Persistence Score) were determined for each chemical, and then summed to calculate a total Physicochemical Properties Score for each chemical. The calculation of these scores is described as follows.

2.4.1. Mobility Score—Chemical mobility in water was assessed based upon three physicochemical properties that describe chemical solvency in water: the octanol/water partition coefficient (K_{OW}), the soil adsorption coefficient (K_{OC}), and aqueous solubility. K_{OW} describes the partitioning of a chemical between water and a carbon-based media (octanol), while K_{OC} describes the partitioning of a chemical between water and organic carbon in soil. K_{OW} and K_{OC} are generally represented on a log10 scale. Aqueous solubility is the maximum amount of a chemical that will dissolve in water in the presence of pure chemical. Chemicals with low K_{OW} , low K_{OC} , or high aqueous solubility are more likely to solubilize and move with water, and therefore were ranked as having greater potential to affect drinking water resources.

For input into the MCDA, we used empirically measured values (provided in EPI Suite) whenever available. Otherwise, we used the following estimated values from EPI Suite: log K_{OW} estimated using the KOWWIN™ model, log K_{OC} estimated using the KOCWIN™ molecular connectivity index method, and aqueous solubility estimated using the

WSKOWWIN™ model. Using the thresholds designated in Table 1, each of these properties was assigned a score of 1–4. The highest of these three scores (K_{OW} , K_{OC} , or solubility) was designated as the Mobility Score for each chemical.

2.4.2. Volatility Score—Chemical volatility was assessed based on the Henry's law constant, which is the ratio of the concentration of a chemical in air to the concentration of that chemical in water at equilibrium. Chemicals with low Henry's law constants are less likely to leave water via volatilization, and were therefore ranked as having greater potential to affect drinking water resources.

For input into the MCDA, we used empirically measured values (provided in EPI Suite) whenever available. Otherwise, we used Henry's law constants that were estimated using the EPI Suite HENRYWIN™ model, which generates values using two different methods (group contribution and bond contribution); the lower of these two estimated values was used as input into the MCDA. Using the thresholds designated in Table 1, the Henry's law constant for each chemical was assigned a score of 1–4. This value was designated as the Volatility Score for each chemical.

2.4.3. Persistence Score—Chemical persistence was assessed based on estimated half-life in water, which describes how long a chemical will persist in water before it is degraded. Chemicals with longer half-lives are more persistent, and were therefore ranked as having greater potential to impact drinking water resources.

EPI Suite estimates biodegradation time using the BIOWIN™ 3 model, which provides an indication of a chemical's environmental biodegradation rate in relative terms (e.g. hours, days, weeks, etc.), assuming aerobic conditions. These semi-quantitative BIOWIN3 estimates are converted to numerical half-life values for use in EPI Suite's Level III Fugacity model. For input into the MCDA, we used the same estimated half-life in water that is used in the Level III Fugacity model. Using the thresholds designated in Table 1, the half-life in water of each chemical was assigned a score of 1–4. This value was designated as the Persistence Score for each chemical.

2.4.4. Total Physicochemical Properties Score—For each chemical, the Mobility Score, Volatility Score, and Persistence Score (each on a scale of 1 to 4) were summed to calculate a total Physicochemical Properties Score. Higher Physicochemical Properties Scores indicate chemicals that are more likely to be transported in water, with a maximum possible score of 12.

2.5. Standardizing scores within each dataset

Within each MCDA (noncancer or cancer), the three criteria scores (Toxicity, Occurrence, Physicochemical Properties) were each standardized to the dataset by scaling to the highest and lowest respective score within the given subset of chemicals. The following equation was used: $S_{x\_final} = (S_x - S_{min}) / (S_{max} - S_{min})$ in which S_x is the raw score for a particular chemical, S_{max} is the highest observed raw score within the set of chemicals, and S_{min} is the lowest observed raw score within the set of chemicals. S_{x_final} is the standardized score for the chemical. Each standardized score (Toxicity, Occurrence, Physicochemical Properties)

falls on a scale of 0 to 1, and represents a relative ranking within the given subset of chemicals.

2.6. Total Hazard Potential Score

Within each MCDA (noncancer or cancer), the standardized Toxicity Score, Occurrence Score, and Physicochemical Properties Score were summed to calculate a Total Hazard Potential Score for each chemical. The Total Hazard Potential Scores fall on a scale of 0 to 3, with higher scores indicating chemicals that may be more likely to affect drinking water resources.

A sensitivity analysis was conducted to evaluate the influence of each of the individual parameters (toxicity value, frequency of use, and each of the physicochemical properties) on the Total Hazard Potential Score. For the sensitivity analysis, we selected a single chemical from the nationwide Noncancer MCDA and examined how the score for that chemical changed when each of parameters was increased or decreased over a realistic range. Results demonstrate that each of the major criteria (toxicity, frequency of use, and physicochemical properties) has a relatively equal contribution to the Total Hazard Potential Score, which was expected because these criteria were weighted equally in the overall score calculation. It is also evident that each of the physicochemical parameters (K_{OW} , K_{OC} , aqueous solubility, Henry's law constant, and half-life in water) is capable of shifting the Physicochemical Properties Score from lower to higher, if the value for that parameter falls on the extreme end of the spectrum for the thresholds used in this analysis; however, high scores for all three subcriteria (Mobility Score, Volatility Score, and Persistence Score) are necessary in order to obtain the maximum possible Physicochemical Properties Score. Results of the sensitivity analysis are provided in the Supporting Information.

2.7. Selection of chemicals for MCDA

2.7.1. Nationwide analysis—To select chemicals for the nationwide analysis, we first identified all chemicals that were reported in EPA's FracFocus 1.0 project database, using the query described in the Supporting Information. This list of chemicals was then cross-referenced against the compilation of chemicals that have toxicity and physicochemical properties data available from the draft database of EPA's hydraulic fracturing study. The availability of these data is depicted in Venn diagrams in Fig. 2. By focusing on the chemicals that have data available for all three of these criteria (toxicity, occurrence, and physicochemical properties), we identified 37 chemical for inclusion in the nationwide noncancer MCDA, and 10 chemicals for inclusion in the nationwide cancer MCDA. Of the 10 chemicals considered in the cancer MCDA, eight of these chemicals were also considered in the noncancer MCDA. All of these chemicals, along with the toxicity, occurrence, and physicochemical property data that were used in the analysis, are listed in Table 2 (noncancer MCDA) and Table 3 (cancer MCDA).

