			Chronic oral RfVs[b]			OSFs[d]	
Chemical Name	**CASRN**	**% of Disclosures[a]**	**RfV (mg/kg-day)**	**Source of RfV**	**Critical Effect[c]**	**OSF (per mg/kg-day)**	**Source of OSF**
Di(2-ethylhexyl) phthalate*	117-81-7		0.02	IRIS	Increased relative liver weight	0.014	IRIS
Chlorine	7782-50-5		0.1	IRIS	No adverse effect level		
p-Xylene*	106-42-3		0.2	ATSDR	Neurotoxicity		
Zinc	7440-66-6		0.3	IRIS	Decreases in erythrocyte Cu, Zn-superoxide dismutase (ESOD) activity in humans		
Lead*	7439-92-1		0.5 µg/day [e]	CalEPA	Reproductive toxicity	0.0085	CalEPA
Chromium (III)	16065-83-1		1.5	IRIS			

CASRN = Chemical Abstract Service Registry Number; RfV = Reference value; IRIS = Integrated Risk Information System; PPRTV = Provisional Peer-Reviewed Toxicity Value; HHBP = Human Health Benchmarks for Pesticides; ATSDR = Agency for Toxic Substances and Disease Registry; CalEPA = California Environmental Protection Agency; CICAD = Concise International Chemical Assessment Documents; QSAR = Quantitative structure-activity relationship; TOPKAT = Toxicity Prediction by Komputer Assisted Technology; ACToR = EPA's Aggregated Computational Toxicology Online Resource

[a] The FracFocus frequency of use data presented in this chapter is based on 35,957 FracFocus disclosures that were deduplicated, within the study time period (January 1, 2011 to February 28, 2013), and with ingredients that have a valid CASRN.

[b] Reference value (RfV): An estimate of an exposure for a given duration to the human population (including susceptible subgroups) that is likely to be without an appreciable risk of adverse health effects over a lifetime. RfVs considered in this analysis include chronic oral reference doses (RfDs) from IRIS, PPRTV, and HHBP; chronic oral minimal risk levels (MRLs) from ATSDR; maximum allowable daily levels (MADLs) from CalEPA; and tolerable daily intake (TDI) from CICAD. See Section 9.4.1.

[c] Critical effect: The first adverse effect, or its known precursor, that occurs to the most sensitive species as the dose rate of an agent increases.

[d] Oral slope factor (OSF): 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 units of 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 less than 1 in 100. OSFs considered in this analysis include values from IRIS, PPRTV, HHBP, and CalEPA. See Section 9.4.1.

[e] CalEPA MADLs are in units of µg/day, while all other chronic oral RfVs in this table are in units of mg/kg-day.

9.6 Hazard Evaluation of Selected Subsets of Hydraulic Fracturing Chemicals Using Multi-Criteria Decision Analysis (MCDA): Integrating Toxicity, Occurrence, and Physicochemical Data

Based on the information presented in Section 9.5, it is clear that there are a variety of chemicals used in hydraulic fracturing fluids or detected in produced water that are known to be hazardous to human health. However, there are gaps in our understanding of the potential for human exposure to these chemicals. Although there are subsurface and surface pathways by which these chemicals may be introduced into drinking water resources—including spills, leaks, mechanical integrity failures, intersection of the fracture network with groundwater, or discharge of wastewater, as described in previous chapters of this report—there are significant limitations associated with the publicly available data on these potential impacts, and the potential for human exposure has not been systematically characterized. This makes it difficult to determine which chemicals are of the greatest concern for human exposure in drinking water, and creates a challenge for hazard evaluation.

Although exposure assessment data are limited, some of the chemicals identified by EPA have other data available that might provide preliminary insight into relative hazard potential. This includes data on toxicity, frequency of use in hydraulic fracturing fluids, detected concentrations in produced water, and data on physicochemical properties. By integrating these types of data, we can place the severity of potential impacts (i.e., the toxicity of specific chemicals) into the context of factors that affect the likelihood of impacts (i.e., frequency of use, environmental fate and transport).

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; Mitchell et al., 2013b; Huang et al., 2011; Linkov et al., 2011). 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 (Huang et al., 2011). A recent publication by Yost et al. (In Press) described the use of an MCDA framework to evaluate the hazard potential of chemicals associated with hydraulic fracturing.

Here, to demonstrate one possible method for exploring the potential hazards of these chemicals, we use an adaptation of the MCDA framework developed by Yost et al. (In Press) to analyze and rank selected subsets of chemicals that have data available.[1] Chemicals were assigned scores based on toxicity, occurrence, and physicochemical properties that describe transport in water. These scores were then combined to develop a relative ranking of chemicals based on hazard potential.

The MCDA scores provide a preliminary evaluation of hazard potential, and serve as a qualitative metric for making comparison between chemicals when exposure assessment data is limited or unavailable. 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, and should not be used in place of

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[1] Yost et al. (In Press) used the MCDA framework to analyze and rank the hazards of chemicals used in hydraulic fracturing fluids, using data from the FracFocus 1.0 project database as the metric of occurrence. This chapter uses that same framework for the analysis of chemicals used in hydraulic fracturing fluids. For chemicals detected in produced water, this chapter modifies the MCDA framework by using measured concentration in produced water as the metric of occurrence.

site-specific data on chemical exposures. An overview of the MCDA framework and selection of chemicals for inclusion in the MCDA is described below.

9.6.1 Overview of the MCDA Framework for Hazard Evaluation

The MCDA framework employed in this chapter was designed specifically to fit the scope of EPA's hydraulic fracturing study (Yost et al., In Press). A basic schematic of the model is shown in Figure 9-5, and the methods for assigning scores are outlined below. Under the MCDA framework, each chemical was assigned three scores:

1. A Toxicity Score;
2. An Occurrence Score; and
3. 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, and offer a means of making comparisons between chemicals.

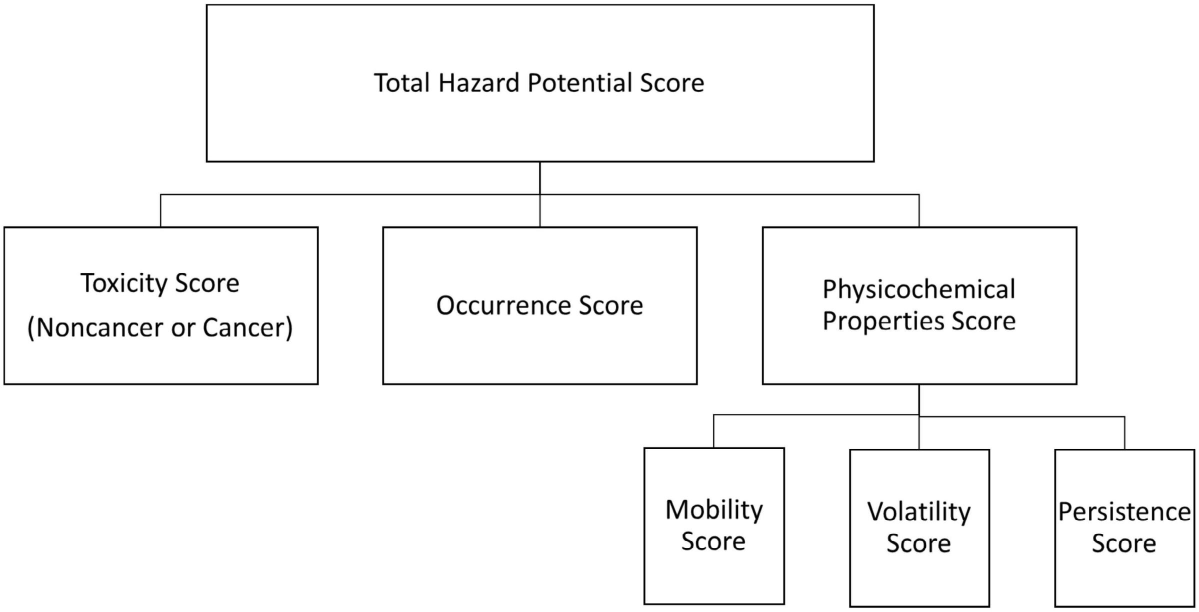

Figure 9-5. Overview of the MCDA framework for hazard evaluation.
Source: Yost et al. (In Press).

9.6.2 Selection of Chemicals for Hazard Evaluation in the MCDA Framework

From the overall list of 1,606 chemicals identified in this assessment, subsets of chemicals were selected for hazard evaluation in the MCDA framework if they had sufficient data for inclusion, using an adaptation of the criteria outlined by Yost et al. (In Press). Specifically, chemicals were selected if they had the following information available:

1. Had a chronic oral RfV or OSF from a US federal source (IRIS, PPRTV, ATSDR, HHBP);
2. Had available data on frequency of use in hydraulic fracturing fluids (data available from the EPA FracFocus 1.0 project database) or measured concentrations in produced water (data available from Appendix E)[1]; and
3. Had data on physicochemical properties available from EPI Suite.

The rationale for applying these criteria is as follows:

1. Federal toxicity values generally undergo more extensive peer review compared to other sources of toxicity values, and are based on the best available scientific information. For this reason, EPA generally prefers to apply RfVs and OSFs from US federal sources for human health risk assessment.
2. Data on frequency of use (in hydraulic fracturing fluids) or measured concentration (in produced water) provide a metric to help assess the likelihood of chemical occurrence in the hydraulic fracturing water cycle.
3. Information on physicochemical properties enables estimation of the likelihood a chemical will be transported in water.

Chemicals used in hydraulic fracturing fluids and chemicals detected in produced water were evaluated separately using the MCDA framework. To explore the different types of toxicity values identified by EPA, two versions of the MCDA were performed on each of these subsets of chemicals: a noncancer MCDA, in which the Toxicity Score is calculated using chronic oral RfVs; and a cancer MCDA, in which the Toxicity Score is calculated using OSFs. For chemicals used in hydraulic fracturing fluids, the noncancer MCDA was repeated for specific subsets of chemicals used in three states that have a significant amount of hydraulic fracturing activity: Texas, Pennsylvania, and North Dakota. Thus, seven iterations of the MCDA were performed: 1-4) noncancer MCDAs for chemicals used in hydraulic fracturing fluids on a national or state-specific basis, 5) a cancer MCDA for chemicals used in hydraulic fracturing fluids, 6) a noncancer MCDA for chemicals detected in produced water, and 7) a cancer MCDA for chemicals detected in produced water.

In total, 42 chemicals used in hydraulic fracturing fluid and 29 chemicals detected in produced water had sufficient information available for inclusion in noncancer MCDAs (Figure 9-6), while 10 chemicals used in hydraulic fracturing fluid and 7 chemicals detected in produced water had sufficient information available for inclusion in cancer MCDAs (Figure 9-7).

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[1] Chemicals in produced water were considered for the MCDA if they had average or median measured concentrations from any of the tables in Appendix E. Chemicals with only a maximum or minimum concentration listed in Appendix E were not considered for the MCDA.

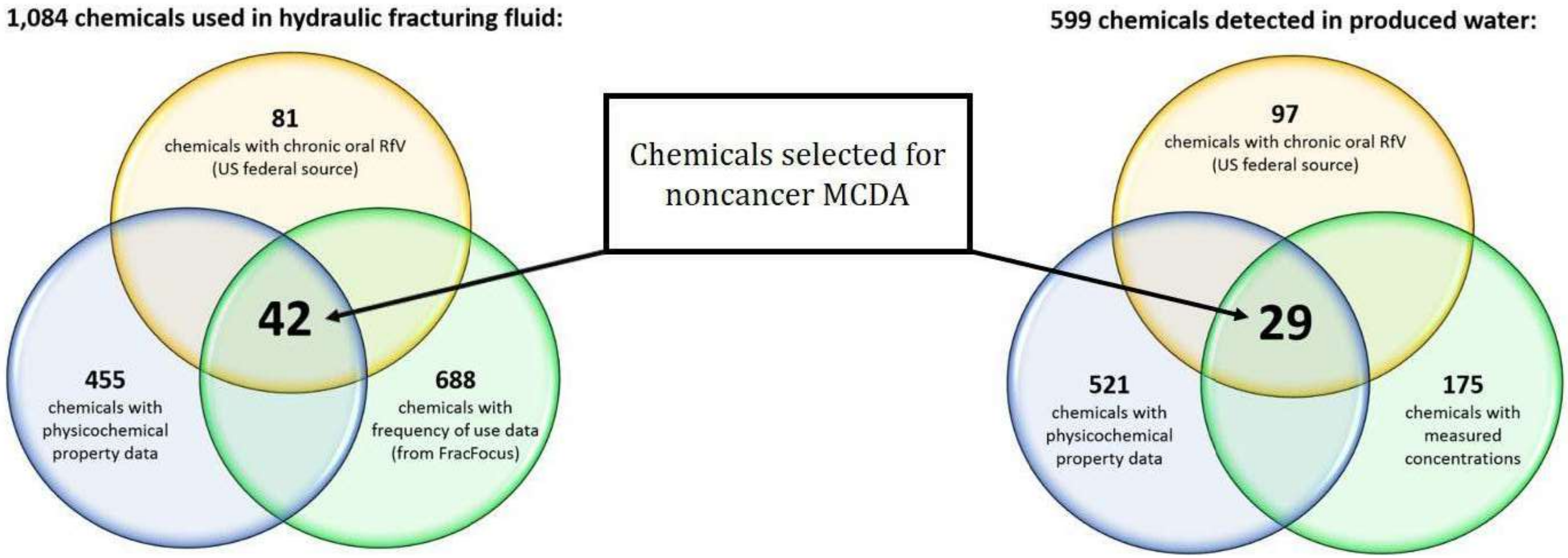

Figure 9-6. The subsets of chemicals selected for hazard evaluation using the noncancer MCDA framework included 42 chemicals used in hydraulic fracturing fluids and 29 chemicals detected in produced water.

For chemicals used in hydraulic fracturing fluids, subsets of these chemicals were also considered in state-specific analyses for Texas (36 chemicals), Pennsylvania (20 chemicals), and North Dakota (21 chemicals).