2.7.2. State-specific analyses (Texas, Pennsylvania, and North Dakota)—For state-specific case studies, we identified subsets of chemicals that were used in Texas, Pennsylvania, and North Dakota from EPA's FracFocus 1.0 project database, using the query described in the Supporting Information. Of the chemicals identified from FracFocus

1,056 have reported use in Texas, 220 have reported use in Pennsylvania, and 283 have reported use in North Dakota. These chemicals were cross-referenced against the compilation of chemicals that have toxicity and physicochemical property data available from the draft database of EPA's hydraulic fracturing study. In total, we identified 31 chemicals used in Texas, 18 chemicals used in Pennsylvania, and 20 chemicals used in North Dakota that had sufficient data available for inclusion in state-specific noncancer MCDAs. These chemicals are a subset of those identified in Fig. 2, and are indicated in Table 2.

3. Results and discussion

3.1. Noncancer MCDA results (Nationwide analysis)

For the nationwide analysis, a graphic of the noncancer MCDA results is presented in Fig. 3. Of the 37 chemicals in hydraulic fracturing fluid that were considered in the noncancer MCDA, propargyl alcohol received the highest Total Hazard Potential Score. Propargyl alcohol was reported in 33% of disclosures in EPA's analysis of FracFocus 1.0, making it one of the most widely reported chemicals that was considered in this analysis, and it also had one of the lowest chronic oral RfVs, of 0.002 mg/kg-day. It is hydrophilic and has relatively low volatility, indicating that it is likely to be readily transported in water. Given these parameters, propargyl alcohol received the highest overall ranking based on hazard potential across all of the metrics that were considered in the nationwide noncancer MCDA.

The other chemicals that fell in the upper quartile in terms of nationwide frequency of use received lower Total Hazard Potential Scores relative to propargyl alcohol, due to having higher chronic oral RfVs and/or physicochemical properties that are less conducive to transport in water. 2-butoxyethanol and N,N-dimethylformamide—reported in 23% and 9% of disclosures, respectively—tied for the second highest score, as both have chronic oral RfVs of 0.1 mg/kg-day and are expected to be readily transported in water. Naphthalene, reported in 19% of disclosures, has an RfV of 0.02 mg/kg-day, and is expected to have somewhat lower transport in water relative to other chemicals because it is moderately hydrophobic and moderately volatile. Methanol (2 mg/kg-day), ethylene glycol (2 mg/kg-day), formic acid (0.9 mg/kg-day), and formaldehyde (0.2 mg/kg-day)—which were reported in 73%, 47%, 11%, and 7% of disclosures, respectively—are all expected to be highly mobile in water and have low volatility, but have higher chronic oral RfVs compared to many of the other chemicals in the assessment. Didecyldimethylammonium chloride (0.1 mg/kg-day), reported in 8% of disclosures, is expected to have reduced mobility in water due to its more hydrophobic properties.

In addition to propargyl alcohol, the other chemicals occurring in the lowest quartile of RfVs received moderate to high Total Hazard Potential Scores overall. Acrylamide (0.002 mg/kg-day) was reported in only 1% of disclosures, but has physicochemical properties that are very conducive to transport in water, and therefore tied for the second highest Total Hazard Potential Scores. Benzyl chloride (0.002 mg/kg-day) and epichlorohydrin (0.006 mg/kg-day) were reported in 6% and 1% of disclosures, respectively, but scored slightly lower than acrylamide with regards to their physicochemical properties. Other chemicals, including (E)-crotonaldehyde (0.001 mg/kg-day), benzene (0.004 mg/kg-day), dichloromethane (0.006

mg/kg-day), aniline (0.007 mg/kg-day), furfural (0.01 mg/kg-day), and 2-(thiocyanomethylthio)benzothiazole (0.01 mg/kg-day), received lower Total Hazard Potential Scores because they were reported less frequently (each in <0.1% of disclosures).

3.2. Cancer MCDA results (Nationwide analysis)

A graphic of the cancer MCDA results is presented in Fig. 4. Of the 10 chemicals in hydraulic fracturing fluid that were considered in the cancer MCDA, acrylamide received the highest Total Hazard Potential Score. Acrylamide has an OSF of 0.5 per mg/kg-day, which is one of the higher OSFs in this suite of chemicals, and has physicochemical properties that are highly conducive to transport in water. Acrylamide was reported in approximately 1% of disclosures in EPA's analysis of FracFocus 1.0, indicating that it is not used frequently in hydraulic fracturing fluid formulations; however, because none of the chemicals within this subset were reported with great frequency in FracFocus 1.0 (Table 3), this nevertheless places acrylamide in the top quartile in terms of frequency of use. Therefore, acrylamide received the highest overall ranking across all of the metrics that were considered in the cancer MCDA. Acrylamide also received one of the highest scores in the noncancer MCDA, as discussed in Section 3.1.

Within the cancer MCDA, the other two chemicals that fell in the upper quartile in terms of frequency of use were benzyl chloride and epichlorohydrin, which were reported in approximately 6% and 1% of disclosures. These two chemicals both received moderate Total Hazard Potential Scores. Benzyl chloride has an OSF of 0.17 per mg/kg-day, while epichlorohydrine has an OSF of 0.0099 per mg/kg-day. Both are expected to have reduced transport in water relative to other chemicals due to volatility.

All OSFs used in this analysis were from EPA's IRIS database (Table 3). Of the 10 chemicals considered in the cancer MCDA, only benzene is classified by IRIS as a known human carcinogen (US EPA, 1998). The other chemicals are classified by IRIS as likely or probable human carcinogens. These cancer weight of evidence characterizations are compiled on the draft database of EPA's hydraulic fracturing study (US EPA, 2015c). The most potent of the likely or probable carcinogens considered in this analysis are quinoline (OSF of 3 per mg/kg-day) and bis(2-chloroethyl) ether (OSF of 1.1 per mg/kg-day). Neither of these two chemicals is used frequently on a nationwide basis; quinoline was reported in approximately 0.02% of disclosures, while bis(2-chloroethyl)ether was reported in approximately 0.7% of disclosures. Both of these chemicals are expected to be readily transported in water.

3.3. State-specific noncancer MCDA results (Texas, Pennsylvania, and North Dakota)

Graphics of the state-specific noncancer MCDA results are presented in Fig. 5 (Texas), Fig. 6 (Pennsylvania), and Fig. 7 (North Dakota). By comparing these results to each other and to the nationwide noncancer analysis (Fig. 3), it is evident that there are some regional differences in the Total Hazard Potential Scores, although many chemicals were commonly used and received similar overall rankings.

Methanol, ethylene glycol, and 2-butoxyethanol were among the most frequently reported chemicals in all three state-specific analyses (Table 2), while other chemicals differed

distinctly between states. For instance, propargyl alcohol was frequently reported in Texas (39% of disclosures) and Pennsylvania (58% of disclosures), but not North Dakota (1% of disclosures). Likewise, naphthalene was reported frequently in Texas (14% of disclosures) and North Dakota (43% of disclosures), but not in Pennsylvania (1% of disclosures). The most toxic chemicals (occurring in the lowest quartile of chronic oral RfVs) common among all three states include propargyl alcohol, benzyl chloride, acrylamide, and naphthalene. Other chemicals in the lowest quartile of chronic oral RfVs in these states include epichlorohydrine (Texas and Pennsylvania), 1,4-dioxane (Texas and North Dakota), benzene, aniline, and 2-(2-Butoxyethoxy)ethanol (Texas).

Overall, in Texas, propargyl alcohol received the highest possible Total Hazard Potential Score, with 2-butoxyethanol, naphthalene, N,N-dimethylformamide, and acrylamide tied for the second highest score. In Pennsylvania, propargyl alcohol also received the highest possible Total Hazard Potential Score, with 2-butoxyethanol receiving second highest score. In North Dakota, 2-butoxyethanol received the highest Total Hazard Potential Score, with naphthalene receiving the second highest score.

3.4. Comparison with field data

The purpose of the MCDA framework is to provide preliminary insight into chemical hazard potential in the absence of known exposure information. To provide environmental context to these results, it is pragmatic to compare the MCDA rankings to existing chemical data from the field. Although water quality data is sparse for areas of hydraulic fracturing activity, we note that several chemicals highlighted in the MCDAs have been recently reported in groundwater and drinking water wells in such areas.

One example is 2-butoxyethanol, which was highlighted in the nationwide and state-specific MCDAs due to high frequency of use and expected transport in water. 2-butoxyethanol was detected by Llewellyn et al. (2015) along with a mixture of unresolved organic compounds in water wells near several hydraulically fractured wells in the Marcellus Shale in Pennsylvania. These authors reported that a similar chemical signature was detected in flowback and produced water samples from hydraulically fractured wells in the Marcellus Shale.² Following multiple lines of evidence, the authors concluded that the contaminants likely originated from a surface spill or leak related to hydraulic fracturing activity, and migrated into the aquifer via shallow to intermediate flow paths in the bedrock. 2-butoxyethanol was also among the chemicals reported in a recent study by DiGiulio and Jackson (2016) in groundwater monitoring wells adjacent to hydraulically fractured wells in the Pavillion Field in Wyoming. These authors noted that 2-butoxyethanol is extensively used in hydraulic fracturing fluids in the Pavillion Field. There is evidence that underground sources of drinking water in this area have been impacted by the injection of stimulation fluids, leaking unlined storage pits, and the apparent upward migration of solutes into groundwater.

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²“Flowback” refers to fluids predominantly containing hydraulic fracturing fluid that return from a well to the surface. “Produced water” is a general term used to refer to water that flows from an oil or gas well, which may contain hydraulic fracturing fluids in addition to natural waters from the formation. Flowback is a type of produced water.

In the Pavillion Field monitoring wells, DiGiulio and Jackson (2016) also reported other various alcohols that are frequently used in hydraulic fracturing fluids, including methanol, ethanol, and isopropyl alcohol. Methanol, ethanol, isopropyl alcohol, and propargyl alcohol were also reported in a study by Hildenbrand et al. (2015), who surveyed 550 groundwater wells overlying and adjacent to the Barnett shale in Texas. Hildenbrand et al. were unable to determine the source of these chemicals, but reported that detections coincided with areas of intensive hydraulic fracturing activity. In our study, propargyl alcohol and methanol were highlighted in the nationwide and state-specific noncancer MCDAs as having high frequency of use and expected transport in water, with propargyl alcohol having a lower RfV (i.e., more toxic) relative to other chemicals. Ethanol and isopropyl alcohol were not considered in the MCDA, because these chemicals lack chronic oral RfVs or OSFs from the sources considered in EPA's hydraulic fracturing study; however, ethanol and isopropyl alcohol are frequently used in hydraulic fracturing fluids (reported by FracFocus 1.0 in approximately 31% and 47% of nationwide disclosures, and 27% and 49% of disclosures in Texas, respectively; see Supporting Information), and are expected to be readily transported in water (US EPA, 2015c).

Another example is naphthalene, which was highlighted in the noncancer MCDA, and was detected in groundwater monitoring wells in by DiGiulio and Jackson (2016). The authors reported that naphthalene was used in hydraulic fracturing fluids in the Pavillion Field, and concluded that naphthalene in the monitoring wells likely had anthropogenic origins, as high molecular weight hydrocarbons would not be expected to occur naturally in the waters of this particular formation. DiGiulio and Jackson also reported other organic chemicals in the groundwater wells that have known use in hydraulic fracturing fluids at the site, but which did not have sufficient data for inclusion in the MCDA—for instance, 1,2,4-trimethylbenzene and diethylene glycol, both of which currently lack chronic oral RfVs or OSFs. These two chemicals are both used frequently (13% and 7% of FracFocus 1.0 disclosures nationwide, respectively; see Supporting Information). Diethylene glycol is expected to be highly mobile in water, while 1,2,4-trimethylbenzene is expected to be less mobile in water due to moderately hydrophobic and volatile properties (US EPA, 2015c).

Other chemicals detected in these field studies received relatively low scores in our MCDA, highlighting some of the limitations of this model. For instance, consider dichloromethane, which was reported infrequently as a chemical ingredient by FracFocus 1.0 (Tables 2–3), but was identified as a frequent contaminant in groundwater wells overlying the Barnett shale (Hildenbrand et al., 2015). The authors of the field study speculated that dichloromethane may be used at hydraulic fracturing well pads as an industrial degreaser, which may have led to the migration of this chemical into groundwater (Hildenbrand et al., 2015). Because our MCDA framework is only designed to target chemicals that are injected into the well, the application of dichloromethane as a degreaser at the well pad is outside the scope of our analysis. Dichloromethane received a moderate score in the noncancer MCDA, and the lowest possible score in the cancer MCDA, due primarily to volatility and low frequency of use in hydraulic fracturing fluids (Figs. 3–4).