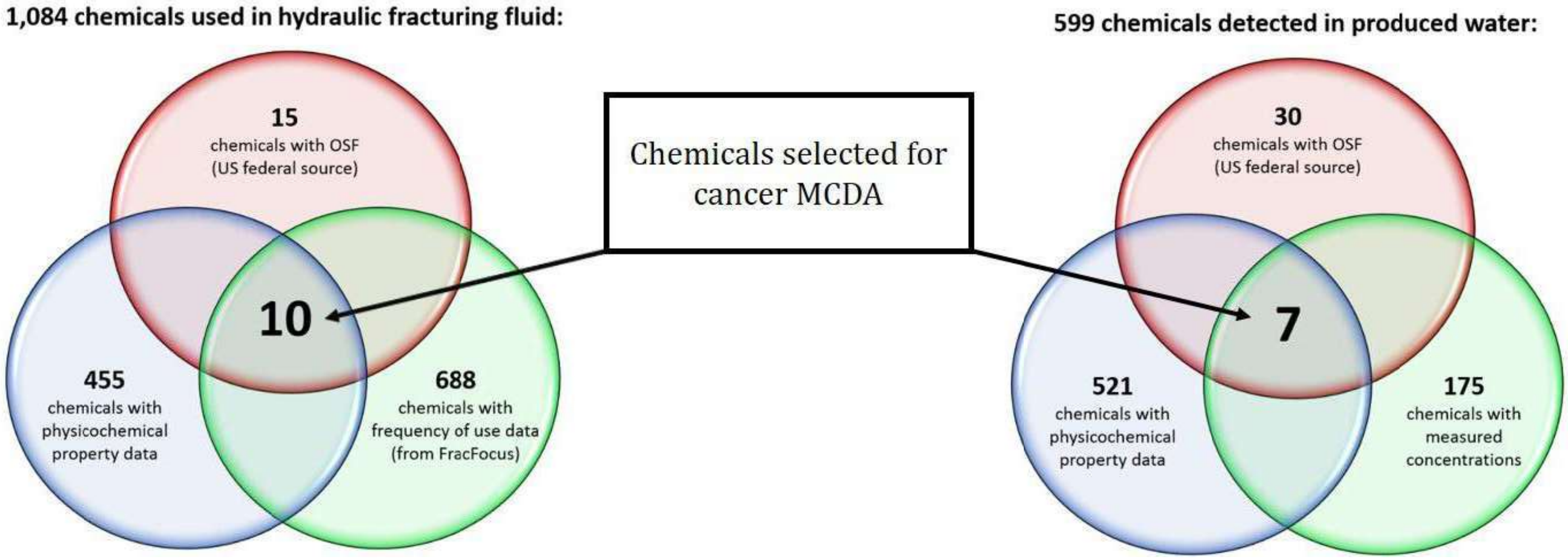

Figure 9-7. The subsets of chemicals selected for hazard evaluation using the cancer MCDA framework included 10 chemicals used in hydraulic fracturing fluids, and 7 chemicals detected in produced water.

9.6.3 Calculation of MCDA Scores

For each iteration of the MCDA, chemicals were assigned scores based on toxicity, occurrence, and physicochemical properties according to the protocol outlined by Yost et al. (In Press). These scores were then standardized to the highest and lowest score within the given subset of chemicals, and then summed to determine a total score and relative ranking for each chemical. The methods used to assign each score and calculate a total score are outlined below.

9.6.3.1 Toxicity Score (Noncancer MCDA)

For each noncancer MCDA, Toxicity Scores were calculated based on chronic oral RfVs from US federal sources (IRIS, PPRTV, ATSDR, and HHBP). If a chemical had a chronic oral RfV available from more than one of these sources, a single value was selected in this order, as described in Section 9.4: HHBP (pesticides), IRIS, PPRTV, ATSDR. Toxicity Scores for the noncancer MCDA were then assigned based on a relative ranking. Within each suite of chemicals considered in this analysis (chemicals used in hydraulic fracturing fluids, or chemicals detected in produced water), RfVs were ranked based on quartiles, and each chemical was assigned a Toxicity Score of 1 to 4 (Table 9-11). 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).

9.6.3.2 Toxicity Score (Cancer MCDA)

For each cancer MCDA, Toxicity Scores were calculated based on OSFs from US federal sources (IRIS, PPRTV, and HHBP). If a chemical had an OSF available from more than one of these sources, a single value was selected in this order, as described in Section 9.4: HHBP (pesticides), IRIS, PPRTV. Toxicity Scores for the cancer MCDA were assigned based on a relative ranking. Within each suite of chemicals considered in this analysis (chemicals used in hydraulic fracturing fluids, or chemicals detected in produced water), OSFs were ranked based on quartiles, and each chemical was assigned a Toxicity Score of 1 to 4 (Table 9-11). 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 of exposure).

9.6.3.3 Occurrence Score

For each of the noncancer and cancer MCDAs, an Occurrence Score was calculated based on the frequency or concentration at which each chemical was reported within the hydraulic fracturing water cycle. For chemicals used in hydraulic fracturing fluids, the Occurrence Score was based on the number of well disclosures for each chemical in the EPA FracFocus 1.0 project database. For chemicals detected in produced water, the Occurrence Score was based on the average or median measured concentration reported in Appendix E. If an average or median concentration of a chemical was reported by multiple studies in Appendix E, the highest of these reported average or median concentrations was used for this calculation. Once a value was determined for each chemical, Occurrence Scores were then assigned based on a relative ranking. Within each suite of chemicals considered in this analysis (chemicals used in hydraulic fracturing fluids, or chemicals detected in produced water), chemical occurrence was ranked based on quartiles, with each chemical assigned an Occurrence Score of 1 to 4 (Table 9-11).

9.6.3.4 Physicochemical Properties Score

For each of the noncancer and cancer MCDAs, a Physicochemical Properties Score was calculated based upon inherent physicochemical properties that describe the likelihood that a chemical will be transported in water. The total Physicochemical Properties Score was calculated as the sum of three subcriteria scores: a Mobility Score, a Volatility Score, and a Persistence Score. The Mobility Score 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. The Volatility Score was assessed based on the Henry's law constant, which describes partitioning of a chemical between water and air. The Persistence Score was assessed based on estimated half-life in water, which describes how long a chemical will remain in water before it is degraded.

For input into the MCDA, experimentally measured physicochemical property values (provided in EPI Suite) were used whenever available. Otherwise, estimated values from EPI Suite were used. To classify these values and assign a score, these numerical values were compared against threshold values (Table 9-11). Each chemical was assigned a Mobility Score, Volatility Score, and Persistence Score (each on a scale of 1 to 4), which were then summed to calculate the Physicochemical Properties Score. The threshold values in Table 9-11 are based upon previously published values employed by existing exposure assessment models, including the EPA's Design for the Environment Alternatives Assessment Criteria for Hazard Evaluation (U.S. EPA, 2011b), the EPA's Pollution Prevention (P2) Framework (U.S. EPA, 2012i), and a peer-reviewed publication by Mitchell et al. (2013b). More details on the Physicochemical Properties Score calculation are provided in the Chapter 9 Annex, Section 9.8.1.

9.6.4 Total Hazard Potential Score

Within each iteration of the MCDA, 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, or Physicochemical Properties) falls on a scale of 0 to 1, and represents a relative ranking within the given subset of chemicals.

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. Examples of the Total Hazard Potential Score calculation can be found in the Chapter 9 Annex, Section 9.8.2.

Table 9-11. Thresholds used for developing the Toxicity Score, Occurrence Score, and Physicochemical Properties Score in this MCDA framework.
Adapted from Yost et al. (In Press).

Criteria	**Sub-criteria**	**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 (% of disclosures in EPA's FracFocus 1.0 project database) or Measured concentration in produced water (µg/L; Appendix E)	<1st quartile	≥1st quartile to <2nd quartile	≥2nd quartile to <3rd quartile	≥3rd quartile
Physico-chemical 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 $\leq 10^{-1}$	$>10^{-5}$ to $\leq 10^{-3}$	$\leq 10^{-5}$
	Persistence	Half-life in water (days)	<16	≥16 to <60	≥60 to <180	≥180

9.6.5 MCDA Results

For each iteration of the MCDA, we first present the data used for input into the MCDA, including data on toxicity, occurrence, and physicochemical properties. We then present the results of each MCDA, which show a relative ranking of chemicals based on integration of these data. Lastly, we discuss the key limitations of this MCDA approach, which is intended as a preliminary analysis only.

9.6.5.1 Results: Noncancer MCDA for Chemicals Used in Hydraulic Fracturing Fluids

A total of 42 chemicals used in hydraulic fracturing fluids were evaluated in a noncancer MCDA (Table 9-12). Chronic oral RfVs within this suite of chemicals range from 0.001−20 mg/kg-day, with (E)-crotonaldehyde having the lowest chronic oral RfV and 1,2-propylene glycol having the highest. These RfVs were derived based on health effects including immune system effects, changes in body weight, changes in blood chemistry, cardiotoxicity, neurotoxicity, liver and kidney toxicity, and reproductive and developmental toxicity. The total UFs used in the derivation of these chronic oral RfVs (Table 9-12) reflect varying degrees of confidence surrounding the data sets for these chemicals. Three of the chemicals with the lowest chronic oral RfVs [(E)-crotonaldehyde, propargyl alcohol, benzyl chloride] have total UFs of 3000, indicating a relatively large amount of uncertainty in these values. Comparatively, chemicals such as benzene, acrylamide, and dichloromethane also have low chronic oral RfVs, but with much less uncertainty reflected in the values.

Figure 9-8 presents the results of a noncancer MCDA for these 42 chemicals in hydraulic fracturing fluids. Of these 42 chemicals, propargyl alcohol received the highest overall Total Hazard Potential Score. Propargyl alcohol was reported in 33% of disclosures nationally in the EPA FracFocus 1.0 project database, making it one of the most widely used chemicals that was considered in this analysis. It has physicochemical properties that are conducive to transport in water, and a low RfV. Given these properties, propargyl alcohol received the highest overall ranking based on hazard potential across all of the metrics that were considered in the MCDA.

Several of the other chemicals that received high Occurrence Scores also received among the highest Total Hazard Potential Scores, including 2-butoxyethanol, naphthalene, 1,2,4-trimethylbenzene, N,N-dimethylformamide, and formaldehyde (reported in 23%, 19%, 13%, 9%, and 7% of disclosures, respectively). Methanol, ethylene glycol, and formic acid (73%, 47%, and 11% of disclosures, respectively) received lower Total Hazard Potential Scores as a result of having higher RfVs. Likewise, didecyldimethylammonium chloride and dodecylbenzenesulfonic acid (8% and 7% of disclosures, respectively) received lower Total Hazard Potential Scores as a result of having higher RfVs and more hydrophobic properties.

The other chemicals that received high Toxicity Scores (i.e., had low chronic oral RfVs) received moderate to high Total Hazard Potential Scores overall. Acrylamide was reported in only 1% of disclosures, but has physicochemical properties that are very conducive to transport in water, and therefore received one of the highest overall Total Hazard Potential Scores. 1,2,4-Trimethylbenzene, benzyl chloride, and epichlorohydrin (13%, 6%, and 1% of disclosures in the EPA FracFocus 1.0 project database, respectively) scored slightly lower than acrylamide with regards to physicochemical properties. Other chemicals, including 1,2,3-trimethylbenzene, 1,3,5-trimethylbenzene, (E)-crotonaldehyde, benzene, dichloromethane, aniline, furfural, and 2-(Thiocyanomethylthio)benzothiazole, received lower overall scores because they are used more infrequently (the trimethylbenzenes were reported in <1% of disclosures, and the rest reported in <0.1% of disclosures).

9.6.5.2 Results: Noncancer MCDA for Chemicals Used in Hydraulic Fracturing Fluids (State-specific analysis for Texas, Pennsylvania, and North Dakota)

To investigate the extent of regional differences and examine the applicability of the MCDA model at the regional scale, we repeated the noncancer MCDA for hydraulic fracturing fluids for subsets of chemicals used in three representative states that have a significant amount of hydraulic fracturing activity: Texas, Pennsylvania, and North Dakota. The chemicals used in these state-specific analyses are subsets of the chemicals used nationally, and are indicated in Table 9-12. Some of the chemicals considered in the national analysis were not included in the state-specific analyses because they were not disclosed to FracFocus 1.0 as used in these states.

Results are presented in Figure 9-9 (Texas), Figure 9-10 (Pennsylvania), and Figure 9-11 (North Dakota). By comparing these results to each other and to the national noncancer MCDA (Figure 9-8), 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, 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 1,2,4-trimethylbenzene. Other chemicals receiving high Toxicity Scores in these states include epichlorohydrine (Texas and Pennsylvania), 1,3,5-Trimethylbenzene (Texas and Pennsylvania), 1,4-dioxane (North Dakota), naphthalene (North Dakota), benzene, aniline, and 1,2,3-Trimethylbenzene (Texas).

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

The results of these state-specific MCDAs support the concept presented in Chapter 5 that there is no single hydraulic fracturing fluid formulation, and that the chemicals of most potential concern will vary between regions or even between wells.

Table 9-12. Data on the selected subset of chemicals in hydraulic fracturing fluids used for input into a noncancer MCDA.
Chemicals within the table are ordered from most toxic to least toxic based on chronic oral RfV.

		Noncancer toxicity (chronic oral RfV)[a]			% disclosures in EPA FracFocus 1.0 project database[b]				Mobility			Volatility	Persist-ence
Chemical Name	**CASRN**	**RfV (mg/ kg-day)**	**Total UF**	**Source**	**National**	**TX**	**PA**	**ND**	**Log K_{OW}**	**Log K_{OC}**	**Solu-bility (mg/L)**	**Henry's Law Constant**	**Half-life in water (days)**
(E)-Crotonaldehyde	123-73-9	0.001	3000	PPRTV	0.06%				0.6	0.254	41480	1.94E-05	15
Propargyl alcohol	107-19-7	0.002	3000	IRIS	33%	39%	58%	1%	-0.38	0.28	935500	1.15E-06	15
Benzyl chloride	100-44-7	0.002	3000	PPRTV	6%	7%	5%	0.80%	2.3	2.649	1030	4.12E-04	15
Acrylamide	79-06-1	0.002	30	IRIS	1%	2%	1%	1%	-0.67	0.755	504000	1.70E-09	15
Benzene	71-43-2	0.004	300	IRIS	0.006%	0.01%			2.13	1.75	2000	5.55E-03	37.5
Epichlorohydrin	106-89-8	0.006	1000	PPRTV	1%	0.20%	0.08%		0.45	1	50630	3.04E-05	15
Dichloromethane	75-09-2	0.006	30	IRIS	0.02%				1.25	1.44	10950	3.25E-03	37.5
Aniline	62-53-3	0.007	1000	PPRTV	0.02%	0.05%			0.9	1.6	20820	2.02E-06	15
1,2,4-Trimethylbenzene	95-63-6	0.01	300	IRIS	13%	11%	1%	25%	3.63	2.788	79.59	6.16E-03	37.5
1,3,5-Trimethylbenzene	108-67-8	0.01	300	IRIS	0.5%	0.80%	1%		3.42	2.82	120.3	8.77E-03	37.5
1,2,3-Trimethylbenzene	526-73-8	0.01	300	IRIS	0.4%	0.80%			3.66	2.8	75.03	4.36E-03	37.5
2-(Thiocyanomethyl-thio)benzothiazole	21564-17-0	0.01	300	HHBP	0.006%				3.3	3.528	41.67	6.49E-12	37.5
Furfural	98-01-1	0.01	3000	HHBP	0.003%				0.41	0.784	53580	3.77E-06	15
Naphthalene	91-20-3	0.02	3000	IRIS	19%	14%	1%	43%	3.3	2.96	142.1	4.40E-04	37.5