Furthermore, our MCDA framework does not address chemicals that are released from the surface environment as a result of hydraulic fracturing activity. An example of this is

benzene, which is used infrequently in hydraulic fracturing fluids (Tables 2–3), but is associated with oil and gas extraction due to natural occurrence in hydrocarbon formations. Benzene, toluene, ethylbenzene, and xylenes (BTEX) are frequently reported in flowback and produced water from hydraulic fracturing operations (Abualfaraj et al., 2014; Hayes, 2009; Orem et al., 2014), and have been reported in groundwater in conjunction with hydraulic fracturing activity (DiGiulio and Jackson, 2016; Gross et al., 2013; Hildenbrand et al., 2015). Given the infrequent reported use of benzene in hydraulic fracturing fluids, it is more likely that these contamination incidents are the result of the natural occurrence and mobilization of BTEX from the hydrocarbon formation, rather than the use of benzene as a chemical ingredient. Benzene received low scores in both the noncancer and cancer MCDAs, due primarily to its low frequency of use.

3.5. Limitations and uncertainty

As a result of fundamental data limitations, very few chemicals used in hydraulic fracturing fluids had all of the data necessary to evaluate using this MCDA approach. The greatest limiting factor was the low number of chemicals with chronic oral toxicity values from US federal sources (73 with chronic oral RfVs, 15 with OSFs; Fig. 2). The lack of toxicity values and other relevant toxicity information for many of the chemicals used in hydraulic fracturing fluids has been discussed in several recent studies (Elliott et al., 2016; Stringfellow et al., 2014; Wattenberg et al., 2015; Yost et al., 2016). Such data limitations are not unique to the hydraulic fracturing industry; in fact, there are currently thousands of chemicals in use across many other industries that have not undergone significant toxicological evaluation (Judson et al., 2009). Nevertheless, this represents a potentially significant data gap with respect to human health risk assessment. In the absence of toxicity information, risk assessors have limited ability to assess the potential public health implications surrounding the use of these chemicals, and potential impacts on drinking water resources may not be assessed adequately.

A relatively large number of chemicals had available data on frequency of use from FracFocus 1.0 (692 chemicals; Fig. 2). However, FracFocus 1.0 data does not represent a complete record of hydraulic fracturing chemical usage in the US, and is subject to numerous uncertainties. For instance, disclosure to FracFocus 1.0 was voluntary in many states during the course of EPA's study, and therefore there may be regions of the US that are not represented in this nationwide analysis. Furthermore, companies submitting to FracFocus 1.0 were not required to report the identity of chemicals they claimed as confidential business information (CBI) under the Toxic Substances Control Act. EPA's analysis of FracFocus 1.0 indicated that approximately 70% of well disclosures had at least one chemical that was claimed as CBI, with CBI chemicals constituting approximately 11% of all ingredient records that were disclosed to FracFocus 1.0 (US EPA, 2015a). Thus, there may be chemicals that are used frequently in hydraulic fracturing fluids that were not identified by EPA's analysis of FracFocus 1.0. If comprehensive chemical usage data were available for the chemicals considered in this study, the frequency of use estimates used in the MCDA would likely change, and there may have been additional chemicals that met the criteria for inclusion in the analysis.

Finally, physicochemical properties from EPI Suite were available for less than half of the chemicals used in hydraulic fracturing fluids (453 chemicals; Fig. 2). These values are useful for making comparisons between chemicals, but are subject to inherent uncertainty. Although measured physicochemical properties were used whenever available, many of the values used in the MCDA were estimated by EPI Suite. It is also important to consider that chemical fate and transport will be influenced by environmental and site-specific conditions. For instance, the half-lives used to develop the Physicochemical Properties Score are estimated values that assume aerobic conditions, and thus may underestimate the expected half-life under anaerobic conditions (e.g. in a groundwater contaminant plume). If chemicals are present in a mixture, as inevitably occurs in hydraulic fracturing fluids and in the subsurface environment, fate and transport will be influenced by changes in solubility or degradation resulting from interactions with other chemicals. Toxicity may also be altered in a chemical mixture, as a result of additive, synergistic, or antagonistic activity between chemicals. These various scenarios are outside the scope of this analysis, but should be taken into consideration for site-specific hazard evaluation.

In addition to these fundamental data limitations, there are also limitations with respect to the scope of the MCDA. As discussed in Section 4, this MCDA is designed to target chemicals used in hydraulic fracturing fluids; therefore, it does not address chemicals that are used at hydraulic fracturing sites for other purposes (e.g. industrial degreasers on the well pad), nor does it address naturally occurring chemicals that may be present in flowback or produced water (e.g. BTEX). Likewise, the physicochemical properties used in the MCDA were chosen specifically to reflect chemical transport in water, and therefore this analysis does not attempt to address the numerous other physicochemical variables that may impact exposure. For instance, hydrophobic chemicals may serve as long-term sources of pollution by sorbing to soils or sediments at contaminated sites; volatile chemicals may serve as air pollution hazards. This analysis also does not attempt to address bioavailability or toxicokinetics, which may be influenced by physicochemical properties such as log K_{OW} . For instance, chemicals with log K_{OW} of 2–4 tend to absorb well through biological membranes, while chemicals with log K_{OW} > 4 tend not to absorb well, and those with log K_{OW} of 5–7 tend to bioconcentrate (US EPA, 2012c).

It is also important to acknowledge the limitations of the MCDA approach itself. The scores assigned by the MCDA framework are only relevant for making comparisons within the defined set of chemicals that were used in the analysis, and therefore do not stand alone as an analysis of hazard potential for a given chemical. A more data-informed hazard evaluation of these chemicals would require knowledge of site-specific variables, including knowledge of the chemicals used at a given well site, the toxicological and physicochemical properties of these chemicals, the amount of fluid being used and recovered, the likelihood of well integrity failures, and the likelihood of spills and other unintentional releases.

Thus, while this MCDA framework provides a simple and transparent tool for exploring the relative hazard potential of chemicals used in hydraulic fracturing fluids, it is not intended to provide a comprehensive analysis. Despite the limitations, the data used for input in the MCDA represents some of the best information currently available, and are useful for making comparisons across chemicals.