		Noncancer toxicity (chronic oral RfV)[a]			% disclosures in EPA FracFocus 1.0 project database[b]				Mobility			Volatility	Persistence
Chemical Name	**CASRN**	**RfV (mg/ kg-day)**	**Total UF**	**Source**	**National**	**TX**	**PA**	**ND**	**Log K_{OW}**	**Log K_{OC}**	**Solubility (mg/L)**	**Henry's Law Constant**	**Half-life in water (days)**
Chlorobenzene	108-90-7	0.02	1000	IRIS	0.003%	0.01%			2.84	2.15	400.5	3.11E-03	15
2-(2-Butoxyethoxy) ethanol	112-34-5	0.03	3000	PPRTV	0.6%	0.40%	4%		0.56	1	71920	7.20E-09	8.67
1,4-Dioxane	123-91-1	0.03	300	IRIS	0.3%	0.50%		0.80%	-0.27	0.421	213900	4.80E-06	15
1,3-Dichloropropene	542-75-6	0.03	100	IRIS	0.02%				2.04	1.82	1994	3.55E-03	37.5
Bisphenol A	80-05-7	0.05	1000	IRIS	0.006%	0.01%			3.32	4.576	172.7	9.16E-12	37.5
Toluene	108-88-3	0.08	3000	IRIS	0.7%	1%			2.73	2.07	573.1	6.64E-03	15
Ethylenediamine	107-15-3	0.09	100	PPRTV	0.01%	0.02%			-2.04	1.172	1000000	1.73E-09	15
2-Butoxyethanol	111-76-2	0.1	10	IRIS	23%	27%	21%	15%	0.83	0.451	64470	1.60E-06	8.67
N,N-Dimethylformamide	68-12-2	0.1	1000	PPRTV	9%	10%	11%	0.60%	-1.01	0	977900	7.39E-08	15
Didecyldimethylammonium chloride	7173-51-5	0.1	100	HHBP	8%	7%	12%	0.05%	4.66	5.546	0.9	6.85E-10	15
1-Butanol	71-36-3	0.1	1000	IRIS	1%	2%		0.70%	0.88	0.5	76700	8.81E-06	8.67
Cumene	98-82-8	0.1	1000	IRIS	0.5%	0.80%	1%		3.66	2.844	75.03	1.15E-02	15
Ethylbenzene	100-41-4	0.1	1000	IRIS	0.4%	0.50%		0.10%	3.15	2.23	228.6	7.88E-03	15
Acetophenone	98-86-2	0.1	3000	IRIS	0.04%	0.04%			1.58	1.8	4484	1.04E-05	15
Formaldehyde	50-00-0	0.2	100	IRIS	7%	8%	4%	8%	0.35	0	57020	3.37E-07	15
Xylenes	1330-20-7	0.2	1000	IRIS	2%	3%	1%	0.20%	3.2	2.25	207.2	7.18E-03	15

		Noncancer toxicity (chronic oral RfV)[a]			% disclosures in EPA FracFocus 1.0 project database[b]				Mobility			Volatility	Persist-ence
Chemical Name	CASRN	RfV (mg/ kg-day)	Total UF	Source	National	TX	PA	ND	Log K_{OW}	Log K_{OC}	Solu-bility (mg/L)	Henry's Law Constant	Half-life in water (days)
o-Xylene	95-47-6	0.2	30	ATSDR	0.05%	0.1%			3.12	2.25	224.1	5.18E-03	15
Phenol	108-95-2	0.3	300	IRIS	0.4%	0.80%		0.05%	1.46	1.9	26160	3.33E-07	15
2-Methyl-1-propanol	78-83-1	0.3	1000	IRIS	0.3%			4%	0.76	0.465	97120	9.78E-06	15
Dodecylbenzenesulfonic acid	27176-87-0	0.5	100	HHBP	7%	10%	2%	8%	4.71	4.066	0.8126	6.27E-08	15
Formic acid	64-18-6	0.9	300	PPRTV	11%	14%	8%	11%	-0.54	0	955200	1.67E-07	8.67
Ethyl acetate	141-78-6	0.9	1000	IRIS	0.4%	0.70%			0.73	0.747	29930	1.34E-04	15
Acetone	67-64-1	0.9	1000	IRIS	0.2%	0.02%		1%	-0.24	0.374	219900	3.50E-05	15
Methanol	67-56-1	2	100	IRIS	73%	80%	69%	54%	-0.77	0.44	1000000	4.55E-06	8.67
Ethylene glycol	107-21-1	2	100	IRIS	47%	60%	35%	37%	-1.36	0	1000000	6.00E-08	8.67
Hexanedioic acid	124-04-9	2	300	PPRTV	0.70%	1%			0.08	1.386	167300	4.71E-12	8.67
Benzoic acid	65-85-0	4	1	IRIS	0.06%	0.10%	0.04%		1.87	1.5	2493	3.81E-08	15
1,2-Propylene glycol	57-55-6	20	300	PPRTV	4%	4%	8%	8%	-0.92	0.36	811100	1.29E-08	8.67

CASRN = Chemical Abstract Service Registry Number; 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; K_{OW} = octanol-water partitioning coefficient; K_{OC} = soil adsorption coefficient

[a] Reference value (RfV): An estimate of an exposure for a given duration to the human population (including susceptible subgroups) that is likely to be without an appreciable risk of adverse health effects over a lifetime. RfVs considered in the MCDA include chronic oral reference doses (RfD) from IRIS, PPRTV, and HHBP; and chronic oral minimal risk levels (MRLs) from ATSDR.

[b] The FracFocus frequency of use data presented in this chapter is based on 35,957 FracFocus disclosures that were deduplicated, within the study time period (January 1, 2011 to February 28, 2013), and with ingredients that have a valid CASRN.

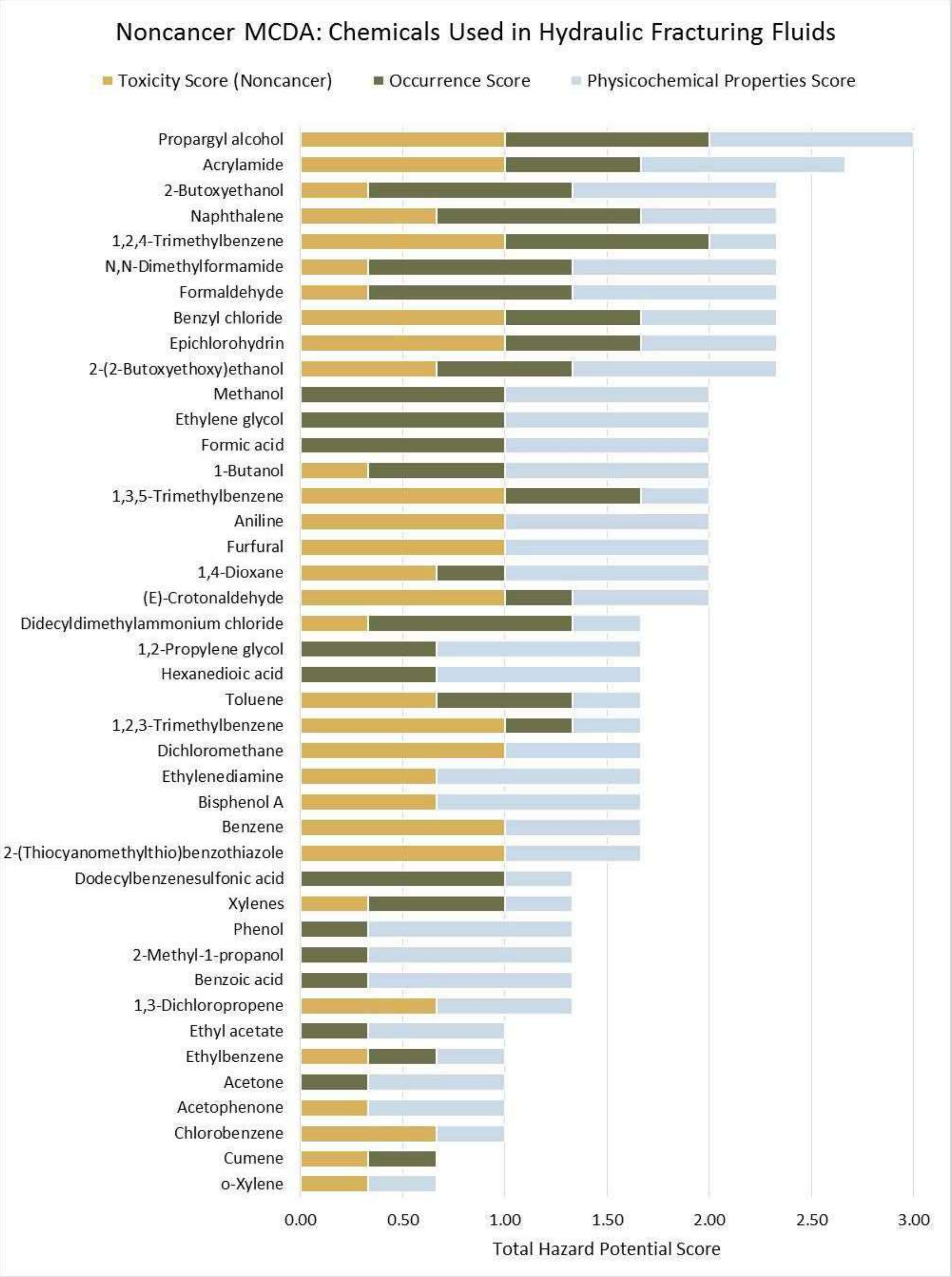

Figure 9-8. Noncancer MCDA results for 42 chemicals used in hydraulic fracturing fluids (national analysis), showing the Toxicity Score, Occurrence Score, and Physicochemical Properties Score for each chemical.

Chemicals are ordered from high to low based on Total Hazard Potential Score. See Section 9.6.4 for details on the calculation.

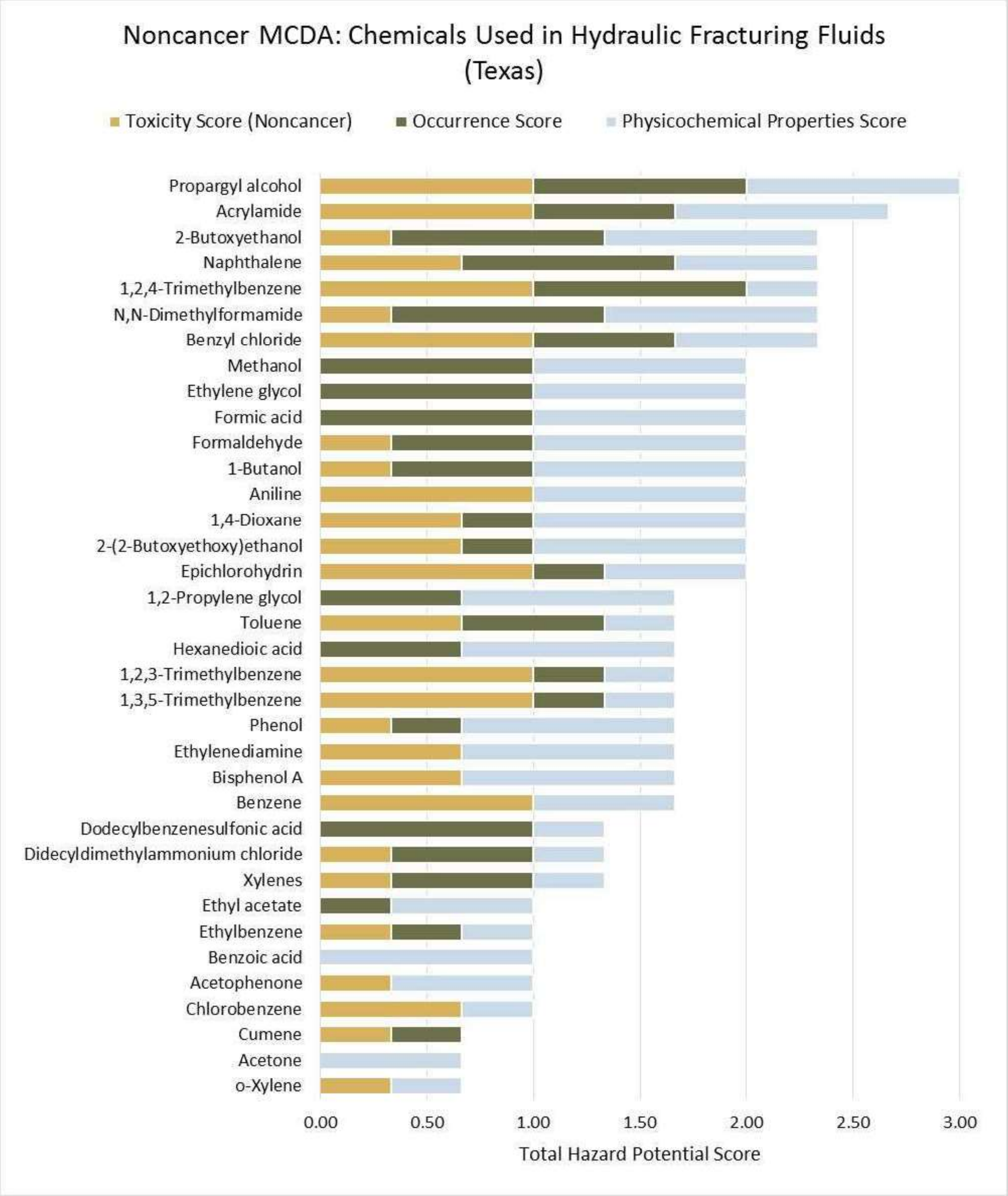

Figure 9-9. Noncancer MCDA results for 36 chemicals used in hydraulic fracturing fluids in Texas (state-specific analysis), showing the Toxicity Score, Occurrence Score, and Physicochemical Properties Score for each chemical.

Chemicals are ordered from high to low based on Total Hazard Potential Score. See Section 9.6.4 for details on the calculation.