3.6. Application and future direction

The MCDA framework presented herein is intended as a preliminary analysis, and illustrates just one possible method for integrating these data to explore potential hazards. For another possible method, we note a recent study by Rogers et al. (2015) which presented a framework for prioritizing chemicals used in hydraulic fracturing fluids based on estimated persistence and mobility in groundwater. The authors used these physicochemical properties to identify chemicals that are predicted to have 10% of the initial concentration remaining at a transport distance of 94 m, which is the national average setback distance between wells and other entities. Those chemicals that were also identified in 0.1% of FracFocus 1.0 disclosures nationwide were concluded by the authors to have elevated exposure potential. Chemicals highlighted by that analysis that were also considered in our MCDA include acrylamide, xylenes, 1,4-dioxane, 1-butanol, 2-butoxyethanol, *N,N*-dimethylformamide, and naphthalene. Although Rogers et al. (2015) did not attempt to develop a rank-ordering of chemicals based on these data, their study illustrates another example of integrating data to estimate potential hazards.

Researchers may find our MCDA framework useful in their efforts to explore the potential hazards of chemicals present at specific field sites. The MCDA framework is flexible, and could be adapted to incorporate different types of toxicity data and/or highlight other variables that may be of interest for risk assessment. For instance, rather than focusing on RfVs and OSFs from US federal sources, one could choose to derive the Toxicity Score using other sources of relevant toxicity information. Additionally, one could choose to perform this analysis using different physicochemical property inputs, to highlight chemical interactions with different environmental media (e.g. hydrophobic or volatile chemicals). Researchers could also choose to apply different weights to each of the three criteria that were considered in this analysis (toxicity, occurrence, physicochemical properties), to reflect expert judgement of each variable's relative importance.

Furthermore, although we elected to focus on chemicals that are used in hydraulic fracturing fluids, this MCDA approach could also be applied to explore the relative hazards of chemicals that have been detected in flowback and produced water. For such an approach, the Occurrence Score could be calculated using metrics such as measured concentration or frequency of detection in flowback/produced water. This would provide a useful compliment to the analysis presented in our study, as it would provide information on the chemicals that are being returned from the well, in addition to the chemicals that are being injected into it. Flowback and produced water may contain hazardous chemicals such as volatile and semi-volatile organic compounds, heavy metals, and radionuclides, many of which are naturally occurring (Abualfaraj et al., 2014; Hayes, 2009; Orem et al., 2014). EPA's hydraulic fracturing study identified 134 chemicals that have been detected in flowback or produced water; toxicological and physicochemical property data for these chemicals are compiled in the publicly available database for the study (US EPA, 2015c). Overall, contamination of drinking water resources depends on site-, chemical-, and fluid-specific factors (Goldstein et al., 2014), and the exact mixture and concentrations of chemicals at a site will depend upon the geology of the formation and the company's sourcing preferences (US EPA, 2015a).

Therefore, potential hazard and risk considerations are best made on a site-specific, well-specific basis.

4. Conclusions

This study illustrates the application of an MCDA framework for comparing the relative hazards of chemicals that are used in hydraulic fracturing fluids. This approach is based on the rationale that no single variable can be used to predict chemical hazards. By combining the multiple lines of data that are available on these chemicals—in this case, data on toxicity, occurrence, and physiochemical properties—we can stratify chemicals according to estimated hazard potential, and gain preliminary insight into those chemicals that may be of more concern than others to drinking water resources.

While it remains challenging to predict the potential impacts of chemicals that are used by the hydraulic fracturing industry, frameworks such as this allow us to explore and compare the relative hazards that may be associated with these chemicals. By performing this analysis on specific subsets of chemicals, we can investigate local or regional differences that may exist with regards to potential hazards. As more data become available on these chemicals and on current industry practices, and as more systematic studies and exposure assessment data become available for areas of hydraulic fracturing activity, hazard evaluation will become more informed.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Abbreviations

MCDA	Multi-criteria decision analysis
RfV	Reference value
RfD	Reference dose
OSF	Oral slope factor
MRL	Minimal risk level
IRIS	Integrated Risk Information System
PPRTV	Provisional Peer-Reviewed Toxicity Values
ATSDR	Agency for Toxic Substances and Disease Registry
HHBP	Human Health Benchmarks for Pesticides

References

- Abualfaraj N, Gurian PL, Olson MS. Characterization of Marcellus shale flowback water. *Environ. Eng. Sci.* 2014; 31:514–524. <http://dx.doi.org/10.1089/ees.2014.0001>.
- ATSDR. Agency for Toxic Substances and Disease Registry (ATSDR) Glossary of terms. 2009. (<http://www.atsdr.cdc.gov/glossary.html>)
- Barati R, Liang J-T. A review of fracturing fluid systems used for hydraulic fracturing of oil and gas wells. *J. Appl. Polym. Sci.* 2014; 131 <http://dx.doi.org/10.1002/app.40735>.
- Brantley SL, et al. Water resource impacts during unconventional shale gas development: The Pennsylvania experience. *Int. J. Coal Geol.* 2014; 126:140–156. <http://dx.doi.org/10.1016/j.coal.2013.12.017>.
- DiGiulio, DC., Jackson, RB. Impact to underground sources of drinking water and domestic wells from production well stimulation and completion practices in the Pavillion, Wyoming. *Field Environ. Sci. Technol.* 2016. <http://dx.doi.org/10.1021/acs.est.5b04970>
- Drollette BD, et al. Elevated levels of diesel range organic compounds in ground-water near Marcellus gas operations are derived from surface activities. *Proc. Natl. Acad. Sci. U. S. A.* 2015; 112:13184–13189. <http://dx.doi.org/10.1073/pnas.1511474112>. [PubMed: 26460018]
- EIA. Annual Energy Outlook 2014 with Projections to 2040. U.S. Energy Information Administration; Washington, D.C.: 2014.
- Elliott EG, Ettinger AS, Leaderer BP, Bracken MB, Deziel NC. A systematic evaluation of chemicals in hydraulic-fracturing fluids and wastewater for reproductive and developmental toxicity. *J. Expo. Sci. Environ. Epidemiol.* 2016:1–10. [PubMed: 25736163]
- Goldstein BD, et al. The role of toxicological science in meeting the challenges and opportunities of hydraulic fracturing. *Toxicol. Sci.* 2014; 139:271–283. <http://dx.doi.org/10.1093/toxsci/kfu061>. [PubMed: 24706166]
- Gross SA, Avens HJ, Banducci AM, Sahmel J, Panko JM, Tvermoes BE. Analysis of BTEX groundwater concentrations from surface spills associated with hydraulic fracturing operations. *J. Air Waste Manage. Assoc.* 2013; 63:424–432. <http://dx.doi.org/10.1080/10962247.2012.759166>.
- Hayes, T. Sampling and Analysis of Water Streams Associated with the Development of Marcellus Shale Gas. Marcellus Shale Coalition; Des Plaines, IL: 2009.
- Hildenbrand ZL, et al. A comprehensive analysis of groundwater quality in the Barnett Shale region. *Environ. Sci. Technol.* 2015; 49:8254–8262. <http://dx.doi.org/10.1021/acs.est.5b01526>. [PubMed: 26079990]
- Hristozov DR, Zabeo A, Foran C, Isigonis P, Critto A, Marcomini A, Linkov I. A weight of evidence approach for hazard screening of engineered nanomaterials. *Nanotoxicology.* 2014; 8:72–87. <http://dx.doi.org/10.3109/17435390.2012.750695>.
- Huang IB, Keisler J, Linkov I. Multi-criteria decision analysis in environmental sciences: Ten years of applications and trends. *Sci. Total Environ.* 2011; 409:3578–3594. <http://dx.doi.org/10.1016/j.scitotenv.2011.06.022>. [PubMed: 21764422]
- Jackson RE, Gorody AW, Mayer B, Roy JW, Ryan MC, Van Stempvoort DR. Groundwater protection and unconventional gas extraction: the critical need for field-based hydrogeological research. *Ground Water.* 2013; 51:488–510. <http://dx.doi.org/10.1111/gwat.12074>. [PubMed: 23745972]
- Judson R, et al. The toxicity data landscape for environmental chemicals. *Environ. Health Perspect.* 2009; 117:685–695. <http://dx.doi.org/10.1289/ehp.0800168>. [PubMed: 19479008]
- Linkov I, Welle P, Loney D, Tkachuk A, Canis L, Kim JB, Bridges T. Use of multicriteria decision analysis to support weight of evidence evaluation. *Risk Anal.* 2011; 31:1211–1225. <http://dx.doi.org/10.1111/j.1539-6924.2011.01585.x>. [PubMed: 21371061]
- Llewellyn GT, et al. Evaluating a groundwater supply contamination incident attributed to Marcellus Shale gas development. *Proc. Natl. Acad. Sci. U. S. A.* 2015; 112:6325–6330. <http://dx.doi.org/10.1073/pnas.1420279112>. [PubMed: 25941400]
- Mitchell J, Pabon P, Collier ZA, Egeghy PP, Cohen-Hubal E, Linkov I, Vallero DA. A decision analytic approach to exposure-based chemical prioritization. *PLoS One.* 2013; 8:e70911. <http://dx.doi.org/10.1371/journal.pone.0070911>. [PubMed: 23940664]