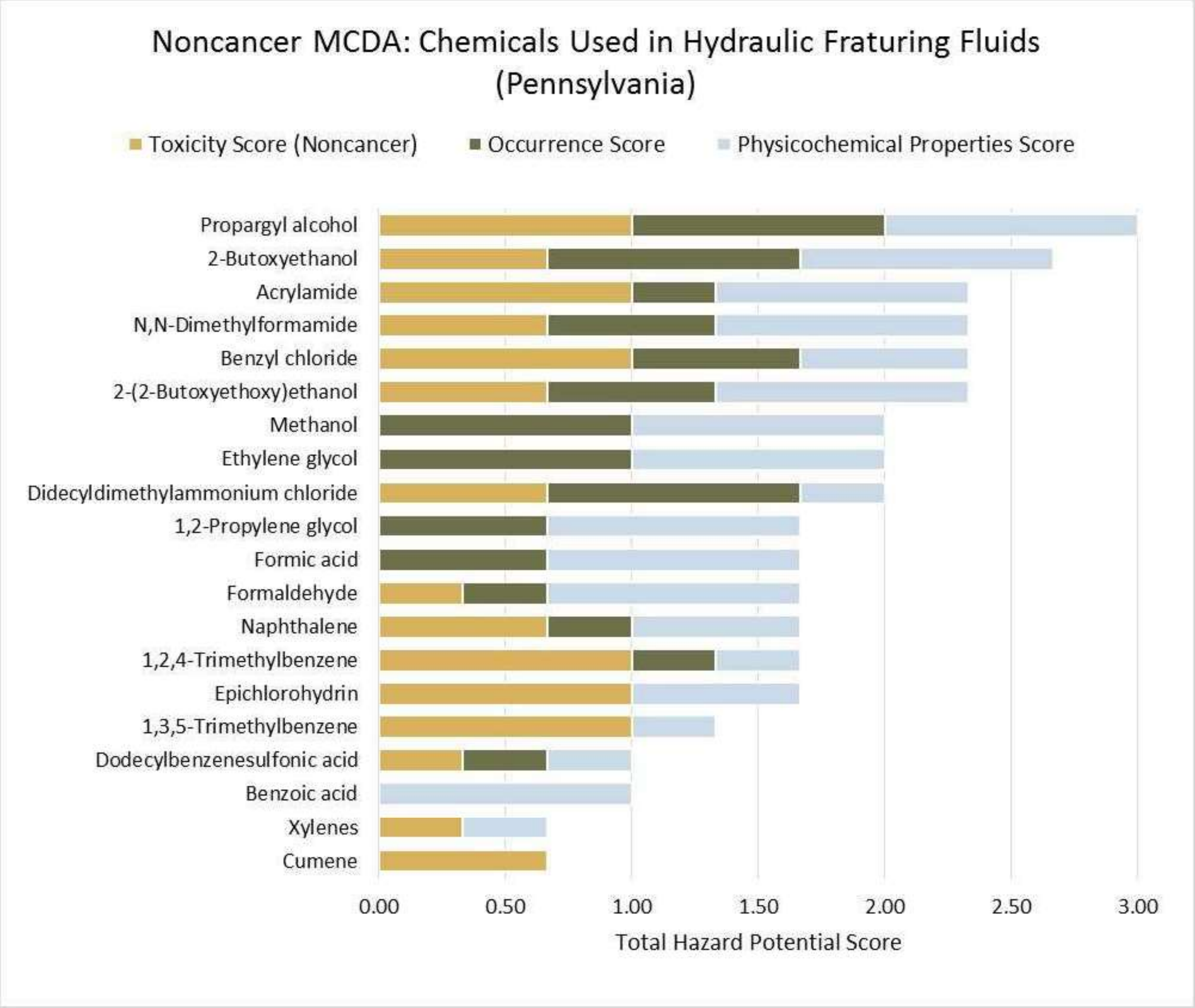

Figure 9-10. Noncancer MCDA results for 20 chemicals used in hydraulic fracturing fluids in Pennsylvania (state-specific analysis), showing the Toxicity Score, Occurrence Score, and Physicochemical Properties Score for each chemical.

Chemicals are ordered from high to low based on Total Hazard Potential Score. See Section 9.6.4 for details on the calculation.

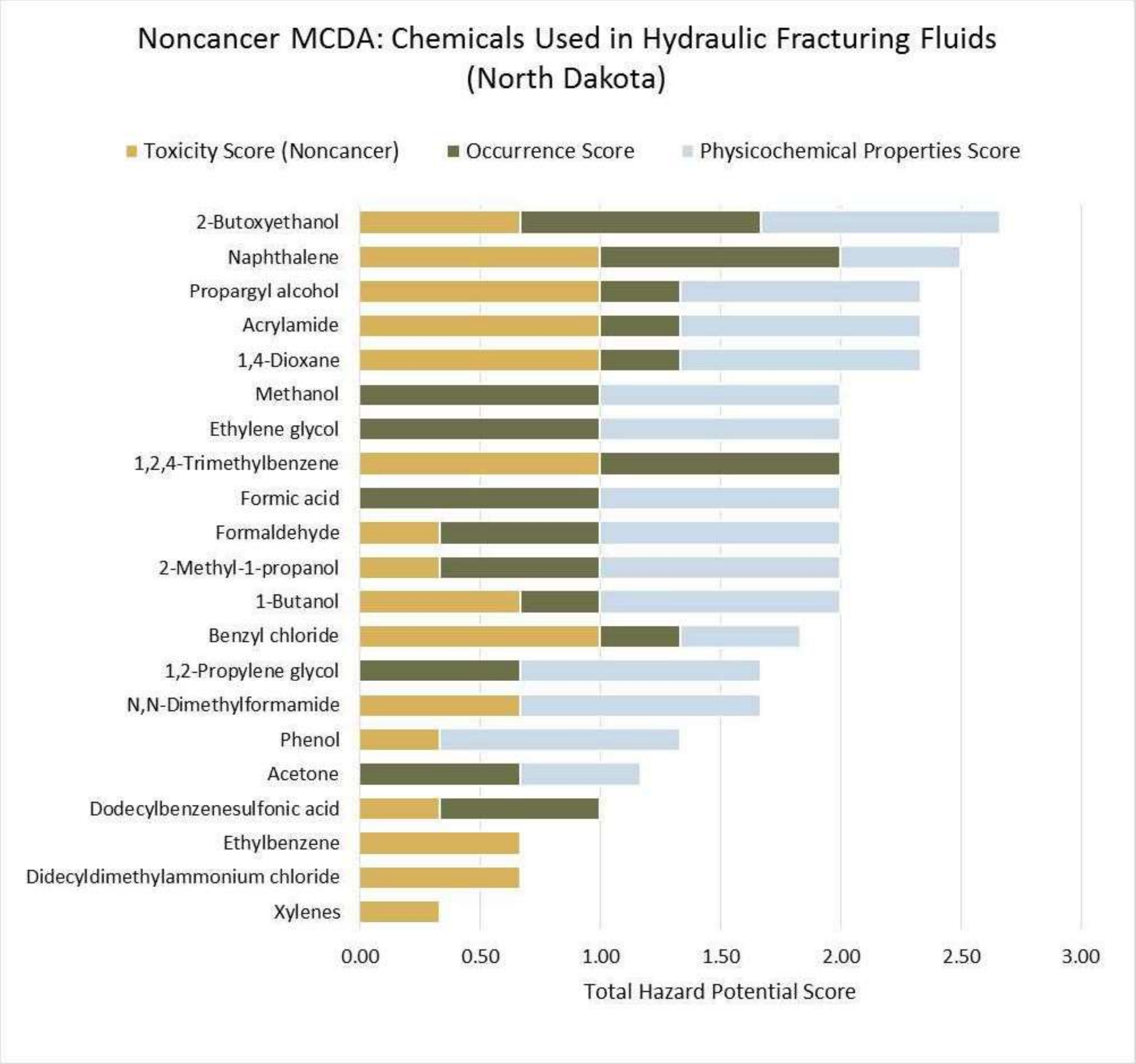

Figure 9-11. Noncancer MCDA results for 21 chemicals used in hydraulic fracturing fluids in North Dakota (state-specific analysis), showing the Toxicity Score, Occurrence Score, and Physicochemical Properties Score for each chemical.

Chemicals are ordered from high to low based on Total Hazard Potential Score. See Section 9.6.4 for details on the calculation.

9.6.5.3 Results: Cancer MCDA for Chemicals Used in Hydraulic Fracturing Fluids

A total of 10 chemicals used in hydraulic fracturing fluids were evaluated in a cancer MCDA (Table 9-13). OSFs for these chemicals ranged from 0.002 to 3 per mg/kg-day, with quinoline having the highest OSF, and dichloromethane having the lowest. Benzene is the only one of these chemicals that is classified as a known human carcinogen by at least one of the sources in Table 9-1, while the other chemicals in this subset are classified as probable carcinogens in humans (Appendix Table G-1e).

Figure 9-12 presents the results from the cancer MCDA for chemicals used in hydraulic fracturing fluids. Of the 10 chemicals that were considered in this analysis, 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 1% of disclosures nationally in the EPA FracFocus 1.0 project database. This nevertheless places acrylamide in the top quartile in terms of frequency of use, as none of the chemicals within this subset were used with great frequency on a national basis.

Bis(2-chloroethyl)ether and quinoline, which are the two most potent carcinogens considered in the analysis and received high Toxicity Score, received the second and third highest Total Hazard Potential Scores within this suite of chemicals. Bis(2-chloroethyl)ether was reported in 0.7% of disclosures, while quinoline was reported in 0.02% of disclosures. Both are expected to be readily transported in water.

In addition to acrylamide, the other two chemicals receiving high Occurrence Scores were benzyl chloride and epichlorohydrin (6% and 1% of disclosures, respectively). 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 received lower Physicochemical Properties Scores relative to other chemicals in this analysis, due in part to volatility.

Table 9-13. Data on the selected subset of chemicals in hydraulic fracturing fluids used for input into a cancer MCDA.
Chemicals within the table are ordered from most potent to least potent based on OSF.

		Cancer-specific toxicity (OSF)[a]		% disclosures in EPA FracFocus 1.0 project database[b]	Mobility			Volatility	Persistence
Chemical Name	**CASRN**	**OSF (per mg/kg-day)**	**Source**	**National**	**Log K_{OW}**	**Log K_{OC}**	**Solubility (mg/L)**	**Henry's Law Constant**	**Half-life in water (days)**
Quinoline	91-22-5	3	IRIS	0.02%	2.03	3.1	1711	1.67E-06	15
Bis(2-chloroethyl) ether	111-44-4	1.1	IRIS	0.7%	1.29	1.88	6435	1.70E-05	37.5
Acrylamide	79-06-1	0.5	IRIS	1%	-0.67	0.755	504000	1.70E-09	15
Benzyl chloride	100-44-7	0.17	IRIS	6%	2.3	2.649	1030	4.12E-04	15
1,4-Dioxane	123-91-1	0.1	IRIS	0.3%	-0.27	0.421	213900	4.80E-06	15
Benzene	71-43-2	0.015-0.055[c]	IRIS	0.006%	2.13	1.75	2000	5.55E-03	37.5
1,3-Dichloropropene	542-75-6	0.05	IRIS	0.02%	2.04	1.82	1994	3.55E-03	37.5
Epichlorohydrin	106-89-8	0.0099	IRIS	1%	0.45	1	50630	3.04E-05	15
Aniline	62-53-3	0.0057	IRIS	0.02%	0.9	1.6	20820	2.02E-06	15
Dichloromethane	75-09-2	0.002	IRIS	0.02%	1.25	1.44	10950	3.25E-03	37.5

CASRN = Chemical Abstract Service Registry Number; IRIS = Integrated Risk Information System; K_{OW} = octanol-water partitioning coefficient; K_{OC} = soil adsorption coefficient

[a] Oral slope factor (OSF): 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 units of 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 less than 1 in 100. OSFs considered in the MCDA include values from IRIS, PPRTV, and HHBP.

[b] The FracFocus frequency of use data presented in this chapter is based on 35,957 FracFocus disclosures that were deduplicated, within the study time period (January 1, 2011 to February 28, 2013), and with ingredients that have a valid CASRN.

[c] IRIS lists the OSF for benzene as a range from 0.015 to 0.055 per mg/kg-day. For input into the MCDA, we used the high end of this range (0.055 per mg/kg-day).

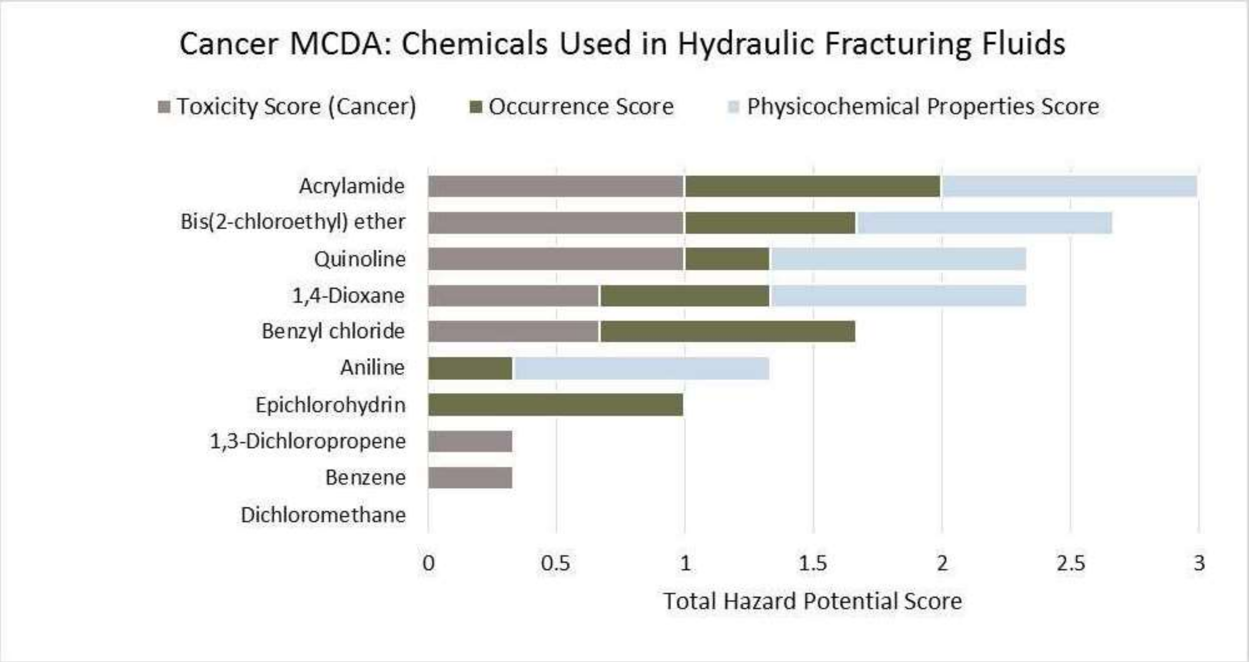

Figure 9-12. Cancer MCDA results for 10 chemicals used in hydraulic fracturing fluids, showing the Toxicity Score, Occurrence Score, and Physicochemical Properties Score for each chemical.

Chemicals are ordered from high to low based on Total Hazard Potential Score. See Section 9.6.4 for details on the calculation.

9.6.5.4 Results: Noncancer MCDA for Chemicals in Produced Water

A total of 29 chemicals detected in produced water were evaluated in a noncancer MCDA (Table 9-14). Of these 29 chemicals, 13 were also included in the noncancer MCDA for hydraulic fracturing fluids. Chronic oral RfVs within this suite of chemicals range from 0.001 to 0.9 mg/kg-day, with pyridine having the lowest chronic oral RfV, and acetone having the highest. Chronic oral exposure to these chemicals may induce a variety of adverse outcomes, including immune system effects, changes in body weight, changes in blood chemistry, pulmonary toxicity, neurotoxicity, liver and kidney toxicity, and reproductive and developmental toxicity. The total UFs used in the derivation of these chronic oral RfVs (Table 9-14) reflect varying degrees of confidence surrounding the data sets for these chemicals.

Figure 9-13 presents the results of a noncancer MCDA for these 29 chemicals detected in produced water. Benzene, pyridine, and naphthalene received the highest Total Hazard Potential Scores, followed by 2-methylnaphthalene. These four chemicals all received high Toxicity Scores and high Occurrence Scores (with maximum average concentrations of 1500 µg/L, 413 µg/L, 238 µg/L, and 1362 µg/L in Barnett, Marcellus, or Powder River Basin produced water, respectively), but received moderate to low Physicochemical Property Scores.

Table 9-14. Data on the selected subset of chemicals detected in produced water used for input into a noncancer MCDA.
Chemicals within the table are ordered from most toxic to least toxic based on chronic oral RfV.