- National Research Council. A Framework to Guide Selection of Chemical Alternatives. The National Academies Press; Washington, D.C.: 2014.
- Orem W, et al. Organic substances in produced and formation water from unconventional natural gas extraction in coal and shale. *Int. J. Coal Geol.* 2014; 126:20–31. <http://dx.doi.org/10.1016/j.coal.2014.01.003>.
- Rogers JD, Burke TL, Osborn SG, Ryan JN. A framework for identifying organic compounds of concern in hydraulic fracturing fluids based on their mobility and persistence in groundwater. *Environ. Sci. Technol. Lett.* 2015; 2:158–164. <http://dx.doi.org/10.1021/acs.estlett.5b00090>.
- Rozell DJ, Reaven SJ. Water Pollution Risk Associated with Natural Gas Extraction from the Marcellus Shale. *Risk Anal.* 2012; 32:1382–1393. <http://dx.doi.org/10.1111/j.1539-6924.2011.01757.x>. [PubMed: 22211399]
- Stringfellow WT, Domen JK, Camarillo MK, Sandelin WL, Borglin S. Physical, chemical and biological characteristics of compounds used in hydraulic fracturing. *J. Hazard. Mater.* 2014; 275:37–54. <http://dx.doi.org/10.1016/j.jhazmat.2014.04.040>. [PubMed: 24853136]
- US EPA. Carcinogenic Effects of Benzene: An Update (Final). US Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment. Washington Office; Washington, DC: 1998.
- US EPA. Human Health Toxicity Values in Superfund Risk Assessments (OSWER Directive 9285.7-53). U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response; Washington, DC: 2003.
- US EPA. Design for the Environment Program Alternatives Assessment Criteria for Hazard Evaluation (Version 2.0). US Environmental Protection Agency; Office of Pollution Prevention and Toxics; Washington, DC: 2011.
- US EPA. Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources. U.S. Environmental Protection Agency, Office of Research and Development; Washington, DC: 2011a.
- US EPA. [Accessed May 21, 2015] Terminology Services (TS): Vocabulary Catalog - IRIS Glossary. 2011b. (http://ofmpub.epa.gov/sor_internet/registry/termreg/searchandretrieve/glossariesandkeywordlists/search.do?details=&glossaryName=IRIS%20Glossary)
- US EPA. Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.11. U.S. Environmental Protection Agency; Washington, D.C.: 2012a.
- US EPA. Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources: Progress Report. U.S. Environmental Protection Agency, Office of Research and Development; Washington, DC: 2012b.
- US EPA. Sustainable Futures / Pollution Prevention (P2) Framework Manual. US Environmental Protection Agency; Office of Chemical Safety and Pollution Prevention; Washington, DC: 2012c.
- US EPA. Analysis of Hydraulic Fracturing Fluid Data from the FracFocus Chemical Disclosure Registry 1.0. U.S. Environmental Protection Agency, Office of Research and Development; Washington, D.C.: 2015a.
- US EPA. Analysis of Hydraulic Fracturing Fluid Data from the FracFocus Chemical Disclosure Registry 1.0: Project Database. U.S. Environmental Protection Agency, Office of Research and Development; Washington, D.C.: 2015b.
- US EPA. Compilation of Physicochemical and Toxicological Information about Hydraulic Fracturing-Related Chemicals (Draft Database). U.S. Environmental Protection Agency; Washington, D.C.: 2015c.
- US EPA. Retrospective Case Study in Killdeer, North Dakota: Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources. Washington, D.C.: 2015d.
- US EPA. Review of State and Industry Spill Data: Characterization of Hydraulic Fracturing-Related Spills. Office of Research and Development. U.S. Environmental Protection Agency; Washington, D.C.: 2015e.
- Vengosh A, Jackson RB, Warner N, Darrah TH, Kondash A. A critical review of the risks to water resources from unconventional shale gas development and hydraulic fracturing in the United States. *Environ. Sci. Technol.* 2014; 48:8334–8348. <http://dx.doi.org/10.1021/es405118y>. [PubMed: 24606408]