		Noncancer toxicity (chronic oral RfV)[a]			Occurrence (concentration in produced water)[b]		Mobility			Volatility	Persistence
Chemical Name	**CASRN**	**RfV (mg/kg-day)**	**Total UF**	**Source**	**Average or Median Conc. (µg/L)**	**Reference**	**Log K_{OW}**	**Log K_{OC}**	**Solubility (mg/L)**	**Henry's Law Constant**	**Half-life in water (days)**
Pyridine	110-86-1	0.001	1000	IRIS	413	Table E-11	0.65	1.6	729800	1.10E-05	15
Benzene	71-43-2	0.004	300	IRIS	1500	Table E-13	2.13	1.75	2000	5.55E-03	37.5
2-Methylnaphthalene	91-57-6	0.004	1000	IRIS	1362	Table E-11	3.86	3.6	41.42	5.18E-04	15
1,2,4-Trimethylbenzene	95-63-6	0.01	300	IRIS	173	Table E-11	3.63	2.788	79.59	6.16E-03	37.5
1,3,5-Trimethylbenzene	108-67-8	0.01	300	IRIS	59	Table E-11	3.42	2.82	120.3	8.77E-03	37.5
Chloroform	67-66-3	0.01	1000	IRIS	28	Table E-11	1.97	1.6	2096	3.67E-03	37.5
Tributyl phosphate	126-73-8	0.01	1000	PPRTV	0.26	Table E-12	4	3.371	7.355	1.41E-06	8.67
Naphthalene	91-20-3	0.02	3000	IRIS	238	Table E-11	3.3	2.96	142.1	4.40E-04	37.5
Di(2-ethylhexyl) phthalate[c]	117-81-7	0.02	1000	IRIS	210	Table E-11	7.6	4.94	0.001132	2.70E-07	15
Chlorobenzene[d]	108-90-7	0.02	1000	IRIS	100	Table E-13	2.84	2.15	400.5	3.11E-03	15
2,4-Dimethylphenol	105-67-9	0.02	3000	IRIS	14.5	Table E-11	2.3	2.692	4068	9.51E-07	15
Pyrene	129-00-0	0.03	3000	IRIS	13	Table E-11	4.88	4.9	0.2249	1.19E-05	60
1,4-Dioxane	123-91-1	0.03	300	IRIS	6.5	Table E-11	-0.27	0.421	213900	4.80E-06	15
Fluorene	86-73-7	0.04	3000	IRIS	8.4	Table E-11	4.1	3.614	20.13	1.59E-03	15
Fluoranthene	206-44-0	0.04	3000	IRIS	6.1	Table E-11	5.16	4.8	0.1297	8.86E-06	60
o-Cresol[e]	95-48-7	0.05	1000	IRIS	28.3	Table E-11	1.95	2.486	9066	1.20E-06	15
Toluene	108-88-3	0.08	3000	IRIS	760	Table E-9	2.73	2.07	573.1	6.64E-03	15

		Noncancer toxicity (chronic oral RfV)[a]			Occurrence (concentration in produced water)[b]		Mobility			Volatility	Persist-ence
Chemical Name	**CASRN**	**RfV (mg/kg-day)**	**Total UF**	**Source**	**Average or Median Conc. (µg/L)**	**Reference**	**Log K_{OW}**	**Log K_{OC}**	**Solubility (mg/L)**	**Henry's Law Constant**	**Half-life in water (days)**
Ethylbenzene	100-41-4	0.1	1000	IRIS	2010	Table E-13	3.15	2.23	228.6	7.88E-03	15
Carbon disulfide	75-15-0	0.1	100	IRIS	400	Table E-11	1.94	1.337	2928	1.44E-02	15
Cumene[f]	98-82-8	0.1	1000	IRIS	120	Table E-11	3.66	2.844	75.03	1.15E-02	15
Benzyl alcohol	100-51-6	0.1	1000	PPRTV	81.5	Table E-11	1.1	1.1	41050	3.37E-07	15
Dibutyl phthalate[g]	84-74-2	0.1	1000	IRIS	41	Table E-11	4.5	3.14	2.351	1.81E-06	8.67
Acetophenone	98-86-2	0.1	3000	IRIS	13	Table E-11	1.58	1.8	4484	1.04E-05	15
Diphenylamine	122-39-4	0.1	100	HHBP	5.3	Table E-11	3.5	2.78	63.61	2.69E-06	37.5
Xylenes	1330-20-7	0.2	1000	IRIS	360	Table E-9	3.2	2.25	207.2	7.18E-03	15
Benzyl butyl phthalate	85-68-7	0.2	1000	IRIS	34.3	Table E-11	4.73	3.72	0.9489	1.26E-06	0.04
Phenol	108-95-2	0.3	300	IRIS	63	Table E-11	1.46	1.9	26160	3.33E-07	15
Caprolactam	105-60-2	0.5	100	IRIS	0.75	Table E-12	0.66	1.3892	28720	2.53E-08	14508
Acetone	67-64-1	0.9	1000	IRIS	145	Table E-10	-0.24	0.374	219900	3.50E-05	15

CASRN = Chemical Abstract Service Registry Number; IRIS = Integrated Risk Information System; PPRTV = Provisional Peer Reviewed Toxicity Values; HHBP = Human Health Benchmarks for Pesticides; K_{OW} = octanol-water partitioning coefficient; K_{OC} = soil adsorption coefficient

[a] Reference value (RfV): An estimate of an exposure for a given duration to the human population (including susceptible subgroups) that is likely to be without an appreciable risk of adverse health effects over a lifetime. RfVs considered in the MCDA include chronic oral reference doses (RfD) from IRIS, PPRTV, and HHBP; and chronic oral minimal risk levels (MRLs) from ATSDR.

[b] From Appendix E.

[c] Di(2-ethylhexyl) phthalate is listed under the name bis(2-ethylhexyl) phthalate in Appendix Table E-11.

[d] Chlorobenzene is listed under the name chloro-benzene in Appendix Table E-13.

[e] o-Cresol is listed under the name 2-methylphenol in Appendix Table E-11.

[f] Cumene is listed under the name isopropylbenzene in Appendix Table E-11.

[g] Dibutyl phthalate is listed under the name dibutyl-n-phthalate in Appendix Table E-11.

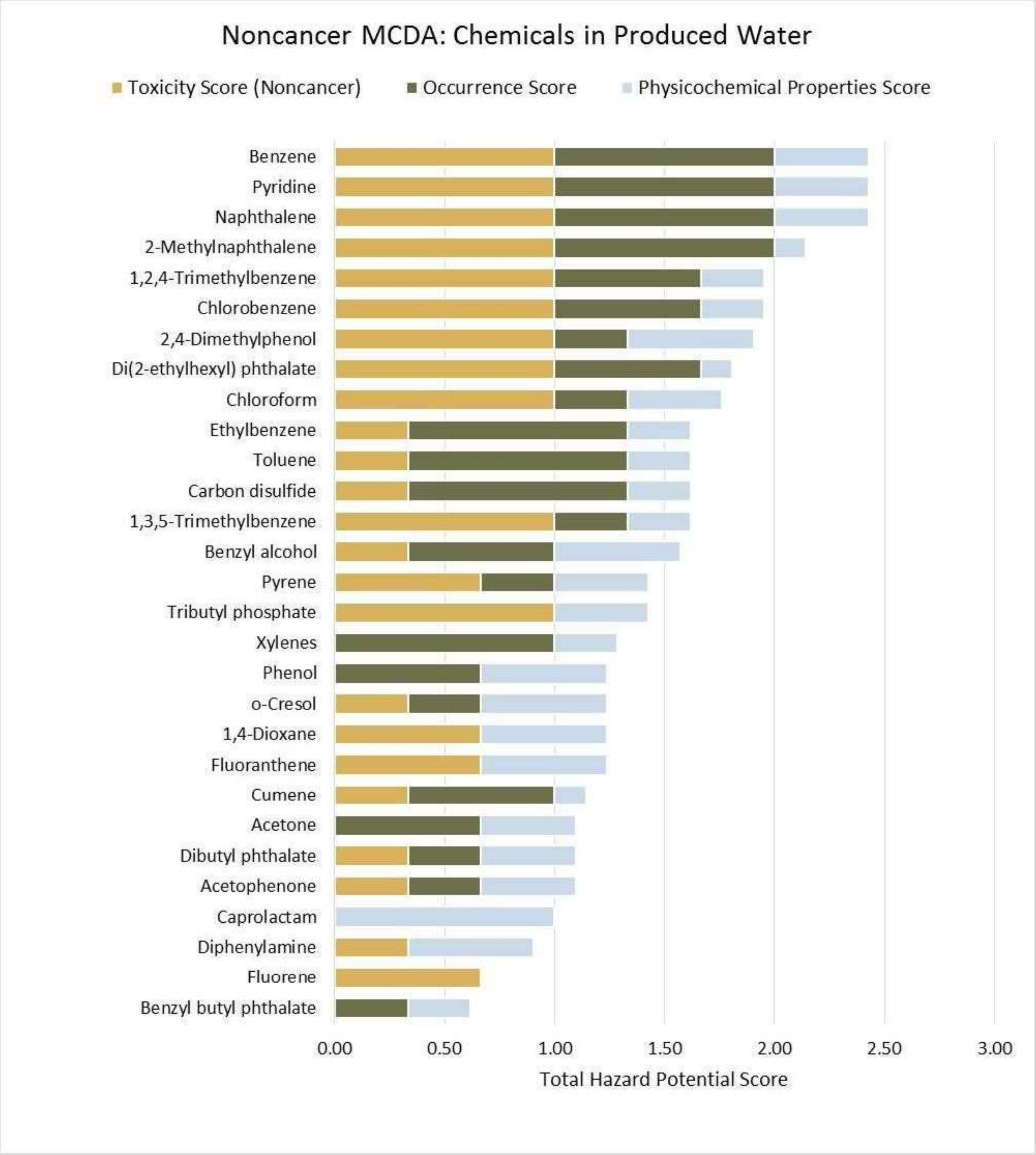

Figure 9-13. Noncancer MCDA results for a subset of 29 chemicals detected in produced water, showing the Toxicity Score, Occurrence Score, and Physicochemical Properties Score for each chemical.

Chemicals are ordered from high to low based on Total Hazard Potential Score. See Section 9.6.4 for details on the calculation.

The other chemicals that received high Toxicity Scores were 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, chloroform, 2,4,-dimethylphenol, tributyl phosphate, di(2-ethylhexyl) phthalate, and chlorobenzene. These chemicals received moderate Total Hazard Potential Scores, as all were detected at lower concentrations compared to other chemicals considered in this analysis and are expected to have moderate transport in water.

The other chemicals that received high Occurrence Scores are ethylbenzene, toluene, xylenes, and carbon disulfide, which were detected at maximum average concentrations of 2010 μg/L, 760 μg/L, 360 μg/L, and 400 μg/L in Barnett, Marcellus, or Powder River Basin produced water. These chemicals received moderate Total Hazard Potential Scores, as all have as all have higher chronic oral RfVs relative to many of the other chemicals in the hazard evaluation, and are all expected to have moderate transport in water relative to the other chemicals.

9.6.5.5 Results: Cancer MCDA for Chemicals in Produced Water

A total of 7 chemicals reported in produced water were evaluated in a cancer MCDA (Table 9-15). OSFs within this suite of chemicals ranged from 7.3 to 0.0049 per mg/kg-day, with benzo(a)pyrene having the highest OSF and N-nitrosodiphenylamine having the lowest. Of these 7 chemicals, benzene and 1,4-dioxane were also included in the cancer MCDA for chemicals used in hydraulic fracturing fluids. Benzene and benzo(a)pyrene are both classified by at least one of the sources in Table 9-1 as a known human carcinogen, while the other chemicals as classified as likely or probable carcinogens in humans (Appendix G: Tables G-1e and G-2e).

Figure 9-14 presents the results of a cancer MCDA for these 7 chemicals in hydraulic fracturing fluids. Benzene and benzo(a)pyrene tied for highest Total Hazard Potential Scores. Of these, benzene was detected at the highest average concentrations in produced water (1500 μg/L in Power River Basin produced water), while benzo(a)pyrene were detected at lower average concentrations (6.7 μg/L in Barnett shale produced water). Benzo(a)pyrine and 1,2-diphenylhydrazine were the most potent carcinogens within this suite of chemicals and received high Toxicity Scores.

The other chemical that received a high Occurrence Score was di(2-ethylhexyl) phthalate, which was detected at an average concentration of 210 μg/L in Barnett Shale produced water. It received a moderate Total Hazard Potential Score because it is hydrophobic and not expected to be readily transported in water.

Table 9-15. Data on the selected subset of chemicals detected in produced water used for input into a cancer MCDA.
Chemicals within the table are ordered from most potent to least potent based on OSF.

		Cancer-specific toxicity (OSF)[a]		**Occurrence (concentration in produced water)[b]**		**Mobility**			**Volatility**	**Persist-ence**
Chemical Name	**CASRN**	**OSF (per mg/kg-day)**	**Source of OSF**	**Average or Median Conc. (µg/L)**	**Reference**	**Log K_{OW}**	**Log K_{OC}**	**Solubility (mg/L)**	**Henry's Law Constant**	**Half-life in water (days)**
Benzo(a)pyrene	50-32-8	7.3	IRIS	6.7	Table E-11	6.13	5.95	0.01038	4.57E-07	60
1,2-Diphenylhydrazine	122-66-7	0.8	IRIS	4.2	Table E-11	2.94	2.98	161.9	4.78E-07	28.17
1,4-Dioxane	123-91-1	0.1	IRIS	6.5	Table E-11	-0.27	0.421	213900	4.80E-06	15
Benzene	71-43-2	0.015-0.055[c]	IRIS	1500	Table E-13	2.13	1.75	2000	5.55E-03	37.5
Di(2-ethylhexyl) phthalate[d]	117-81-7	0.014	IRIS	210	Table E-11	7.6	4.94	0.001132	2.70E-07	15
Tributyl phosphate	126-73-8	0.009	PPRTV	0.26	Table E-12	4	3.371	7.355	1.41E-06	8.67
N-Nitrosodiphenylamine	86-30-6	0.0049	IRIS	8.9	Table E-11	3.13	3.42	94.85	1.21E-06	37.5

CASRN = Chemical Abstract Service Registry Number; IRIS = Integrated Risk Information System; PPRTV = Provisional Peer-Reviewed Toxicity Values; K_{OW} = octanol-water partitioning coefficient; K_{OC} = soil adsorption coefficient

[a] Oral slope factor (OSF): 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 units of 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 less than 1 in 100. OSFs considered in the MCDA include values from IRIS, PPRTV, and HHBP.

[b] From Appendix E.

[c] IRIS lists the OSF for benzene as a range from 0.015 to 0.055 per mg/kg-day. For input into the MCDA, we used the high end of this range (0.055 per mg/kg-day).

[d] Di(2-ethylhexyl) phthalate is listed under the name bis(2-ethylhexyl) phthalate in Appendix Table E-11.