- Vidic RD, Brantley SL, Vandenbossche JM, Yoxtheimer D, Abad JD. Impact of Shale Gas Development on Regional Water Quality. *Science*. 2013; 340 <http://dx.doi.org/10.1126/science.1235009>.
- Wattenberg EV, Bielicki JM, Suchomel AE, Sweet JT, Void EM, Ramachandran G. Assessment of the acute and chronic health hazards of hydraulic fracturing. *Fluids J. Occup. Environ. Hyg.* 2015; 12:611–624. <http://dx.doi.org/10.1080/15459624.2015.1029612>. [PubMed: 25894916]
- Yost EE, Stanek JJ, DeWoskin RS, Burgoon LD. Overview of chronic oral toxicity values for chemicals present in hydraulic fracturing fluids, flowback and produced waters. *Environ. Sci. Technol.* 2016; 50:4788–4797. <http://dx.doi.org/10.1021/acs.est.5b04645>. [PubMed: 27050380]

HIGHLIGHTS

- Data integration was used to explore potential hazards of fracturing fluid chemicals.
- Chemicals were ranked based on toxicity, frequency of use, and mobility in water.
- Lack of toxicity values for the majority of the chemicals is a significant data gap.
- This approach is useful as a preliminary analysis for comparison across chemicals.

Fig. 1.

The MCDA employed in this study is a three-part prioritization model, which incorporates data on toxicity, occurrence, and physicochemical properties.

Selection of chemicals for noncancer toxicity analysis:

Selection of chemicals for cancer analysis:

Chemicals selected for MCDA (nationwide)

Fig. 2.

Venn diagram depicting the availability of data for input into the MCDA (nationwide analysis). Values shown in the diagram reflect all of the toxicity and physicochemical properties data that is available on the draft database of EPA's hydraulic fracturing study (US EPA, 2015c), as well as all of the chemical usage data that is available on EPA's FracFocus 1.0 project database (US EPA, 2015b). Chemicals that had available data for all three criteria (toxicity, occurrence, and physicochemical properties) were selected for inclusion in the MCDA.

Fig. 3. Results of the noncancer MCDA, based on a nationwide analysis (37 chemicals total), depicting the Toxicity, Occurrence, and Physicochemical Properties Scores for each chemical. Chemicals are ordered from high to low based on Total Hazard Potential Score.

Cancer MCDA - Nationwide Analysis

Fig. 4.

Results of the cancer MCDA, based on a nationwide analysis (10 chemicals total), depicting the Toxicity, Occurrence, and Physicochemical Properties Scores for each chemical. Chemicals are ordered from high to low based on Total Hazard Potential Score.

Fig. 5. Results of the noncancer MCDA, based on state-specific analysis for Texas (31 chemicals total), depicting the Toxicity, Occurrence, and Physicochemical Properties Scores for each chemical. Chemicals are ordered from high to low based on Total Hazard Potential Score.

Fig. 6. Results of the noncancer MCDA, based on state-specific analysis for Pennsylvania (18 chemicals total), depicting the Toxicity, Occurrence, and Physicochemical Properties Scores for each chemical. Chemicals are ordered from high to low based on Total Hazard Potential Score.

Fig. 7.

Results of the noncancer MCDA, based on state-specific analysis for North Dakota (20 chemicals total), depicting the Toxicity, Occurrence, and Physicochemical Properties Scores for each chemical. Chemicals are ordered from high to low based on total hazard potential score.

Table 1

Thresholds used for developing the Toxicity Score, Occurrence Score, and Physicochemical Properties Score in the MCDA framework.

Criteria	Subcriteria	Value	Score			
			1	2	3	4
Toxicity (noncancer MCDA)	NA	Chronic oral RfV (mg/kg-day)	>3rd quartile	>2nd quartile to 3rd quartile	>1st quartile to 2nd quartile	1st quartile
Toxicity (cancer MCDA)	NA	OSF (per mg/kg-day)	<1st quartile	1st quartile to <2nd quartile	2nd quartile to <3rd quartile	3rd quartile
Occurrence	NA	Frequency of use, FracFocus 1.0 (% of disclosures)	<1st quartile	1st quartile to <2nd quartile	2nd quartile to <3rd quartile	3rd quartile
Physicochemical properties	Mobility	Log K _{ow}	>5	>3 to 5	>2 to 3	2
		Log K _{oc}	>4.4	>3.4 to 4.4	>2.4 to 3.4	2.4
		Aqueous solubility (mg/L)	<0.1	0.1 to <100	100 to <1000	1000
	Volatility	Henry's law constant	>10 ⁻¹	>10 ⁻³ to 10 ⁻¹	>10 ⁻⁵ to 10 ⁻³	10 ⁻⁵
		Persistence	<16	16 to <60	60 to <180	180
		Half-life in water (days)				

Table 2

Chemical data used for input into the noncancer MCDA.