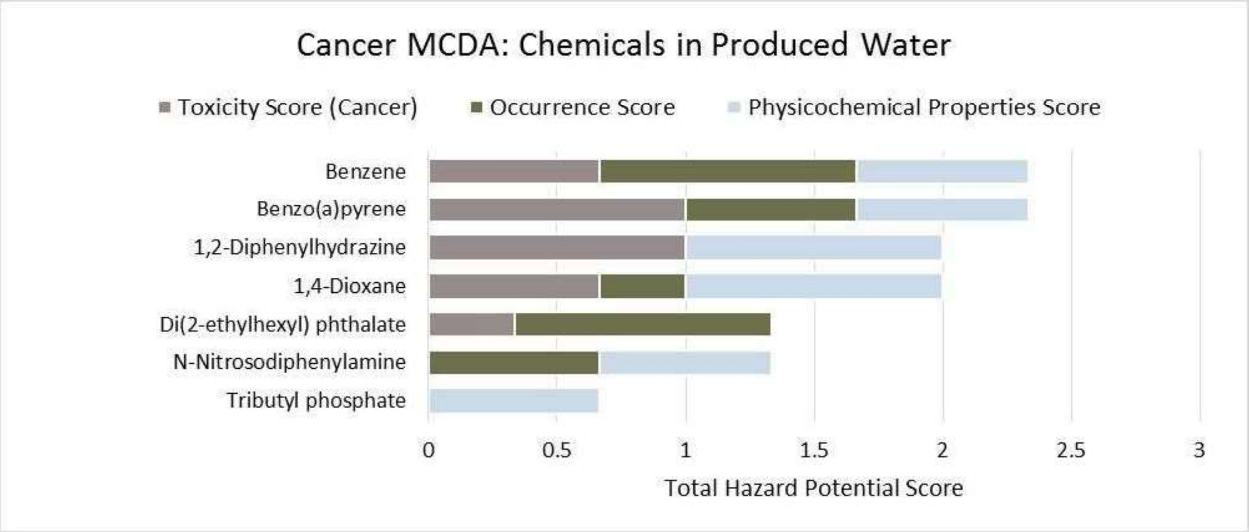

Figure 9-14. Cancer MCDA results for 7 chemicals detected in produced water, showing the Toxicity Score, Occurrence Score, and Physicochemical Properties Score for each chemical. Chemicals are ordered from high to low based on Total Hazard Potential Score. See Section 9.6.4 for details on the calculation.

9.6.6 Limitations and Uncertainty of the MCDA Framework

While this MCDA framework provides a simple and transparent tool for exploring the relative hazard potential of chemicals in the hydraulic fracturing water cycle, it is intended only as a preliminary analysis. It is important to acknowledge the limitations of this analysis, as well as the limitations of the parameters that were used for input in the MCDA.

Chronic oral RfVs and OSFs were selected for the MCDA because they are a primary focus of the toxicological evaluation presented in this chapter. We were interested in placing these values in the context of variables that may impact the likelihood of human exposure. These toxicity values were available for a relatively small fraction of chemicals on EPA's list, which limited the number of chemicals considered in the MCDA.

The FracFocus 1.0 data used in the MCDA does not represent a complete record of hydraulic fracturing chemical usage in the United States, as described in more detail in Chapter 5 and in Section 9.3.1. Frequency of use also does not reflect the volume or concentration of chemical usage, and therefore is an incomplete metric for potential exposure. The EPA FracFocus 1.0 project database provides data on the maximum concentration of chemicals in additives and in hydraulic fracturing fluid, as discussed in Section 5.4, but we elected not to use this data in the MCDA because reported concentrations for each chemical varied widely between disclosures (see Table 5-5 and volume estimates in Figure 5-5), making it difficult to determine a chemical concentration to use in an MCDA. Additionally, many chemicals in the EPA FracFocus 1.0 project database did not have valid concentration data; for instance, the maximum concentrations of a chemical in additive often added up to greater than 100%. We therefore elected to focus on frequency of use as a general metric of chemical occurrence in the hydraulic fracturing water cycle.

The produced water concentrations used in the MCDA are based on the compilation of data presented in Appendix E. While this data reflects the findings of recent studies, it does not represent a complete record of chemicals present in produced water, as described in more detail in Chapter 7 and in Section 9.3.2. Concentrations in produced water also do not necessarily reflect the concentrations in treated wastewater, drinking water wells, or residuals in soil or sediment. Concentrations of these chemicals in treated wastewater or well water would likely be more dilute compared to concentrations in produced water. Concentrations in soils or sediments may be higher, particularly for hydrophobic chemicals.

The physicochemical properties from EPI Suite used in the MCDA are useful for making comparison across chemicals, but these values are also subject to uncertainty. Many of the values used in the MCDA were estimated by EPI Suite, and therefore are subject to the inherent limitations of the EPI Suite model (Section 5.8). Chemical fate and transport will be also influenced by environmental and site-specific conditions, which are outside the scope of this analysis. 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.

There are also fundamental limitations with regards to the scope of the MCDA. The chemicals used in these analyses may not be representative of chemicals at a specific field site. The analysis only examined organic chemicals, as EPI Suite is not able to estimate physicochemical properties of inorganic chemicals. Additionally, the physicochemical properties used in the MCDA were chosen specifically to reflect chemical transport in water, and therefore do not highlight the potential hazards of hydrophobic or volatile chemicals. Hydrophobic chemicals may serve as long-term sources of pollution by sorbing to soils or sediments at contaminated sites, and volatile chemicals may be hazardous when inhaled. 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 (U.S. EPA, 2012i).

9.6.7 Application of the MCDA Framework for Preliminary Hazard Evaluation

The MCDA framework presented here is intended as a preliminary analysis, and illustrates one possible method for integrating data to explore potential hazards. By combining multiple lines of data, 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.

Researchers may find this approach useful in their efforts to explore the potential hazards of chemicals present at specific field sites, particularly in instances when exposure assessment data is not available. The MCDA framework is flexible, and could be adapted to incorporate site-specific data on chemical usage, different types of toxicity data, as well as 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 considered in this analysis (toxicity, occurrence, physicochemical properties), to reflect expert judgement of each variable's relative importance.

9.7 Synthesis

The overall objective of this chapter was to identify and provide information on the toxicological properties of chemicals used in hydraulic fracturing and of hydraulic fracturing wastewater constituents, and to evaluate the potential hazards of these chemicals for drinking water resources. Toward this end, the EPA developed a list of 1,606 chemicals that are reported to be associated with hydraulic fracturing, separating them into subsets based on whether they were reported to have been used in hydraulic fracturing fluids (1,084 chemicals total) or detected in produced water (599 chemicals total). To evaluate the potential hazards of these chemicals, the EPA compiled chronic oral RfVs, OSFs, and qualitative cancer classifications from selected federal, state, and international sources that met the EPA's criteria for consideration in this assessment. This toxicological information was used to conduct an initial identification of the potential human health hazards associated with several subsets of chemicals identified as being of particular interest in previous chapters of this report. Finally, in order to illustrate how data integration could be used to explore potential hazards, an MCDA framework was used to evaluate selected subsets of chemicals based on toxicity, environmental occurrence, and physicochemical properties affecting chemical transport in water.

9.7.1 Summary of Findings

A major finding of this chapter was that chronic oral RfVs and OSFs were not available for the majority of chemicals that the EPA has identified as being associated with hydraulic fracturing activity, indicating that the majority of these chemicals have not undergone significant toxicological evaluation. Similarly, there have been several recent peer-reviewed studies that have attempted to gather toxicological information for subsets of chemicals that are used in hydraulic fracturing fluids, and they have found that many of these chemicals do not have toxicity values available (Elliott et al., 2016; Wattenberg et al., 2015; Stringfellow et al., 2014; Colborn et al., 2011). Taken together, this suggests a potentially significant knowledge gap exists with respect to the scientific community's understanding of the potential human health impacts of these chemicals. With the limited availability of toxicity values, risk assessment is difficult, and potential impacts on drinking water resources may not be assessed adequately. This lack of toxicity values is not unique to the hydraulic fracturing industry; in fact, it has been estimated that there are tens of thousands of chemicals in commercial use that have not undergone significant toxicological evaluation (Judson et al., 2009).

There are a variety of chemicals associated with hydraulic fracturing known to be hazardous to human health. Chronic oral RfVs or OSFs from the sources considered by the EPA in this assessment were available for 98 (9%) of the 1,084 chemicals used in hydraulic fracturing fluids, and 120 (20%) of the 599 chemicals detected in hydraulic fracturing produced water. Potential hazards associated with chronic oral exposure to these chemicals include carcinogenesis, immune system effects, changes in body weight, changes in blood chemistry, cardiotoxicity, neurotoxicity, liver and kidney toxicity, and reproductive and developmental toxicity. Methane is not considered to be toxic when ingested, but may accumulate to explosive levels or act as an asphyxiant. DBPs formed during wastewater treatment can contribute to an increased risk of cancer, anemia, liver and kidney effects, and central nervous system effects, with brominated forms of DBPs considered to be more cytotoxic, genotoxic, and carcinogenic than chlorinated species.

To assess the toxicity of chemicals that lack chronic oral RfVs and OSF, risk assessors will need to turn towards alternative data sources. This chapter explored two alternative data sources that may provide useful information. QSAR-based toxicity estimates—specifically, rat chronic oral LOAEL estimates generated using TOPKAT—were available for many of the chemicals that lacked chronic oral RfVs and OSFs from the sources considered in this assessment, and may be used to rank chemicals based on toxicity when other data are not available. Additionally, many of these chemicals have information available on the EPA's ACToR database, which is an online data warehouse designed to consolidate large and disparate amounts of chemical data. The information available in the ACToR data warehouse ranges from the selected RfVs and OSFs discussed in this assessment, which have undergone extensive peer review, to toxicological data that have undergone little-to-no peer review.

When considering the potential impact of chemicals on drinking water resources and human health, it is important to consider exposure as well as toxicological properties. As discussed in previous chapters of this report and highlighted in this chapter, events such as spills, leaks from storage pits, and discharge of inadequately treated wastewater have led to the entry of hydraulic fracturing-related chemicals into drinking water resources. In some instances, chemical concentrations in surface water or groundwater were in exceedance of MCLs, indicating their presence at levels that could impact human health. While these studies demonstrate the potential entry of these chemicals into drinking water resources, there is a lack of systematic studies examining actual human exposures to these chemicals in drinking water as a result of hydraulic fracturing activity.

In the absence of exposure assessment data, the MCDA framework presented in this chapter provides a preliminary analysis of the relative hazard potential of these chemicals. In this context, occurrence and physicochemical property data were used as metrics to estimate the likelihood that a chemical could reach and impact drinking water, and toxicity data was used as a metric for the potential severity of an impact. This analysis highlighted several chemicals that may be more likely than others to reach drinking water and create a toxicological hazard. Of the chemicals used in hydraulic fracturing fluids that were considered in this analysis, chemicals such as propargyl alcohol stood out as having high potential toxicity, high frequency of use, and physicochemical properties that are conducive to transport in water. Of the chemicals in produced water, chemicals such as benzene, pyridine, 2-methylnaphthalene, and naphthalene stood out as having high potential toxicity, high concentrations in produced water, and physicochemical properties that are conducive to transport in water.

9.7.2 Factors Affecting the Frequency or Severity of Impacts

There are multiple pieces of information that could be taken into account when evaluating the frequency and severity of impacts that these chemicals may have on drinking water resources. This includes knowledge of the chemicals used at a given site, the toxicological and physicochemical properties of these chemicals, the amount of fluid being used and recovered, the likelihood of mechanical integrity failures, the likelihood of spills and other unintentional releases, and the efficiency of chemical removal during wastewater treatment. The MCDA presented in this chapter incorporated parameters that may impact the likelihood of chemical exposure, including frequency of use, measured concentration, and transport in water, and was used to stratify and rank chemicals based on relative hazard potential. However, it should be considered only as a preliminary analysis, and should not be used in place of local data on the concentrations and volumes of chemicals in areas of hydraulic fracturing activity.

Analysis of the chemicals used in hydraulic fracturing fluids indicated that the majority of chemicals on the EPA's list are used in <1% of wells nationally (Figure 9-4). Therefore, potential exposure to the majority of these chemicals is more likely to be a local issue, rather than a national one. Given that the analysis of the EPA FracFocus 1.0 project database presented in this chapter was based on 35,957 disclosures, a chemical used in <1% of wells nationally could still be used in several hundred wells. Chemicals used infrequently on a national basis could still be used more frequently within certain areas or counties, increasing the potential for local exposure to that chemical.

As an example of how an infrequently used chemical could have local impacts, consider (E)-crotonaldehyde, which had one of the lowest chronic oral RfVs among the chemicals considered in the noncancer MCDA for hydraulic fracturing chemicals, and was reported in approximately 0.06% of disclosures in the EPA FracFocus 1.0 project database. If the EPA FracFocus 1.0 project database is a representative sample of all of the wells across the country, then the likelihood of (E)-crotonaldehyde contamination on a national scale is limited. However, this in no way diminishes the likelihood or potential severity of (E)-crotonaldehyde contamination at sites where this chemical is used.

This is in contrast with frequently used chemicals such as methanol. Methanol was reported in 73% of wells in the EPA FracFocus 1.0 project database, and was the most frequently used chemical considered in the noncancer MCDA for chemicals used in hydraulic fracturing fluids. Methanol is soluble and relatively mobile in water, but has a higher chronic oral RfV compared other chemicals considered in this analysis. Therefore, methanol may be expected to have a higher exposure potential on a national basis compared to other chemicals, with a moderate hazard potential due to its relatively high RfV.

Even if no chemicals were added to hydraulic fracturing fluids, there is still a potential for impacts from constituents naturally present in the subsurface which could be brought to the surface in produced water. As described in Section 9.5, many of the naturally occurring chemicals in produced water—e.g., organic chemicals (e.g., BTEX and related hydrocarbons), metals, anions, and TENORM—are hazardous to human health and have been reported in drinking water resources as a result of hydraulic fracturing activity, sometimes at concentrations exceeding MCLs. The constituents of produced water that contribute to the formation of DBPs, specifically bromide, chloride, iodine, and ammonium, are naturally occurring and are characteristic of wastewater from hydraulically fractured wells.

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 and the chemicals used in the oil and gas extraction processes. Therefore, potential hazard and risk considerations are best made on a site-specific, well-specific basis.

9.7.3 Uncertainties

There are notable uncertainties in the chemical and toxicological data limiting a comprehensive assessment of the potential health impacts of hydraulic fracturing on drinking water resources.

For human health risk assessment, a significant data gap is the lack of chronic oral RfVs and OSFs from sources meeting the EPA's criteria for inclusion in this report. For instance, of the 34 chemicals (excluding water, quartz, and sodium chloride) that were reported in ≥10% of disclosures in the EPA FracFocus 1.0 project database, 9 chemicals have chronic oral RfVs available, and none have OSFs (Table 9-2). Without reliable and peer reviewed toxicity values, comprehensive hazard evaluation and hazard identification of chemicals is difficult, and the ability to consider the potential cumulative effects of exposure to chemical mixtures in hydraulic fracturing fluid or produced water may be limited. Although there are other potential sources of toxicity information for many of these chemicals, some of it may be limited or of lesser quality. Consequently, potential impacts on drinking water resources and human health may not be assessed adequately.

An equally significant data gap is the lack of exposure assessment data for drinking water resources in areas of hydraulic fracturing activity. As discussed in Text Box 9-1, data on exposure potential is a critical component of the risk assessment process, and is necessary for risk characterization. In the absence of exposure assessment information, the MCDA framework presented in this chapter may be useful for exploring the potential hazards of hydraulic fracturing-related chemicals, but should be considered as a preliminary analysis only. The MCDA presented in this chapter considered only a small subset of chemicals that had data available, was limited in scope, and may not be representative of the chemicals that are present at a specific field site. It should be emphasized that this MCDA framework represents just one method that can be used to integrate chemical data for hazard evaluation, and is readily adaptable to include different variables, different weights for the variables, and site-specific considerations.

There is also uncertainty surrounding the EPA's list of chemicals associated with hydraulic fracturing activity. As discussed in Section 5.4 and Section 9.3.1, there is incomplete information available on chemicals used in hydraulic fracturing fluids due to industry use of CBI as well as incomplete reporting of chemical use. For instance, the EPA's analysis of the FracFocus 1.0 project database found that approximately 11% of ingredients were reported as CBI, and that more than 70% of FracFocus 1.0 disclosures contained at least one CBI ingredient. There may also be regional limitations in the disclosures submitted to FracFocus 1.0, as 78% of chemical disclosures in came from five states, and 47% were from Texas (U.S. EPA, 2015a). Despite these limitations, FracFocus remains the most complete source for tracking hydraulic fracturing chemical usage in the United States, and therefore was the best available source for the hazard evaluation in this chapter. Although the sources used to compile the chemical list represented the best available data at the time of this study, it is possible that some of these chemicals are no longer used at all, and many of these chemicals may only be used infrequently. Therefore, it may be possible that significantly fewer than 1,084 chemicals are currently used in abundance. As practices evolve, it is likely that chemicals are used or will be used that are not included on this chemical list. Having a better understanding of the chemicals and formulations, including those that are CBI, along with their frequency of use and volumes, would greatly benefit risk assessment and risk management decisions.

Additionally, the list of produced water chemicals identified in this chapter is almost certainly incomplete. As discussed in Chapter 7, chemicals and their metabolites may go undetected because they were not included in the analytical methodology, or because an analytical methodology was not available. Chemical analysis of produced water can also be challenging because high levels of dissolved solids in produced water and wastewater can interfere with chemical detection. As a result, there are likely chemicals of concern in produced water that have not been detected or reported, and are not included on the chemical list presented in this report.

9.7.4 Conclusions

The EPA identified 1,606 chemicals associated with the hydraulic fracturing water cycle, including 1,084 chemicals used in hydraulic fracturing fluids, and 599 chemicals detected in produced water. Toxicity-based chronic oral RfVs and/or OSFs from sources meeting selection criteria were not available for the majority (89%) of the chemicals on this total list. Thirty-seven percent of chemicals on the EPA's list that are used in hydraulic fracturing fluids lack data on their frequency of use. Current understanding of the chemical composition of produced water is constrained by analytical chemistry limitations and by the likelihood that chemical composition will vary between wells. A limited number of studies have detected these chemicals in surface water, groundwater, or well water near areas of hydraulic fracturing activity, suggesting the potential for human exposure; however, actual human exposures to these chemicals in drinking water resources has not been well characterized. Given the large number of chemicals used or detected in various stages of the hydraulic fracturing water cycle, as well as the large number of hydraulically fractured wells nationwide, this missing chemical information represents a significant data gap.

While it remains challenging to fully understand the toxicity and potential public health impacts of these chemicals for drinking water resources, the toxicological data, occurrence data, and physicochemical data compiled in this report provide a resource for assessing the potential hazards of chemicals in the hydraulic fracturing water cycle. The MCDA framework presented here illustrates one method for integrating these data for a preliminary hazard evaluation, which may be useful when exposure assessment data are not available. While the analysis in this chapter is constrained to the assessment of chemicals on a national scale, this approach is readily adaptable for use on a regional or site-specific basis.

This collection of data provides a tool to inform decisions about protection of drinking water resources. Stakeholders may use these results to prioritize chemicals for hazard assessment or for determining future research priorities. Industry may use this information to prioritize chemicals for replacement with less toxic, persistent, and mobile alternatives.

9.8 Annex

9.8.1 Calculation of Physicochemical Property Scores (MCDA Hazard Evaluation)

Section 9.6.3 describes how Physicochemical Properties Scores for the noncancer and cancer MCDAs were calculated based on three subcriteria which affect the likelihood that a chemical will be transported in water: mobility, volatility, and persistence. Calculation of these subcriteria scores was performed as described by Yost et al. (In Press), as follows:

9.8.1.1 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} described the partitioning of a chemical between water and organic carbon in soil. K_{OW} and K_{OC} are generally represented on a logarithmic 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 experimentally 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™ Sabljic molecular connectivity method, and aqueous solubility estimated using the WSKOWWIN™ model. Using the thresholds designated in Table 9-11, 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.

9.8.1.2 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. 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 experimentally 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 9-11, 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.

9.8.1.3 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 transformed or 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 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 9-11, 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.

9.8.1.4 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.

9.8.2 Example of MCDA Score Calculation

The methods used for MCDA score calculation are described in Section 9.6.3. For an example of how the MCDA scores were calculated, consider benzene, which was included in both the noncancer MCDA (national analysis) and cancer MCDA for chemicals used in hydraulic fracturing fluids. This demonstrates how MCDA scores were calculated for benzene for these two different analyses.

9.8.2.1 Score Calculation for Benzene in Noncancer MCDA for Hydraulic Fracturing Fluids

- **Toxicity Score (Noncancer):** Benzene has a chronic oral RfV of 0.004 mg/kg-day (source: IRIS). Across the 42 chemicals that were considered in the noncancer MCDA (national analysis), chronic oral RfVs ranged from 0.001 mg/kg-day [(E)-crotonaldehyde] to 20 mg/kg-day (1,2-propylene glycol). The chronic oral RfV of benzene falls in the lowest (most toxic) quartile of these chemicals, and therefore benzene was assigned a Toxicity Score of 4. When the results were standardized to the highest Toxicity Score (4) and lowest Toxicity Score (1) within the set of chemicals, benzene was calculated to have a final Toxicity Score of 1, as follows:

$$1 = (4 - 1) / (4 - 1)$$

- **Occurrence Score:** Benzene was used in 0.006% of wells nationally. For the 42 chemicals considered in the national noncancer MCDA, frequency of use ranged from 73%

(methanol) to 0.003% (furfural) of wells nationally. Benzene falls in the lowest quartile with regards to frequency of use, and therefore benzene was assigned an Occurrence Score of 1. When the results were standardized to the highest Occurrence Score (4) and lowest Occurrence Score (1) within the set of chemicals, benzene was calculated to have a final Occurrence Score of 0, as follows:

$$0 = (1 - 1) / (4 - 1)$$

- **Physiochemical Properties Score:** Benzene received a Mobility Score of 4 (log K_{OW} = 2.13; log K_{OC} = 1.75; solubility = 2000 mg/l), a Volatility Score of 2 (Henry's law constant = 0.00555), and a Persistence Score of 2 (half-life in water = 37.5 days). This sums to a Total Physicochemical Properties Score of 8. Within the 42 chemicals considered in the national noncancer MCDA, several chemicals received Total Physicochemical Properties Scores of 9, which was the highest observed score. Cumene received a Total Physicochemical Properties Scores of 6, which was the lowest score. When the results were standardized to the highest (9) and lowest (6) of these scores, benzene was calculated to have a final Total Physicochemical Properties Scores of 0.67, as follows:

$$0.67 = (8 - 6) / (9 - 6)$$

- **Total Hazard Potential Score (Noncancer MCDA):** For benzene, the Toxicity Score (1), Occurrence Score (0), and Physicochemical Properties Score (0.67) were summed to calculate a Total Hazard Potential Score of 1.67. The relative contribution of the three criteria scores to this total score is depicted as a graphic in Figure 9-8.

9.8.2.2 Score Calculation for Benzene in Cancer MCDA for Hydraulic Fracturing Fluids

- **Toxicity Score (Cancer):** Benzene has an OSF of 0.055 per mg/kg-day (source: IRIS). Within the entire set of 10 chemicals that was considered in the cancer MCDA, OSFs ranged from 3 (quinoline) to 0.002 (dichloromethane) per mg/kg-day. The OSF of benzene falls in the second quartile of these scores, and therefore was assigned a Toxicity Score of 2. When the results were standardized to the highest Toxicity Score (4) and lowest Toxicity Score (1) within the set of chemicals, benzene was calculated to have a final Toxicity Score of 0.33, as follows:

$$0.33 = (2 - 1) / (4 - 1)$$

- **Occurrence Score:** As described in the noncancer MCDA above, benzene was used in 0.006% of wells nationally. This was the lowest frequency of use among the 10 chemicals that were considered in the cancer MCDA, with benzyl chloride (used in 6% of wells) having the highest. Benzene therefore falls in the lowest quartile with regards to frequency of use, and was assigned an Occurrence Score of 1. When the results were standardized to the highest Occurrence Score (4) and lowest Occurrence Score (1) within the set of chemicals, benzene was calculated to have a final Occurrence Score of 0, as follows:

$$0 = (1 - 1) / (4 - 1)$$

- **Physiochemical Properties Score:** As described in the noncancer MCDA above, benzene received a Total Physicochemical Properties Score of 8. Within the 10 chemicals that were considered in the cancer MCDA, all chemicals either received a Total Physicochemical Properties Score of 8 or 9. When the results were standardized to these high and low scores, benzene was calculated to have a final Total Physicochemical Properties Scores of 0 as follows:

$$0 = (8 - 8) / (9 - 8)$$

- **Total Hazard Potential Score (Cancer MCDA):** The Toxicity Score (0.33), Occurrence Score (0), and Physicochemical Properties Score (0) were summed to calculate a Total Hazard Potential Score of 0.33. The relative contribution of the three criteria scores to this total score is depicted as a graphic in Figure 9-12.

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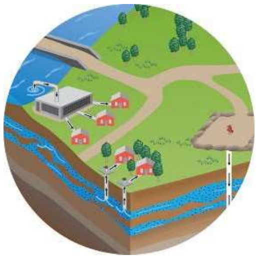
Chapter 10. Synthesis



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10. Synthesis

Introduction

The goals of this report were to assess the potential for activities in the hydraulic fracturing water cycle to impact the quality or quantity of drinking water resources, and to identify factors affecting the frequency or severity of those impacts. Overall, we conclude activities in the hydraulic fracturing water cycle can impact drinking water resources under some circumstances. Impacts can range in frequency and severity, depending on the combination of hydraulic fracturing water cycle activities and local- or regional-scale factors. The following combinations of activities and factors are more likely than others to result in more frequent or more severe impacts:

- Water withdrawals for hydraulic fracturing in times or areas of low water availability, particularly in areas with limited or declining groundwater resources;
- Spills during the management of hydraulic fracturing fluids and chemicals or produced water that result in large volumes or high concentrations of chemicals reaching groundwater resources;
- Injection of hydraulic fracturing fluids into wells with inadequate mechanical integrity, allowing gases or liquids to move to groundwater resources;
- Injection of hydraulic fracturing fluids directly into groundwater resources;
- Discharge of inadequately treated hydraulic fracturing wastewater to surface water resources; and
- Disposal or storage of hydraulic fracturing wastewater in unlined pits, resulting in contamination of groundwater resources.

These conclusions are based on cases of identified impacts and other data, information, and analyses presented in this report. Cases of impacts were identified for all stages of the hydraulic fracturing water cycle. Identified impacts generally occurred near hydraulically fractured oil and gas production wells and ranged in severity, from temporary changes in water quality to contamination making private drinking water wells unusable. The inherent characteristics of groundwater resources make them more vulnerable to impacts from activities in the hydraulic fracturing water cycle compared to surface water.

We see the identification of factors affecting the frequency or severity of impacts, and uncertainties and data gaps in this report as particularly useful for decision makers. Factors often can be managed, changed, or used to identify areas for specific monitoring or modification of practices. Thus, in the short-term, information on factors can help decision makers reduce current vulnerabilities of drinking water resources to activities in the hydraulic fracturing water cycle. In the longer term, reducing the uncertainties and filling the data gaps could enhance science-based decisions to protect drinking water resources in the future.

The purpose of this chapter is to synthesize for decision makers the information on factors, uncertainties, and data gaps presented in this assessment. In Section 10.2, we focus on factors increasing or decreasing the frequency or severity of impacts at each stage of the hydraulic fracturing water cycle. In Section 10. 3, we discuss major uncertainties and data gaps identified in this assessment. Finally, in Section 10.4, we discuss potential uses for this assessment.

10.1 Factors Affecting the Frequency or Severity of Impacts

10.1.1 Water Acquisition

Groundwater and surface water resources serve as both sources of water for hydraulic fracturing and public and private drinking water supplies. Thus, water withdrawals for hydraulic fracturing can impact the quantity or quality of drinking water resources under certain circumstances. Since, by definition, every water withdrawal affects water quantity, we focused in this assessment not on all water withdrawals per se, but rather on those with the potential to limit the availability of drinking water or alter its quality. Whether a withdrawal has this potential depends upon a combination of factors at the local scale. Factors can either increase or decrease the frequency or severity of impacts. In this section on water acquisition, we combine our discussion of frequency and severity because all of the factors we discuss in this section affect both frequency and severity in a similar fashion (i.e., either increase both frequency and severity, or decrease both frequency and severity).

10.1.1.1 Frequency and Severity

The local balance between water withdrawals and water availability is the most important factor determining whether water acquisition impacts are likely to occur or be severe. Impacts are more likely to be frequent or severe where or when hydraulic fracturing water withdrawals are relatively high and water availability is low. In contrast, the same amount of water withdrawn can have a negligible effect if withdrawn in an area of—or at a time of—higher water availability. For this reason, it is important not to focus solely on the amount withdrawn, but the balance between water withdrawals and availability in place and time.

For this assessment, we developed county-level estimates of water use (i.e., water withdrawals) for hydraulic fracturing, which were then compared to an index of readily available fresh water. This readily available fresh water index included unappropriated surface water and groundwater, and appropriated water potentially available for purchase (Tidwell et al., 2013) (Text Box 4-2).[1] In the majority of counties where hydraulic fracturing takes place, hydraulic fracturing water use was less than 1% of this index of readily available fresh water. We did find, however, a small number of counties with higher percentages. There were 45 counties out of the almost 400 surveyed where hydraulic fracturing water use was above 10% of the index. Of these counties, 35 exceeded 30%, and 17 of these counties had hydraulic fracturing water use exceeding the index. All of the counties in this latter category are located in Texas.

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[1] In the western United States, water is generally allocated by the principle of prior appropriation—that is, first in time of use is first in right. New development must use unappropriated water or purchase appropriated water from vested users. In the index of readily available fresh water, it was assumed 5% of appropriated irrigated water could be purchased. See Text Box 4-2 for more details about this analysis.