CASRN	Chemical Name	Toxicity		Occurrence (% of FracFocus 1.0 Disclosures)				Physicochemical Properties				
		RFV (mg/kg-day)	Source of RFV	National	TX	PA	ND	Log K _{ow}	Log K _{oc}	Aqueous solubility (mg/l)	Henry's law constant	Half-life in water (days)
123-73-9	(E)-Crotonaldehyde	0.001	PPRTV (RfD)	0.06%				0.6	0.254	41,480	1.94E-05	15
107-19-7	Propargyl alcohol	0.002	IRIS (RfD)	33%	39%	58%	1%	-0.38	0.28	935,500	1.15E-06	15
100-44-7	Benzyl chloride	0.002	PPRTV (RfD)	6%	7%	5%	0.8%	2.3	2.649	1030	4.12E-04	15
79-06-1	Acrylamide	0.002	IRIS (RfD)	1%	2%	1%	1%	-0.67	0.755	504,000	1.70E-09	15
71-43-2	Benzene	0.004	IRIS (RfD)	0.006%	0.01%			2.13	1.75	2000	5.55E-03	37.5
75-09-2	Dichloromethane	0.006	IRIS (RfD)	0.02%				1.25	1.44	10,950	3.25E-03	37.5
106-89-8	Epichlorohydrin	0.006	PPRTV (RfD)	1%	0.2%	0.08%		0.45	1	50,630	3.04E-05	15
62-53-3	Aniline	0.007	PPRTV (RfD)	0.02%	0.05%			0.9	1.6	20,820	2.02E-06	15
21564-17-0	2-(Thiocyanomethylthio)benzothiazole	0.01	HHBP (RfD)	0.006%				3.3	3.528	41.67	6.49E-12	37.5
98-01-1	Furfural	0.01	HHBP (RfD)	0.003%				0.41	0.784	53,580	3.77E-06	15
91-20-3	Naphthalene	0.02	IRIS (RfD)	19%	14%	1%	43%	3.3	2.96	142.1	4.40E-04	37.5
542-75-6	1,3-Dichloropropene	0.03	IRIS (RfD)	0.02%				2.04	1.82	1994	3.55E-03	37.5
123-91-1	1,4-Dioxane	0.03	IRIS (RfD)	0.3%	0.5%		0.8%	-0.27	0.421	213,900	4.8E-06	15
112-34-5	2-(2-Butoxyethoxy)ethanol	0.03	PPRTV (RfD)	0.6%	0.4%	4%		0.56	1	71,920	7.20E-09	8.67
80-05-7	Bisphenol A	0.05	IRIS (RfD)	0.006%	0.01%			3.32	4.576	172.7	9.16E-12	37.5
108-88-3	Toluene	0.08	IRIS (RfD)	0.7%	1%			2.73	2.07	573.1	6.64E-03	15
107-15-3	Ethylenediamine	0.09	PPRTV (RfD)	0.01%	0.02%			-2.04	1.172	1,000,000	1.73E-09	15
111-76-2	2-Butoxyethanol	0.1	IRIS (RfD)	23%	27%	21%	15%	0.83	0.451	64,470	1.60E-06	8.67
68-12-2	N,N-Dimethylformamide	0.1	PPRTV (RfD)	9%	10%	11%	0.6%	-1.01	0	977,900	7.39E-08	15
7173-51-5	Didecylidimethylammonium chloride	0.1	HHBP (RfD)	8%	7%	12%	0.05%	4.66	5.546	0.9	6.85E-10	15
71-36-3	1-Butanol	0.1	IRIS (RfD)	1%	3%		0.7%	0.88	0.5	76,700	8.81E-06	8.67
98-82-8	Cumene	0.1	IRIS (RfD)	0.5%	0.8%	1%		3.66	2.844	75.03	1.15E-02	15
100-41-4	Ethylbenzene	0.1	IRIS (RfD)	0.4%	0.5%		0.1%	3.15	2.23	228.6	7.88E-03	15
98-86-2	Acetophenone	0.1	IRIS (RfD)	0.04%	0.04%			1.58	1.8	4484	1.04E-05	15
50-00-0	Formaldehyde	0.2	IRIS (RfD)	7%	8%	4%	8%	0.35	0	57,020	3.37E-07	15
1330-20-7	Xylenes	0.2	IRIS (RfD)	2%	3%	1%	0.2%	3.2	2.25	207.2	7.18E-03	15
78-83-1	2-Methyl-1-propanol	0.3	IRIS (RfD)	0.3%			4%	0.76	0.465	97,120	9.78E-06	15

CASRN	Chemical Name	Toxicity				Occurrence (% of FracFocus 1.0 Disclosures)				Physicochemical Properties					
		RFV (mg/kg-day)	Source of RFV	National	TX	PA	ND	Log K _{OW}	Log K _{OC}	Aqueous solubility (mg/l)	Henry's law constant	Half-life in water (days)			
108-95-2	Phenol	0.3	IRIS (RfD)	0.4%	0.8%		0.05%	1.46	1.9	26,160	3.33E-07	15			
27176-87-0	Dodecylbenzenesulfonic acid	0.5	HHBP (RfD)	7%	10%	2%	8%	4.71	4.066	0.8126	6.27E-08	15			
64-18-6	Formic acid	0.9	PPRTV (RfD)	11%	14%	8%	11%	-0.54	0	955,200	1.67E-07	8.67			
141-78-6	Ethyl acetate	0.9	IRIS (RfD)	0.4%	0.7%			0.73	0.747	29,930	1.34E-04	15			
67-64-1	Acetone	0.9	IRIS (RfD)	0.2%	0.02%		1%	-0.24	0.374	219,900	3.50E-05	15			
67-56-1	Methanol	2	IRIS (RfD)	73%	80%	69%	54%	-0.77	0.44	1,000,000	4.55E-06	8.67			
107-21-1	Ethylene glycol	2	IRIS (RfD)	47%	60%	35%	37%	-1.36	0	1,000,000	6.00E-08	8.67			
124-04-9	Hexanedioic acid	2	PPRTV (RfD)	0.7%	1%			0.08	1.386	167,300	4.71E-12	8.67			
65-85-0	Benzoic acid	4	IRIS (RfD)	0.06%	0.1%	0.04%		1.87	1.5	2493	3.81E-08	15			
57-55-6	1,2-Propylene glycol	20	PPRTV (RfD)	4%	4%	8%	8%	-0.92	0.36	811,100	1.29E-08	8.67			

Table 3

Chemical data used for input into the cancer MCDA.

		Toxicity		Occurrence (% of FracFocus 1.0 Disclosures) ^a				Physicochemical properties				
CASRN	Chemical name	OSF (per mg/kg-day)	Source of OSF	National	TX	PA	ND	LogK _{OW}	LogK _{OC}	Aqueous solubility (mg/l)	Henry's law constant	Half-life in water
91-22-5	Quinoline	3	IRIS	0.02%	0.04%			2.03	3.1	1711	1.67E-06	15
111-44-4	Bis(2-chloroethyl) ether	1.1	IRIS	0.7%	0.9%		1%	1.29	1.88	6435	1.70E-05	37.5
79-06-1	Acrylamide	0.5	IRIS	1%	2%	1%	1%	-0.67	0.755	504,000	1.70E-09	15
100-44-7	Benzyl chloride	0.17	IRIS	6%	7%	5%	0.8%	2.3	2.649	1030	4.12E-04	15
123-91-1	1,4-Dioxane	0.1	IRIS	0.3%	0.5%		0.8%	-0.27	0.421	213,900	4.80E-06	15
71-43-2	Benzene	0.055	IRIS	0.006%	0.01%			2.13	1.75	2000	5.55E-03	37.5
542-75-6	1,3-Dichloropropene	0.05	IRIS	0.02%				2.04	1.82	1994	3.55E-03	37.5
106-89-8	Epichlorohydrin	0.0099	IRIS	1%	0.2%	0.08%		0.45	1	50,630	3.04E-05	15
62-53-3	Aniline	0.0057	IRIS	0.02%	0.05%			0.9	1.6	20,820	2.02E-06	15
75-09-2	Dichloromethane	0.002	IRIS	0.02%				1.25	1.44	10,950	3.25E-03	37.5

^aThe cancer MCDA was only performed using the nationwide dataset. State-specific frequency of use for these chemicals is provided here for reference only.