This does not mean impacts to drinking water quantities occurred or will occur in these counties, nor does it mean that impacts did not or will not occur in counties with relatively low percentages. To truly determine whether impacts occurred, water withdrawals and availability need to be compared at the scale of the drinking water resource. For instance, groundwater withdrawals for hydraulic fracturing could affect water levels in nearby private water wells. As a national assessment, we could not often examine impacts at this local scale, although we did cite studies of local impacts where available. Nevertheless, our county level assessment does point to places where the potential for impacts is higher. This information may be useful to focus efforts on reducing the fresh water demand of hydraulic fracturing.

Beyond our county level assessment, we conclude that declining groundwater resources are particularly vulnerable to water quantity and quality impacts from withdrawals. Groundwater recharge rates can be low, and groundwater withdrawals are exceeding recharge in areas of the country (Konikow, 2013). When withdrawals exceed recharge, the result is declining water levels. For this reason, water levels in some aquifers in the United States have declined substantially over the last century (Konikow, 2013). Although irrigated agriculture is often the dominant user of groundwater, hydraulic fracturing withdrawals now also contribute to declining groundwater levels in some areas (e.g., southern Texas; Steadman et al., 2015; Scanlon et al., 2014b) Cumulative groundwater withdrawals can also impact water quality by mobilizing chemicals, such as uranium, from naturally occurring sources in the surrounding rock into the groundwater (DeSimone et al., 2014).

In certain instances, state and local governments have encouraged or mandated the use of surface water in place of groundwater, as evidenced in both Louisiana and North Dakota. In 2008, the state of Louisiana asked oil and gas companies to switch from groundwater to surface water to mitigate stress on the Carrizo-Wilcox aquifer, a critical source of drinking water in the region. Likewise, the state of North Dakota requested the oil industry obtain water from the Missouri river system, and not from stressed groundwater sources. By contrast, surface water availability is limited in other regions and cannot provide an alternative source of water (e.g., western Texas).

Among surface water sources, small streams are particularly vulnerable to impacts. This is the case across the country, even in the eastern United States where surface water is generally more plentiful. An EPA study of the Susquehanna River Basin in northeastern Pennsylvania found that the smallest streams (with less than 10 mi^2 of contributing area–i.e., the watershed area drained by the stream) would be the most likely to be impacted from water withdrawals in the absence of protective passby flows; see discussion below and U.S. EPA (2015e).[1] While the amount of contributing area varies by geographic location due to differences in runoff, the finding that the smallest streams are the most vulnerable to withdrawals holds across all landscapes.

Not only does water availability vary from one location to another, but it can also vary temporally at a given location, often due to variations in precipitation. Because of this dynamic, long-term or seasonal drought can increase the frequency or severity of impacts from withdrawals by decreasing water availability. The EPA study of the Susquehanna River Basin found even larger streams (up to

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[1] Passby flows are low stream flow thresholds below which withdrawals are not allowed.

600 mi^2 of contributing area) would be vulnerable to impacts at times of drought, again absent passby flows (U.S. EPA, 2015e). Dry conditions can also stress groundwater supplies by simultaneously increasing water demand (e.g., irrigation water demand increases in dry conditions) while also decreasing groundwater recharge. Much of the western United States has experienced extended periods of drought over the last decade. Climate change is likely to exacerbate these conditions in certain locations (Meixner et al., 2016).

Conversely, there are factors that can reduce the frequency or severity of impacts. Reuse of hydraulic fracturing wastewater (i.e., produced water managed for reuse, treatment and discharge, or disposal), for example, can reduce demands on fresh water resources.[1] Reuse does not appear to be driven by water scarcity, but rather by the cost of disposal. Operators are likely to dispose of wastewater when it is less expensive than reuse. For instance, greater reuse of wastewater occurs in the Marcellus Shale in Pennsylvania than in the Barnett Shale in Texas, even though water availability is generally higher in the Marcellus region (Figure 10-1). The general lack of disposal wells in Pennsylvania means disposing of wastewater requires trucking to Ohio or other locations with disposal wells. Because of this expense, operators reuse substantial proportions of their wastewater, in contrast to the Barnett Shale where disposal wells are readily available.

The reuse of wastewater to offset fresh water use in hydraulic fracturing is often limited by the amount of wastewater available. The volume of produced water from a single well can be relatively small compared to the volume needed to fracture a well (Figure 10-1a). This means produced water would need to be aggregated from multiple wells to equal the volume needed to hydraulically fracture an additional well. For instance, it would take 10 wells to make enough water to fracture an 11th well if, as has been shown in the Marcellus Shale in Pennsylvania, produced water volumes are 10% of injected volumes (Figure 10-1a). Thus, reuse is a factor that can reduce fresh water demand, but not eliminate it in most cases. Nevertheless, even a marginal decline in fresh water demand can make a difference in the frequency or severity of impacts.

The use of brackish groundwater is also a factor reducing fresh water demand, in some cases to a much greater degree than reuse. In the Permian Basin in western Texas, for instance, brackish water makes up 30 to 80% of water used for hydraulic fracturing, and 20% in the Eagle Ford Shale in southern Texas (Nicot et al., 2012). Our county level estimates suggest brackish water availability could entirely meet current hydraulic fracturing water demand in Texas and many other locations.[2] In 35 counties nationally, hydraulic fracturing water use equaled or exceeded 30% of an index of fresh water availability; when brackish water and wastewater were considered in addition to fresh water availability, only two counties equaled or exceeded 30% (Text Box 4-2).

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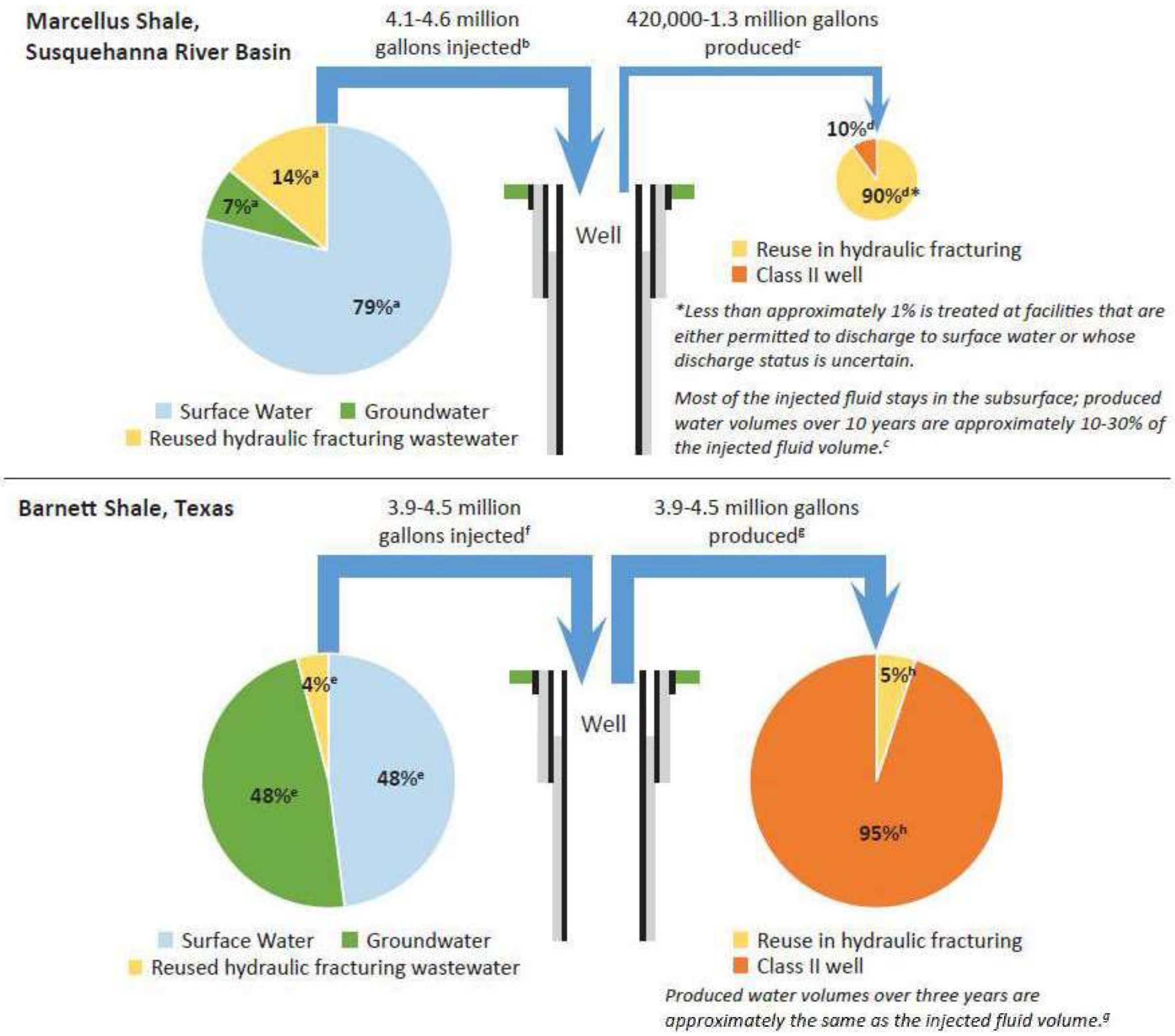
[1] Hydraulic fracturing wastewater is produced water that is managed using practices that include, but are not limited to, reuse in subsequent hydraulic fracturing operations, treatment and discharge, and injection into disposal wells. The term is being used in this study as a general description of certain waters and is not intended to constitute a term of art for legal or regulatory purposes (see Chapter 8 and Appendix J, the Glossary, for more detail).

[2] Brackish water for the purposes of this analysis ranged from 3,000 to 10,000 ppm of total dissolved solids (TDS), and from 50 to 2,500 ft (15-760 m) below the surface (Tidwell et al., 2013). (See Text Box 4-2 for more details.)



**Less than approximately 1% is treated at facilities that are either permitted to discharge to surface water or whose discharge status is uncertain.*

Most of the injected fluid stays in the subsurface; produced water volumes over 10 years are approximately 10-30% of the injected fluid volume.[c]

Produced water volumes over three years are approximately the same as the injected fluid volume.[g]

Figure 10-1. Water budgets representative of practices in (top) the Marcellus Shale in the Susquehanna River Basin in Pennsylvania and (bottom) the Barnett Shale in Texas.

Pie size and arrow thickness represent the relative volume of water as it flows through the hydraulic fracturing water cycle. Water budgets illustrative of typical water management practices in the Marcellus Shale in the Susquehanna River Basin between approximately 2008 and 2013 and the Barnett Shale in Texas between approximately 2011 and 2013. They do not represent any specific well. Sources for the top figure (a) Tables 4-1 and 4-2 (SRBC, 2016)—note, surface water, groundwater, and reuse values of 92%, 8%, and 16% in table normalized to 79%, 7%, 14%, respectively, for this chart (this was done to represent reuse on the same chart as surface water and groundwater—in the original tabular values, reuse is expressed as a percentage of total water used, and surface water and groundwater are expressed in percentages relative to each other); (b) Appendix Table B-5 (U.S. EPA, 2015a); (c) Table 7-2 (Ziemkiewicz et al., 2014)—note: produced water volumes estimated from percentages applied to volumes injected, and value from the West Virginia portion of the Marcellus Shale used in this chart since it was the longest term measurement of produced water volumes; (d) Figure 8-4 (PA DEP, 2015a) and Table 8-6 (Ma et al., 2014; Shaffer et al., 2013). Sources for the bottom figure: (e) Tables 4-1 and 4-2 (Nicot et al., 2014; Nicot et al., 2012)—note, surface water, groundwater, and reuse values of 50%, 50%, and 5% in the tables normalized to 48%, 48%, and 4%, respectively, for this chart (see reason for this above); (f) Appendix Table B-5 (U.S. EPA, 2015a; Nicot et al., 2012; Nicot et al., 2011)—note: see median value for Fort Worth Basin; (g) Table 7-2 (Nicot et al., 2014); (h) Table 8-6 (Nicot et al., 2012)—note, percentage going to disposal wells estimated by subtracting reuse values from 100%.

Finally, passby flows can be a factor reducing the frequency or severity of surface water impacts. Passby flows are low stream flow thresholds below which withdrawals are not allowed. This management practice has been shown to be protective of streams from over-withdrawals in the Susquehanna River Basin in northern Pennsylvania (U.S. EPA, 2015e). This is likely most important for protecting aquatic life in smaller streams, but may also aid in protecting drinking water supplies.

10.1.2 Chemical Mixing and Produced Water Handling

Like water acquisition, activities in the chemical mixing and produced water handling stages of the hydraulic fracturing water cycle can impact drinking water in some instances. We combine our discussion of the two stages here because activities in these stages both affect drinking water resources primarily through spills. The chemical mixing stage encompasses management of fluids on the well pad to create hydraulic fracturing fluid. Chemicals are mixed with a base fluid, typically water, and then injected into the production well. After the pressure is released post-fracturing, produced water flows from the well and needs to be collected and managed in the produced water handling stage.

Chemical mixing and produced water handling activities can impact drinking water resources through spills of chemicals used to make hydraulic fracturing fluid, hydraulic fracturing fluid itself, or produced water reaching surface water or groundwater.[1] There is some information on spill frequencies—although limited—and spill severities are most often uncharacterized. Nevertheless, we could identify factors affecting the frequency or severity of impacts from chemical mixing or produced water spills. In the section below, we discuss these factors, with those affecting frequency first, followed by those affecting severity. We discuss each of the factors individually, but spill events in reality exhibit combinations of these factors. These factors can interact to increase or decrease the frequency or severity of a spill beyond the effect of an individual factor.

10.1.2.1 Frequency

An impact on the quality of a drinking water resource from a spill first depends on a spill occurring. Most spill frequency estimates are of spills in total, and not the subset reaching drinking water resources. Spill estimates from three states (Colorado, North Dakota, and Pennsylvania) ranged from 0.4 to 12.2 reported spills per 100 hydraulically fractured wells (Appendix C.4).[2] The estimates from Pennsylvania and Colorado included hydraulic fracturing chemicals, fluids, and produced water; while the North Dakota estimate was based on spills of hydraulic fracturing chemicals and fluids only.[3] Spill rates can also be expressed on a per-active-well basis. This may be

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[1] In Chapter 5 and elsewhere in this assessment, the chemicals added to the base fluid (most often water) and proppant (most often sand) are referred to as "additives" since this is the term used in FracFocus. Here, this chapter simply refers to them as "chemicals." It does this to discuss chemicals in a unified manner in this combined section on chemical mixing and produced water.

[2] Since most wells are not reported hydraulically fractured in databases, these estimates used spudded, completed, or installed wells as proxies for hydraulically fractured wells. (See Appendix Section C.4 for more detail.)

[3] These estimates from Pennsylvania and Colorado also included spills of diesel fuel and drilling muds, which could not be separated out from the total frequency estimate even though they were generally out-of-scope of this assessment (diesel fuel was in scope if used in hydraulic fracturing fluid).

more appropriate for produced water spills since they can occur years or even decades after hydraulic fracturing. An analysis of North Dakota produced water spills found there were approximately 5 to 7 spills of produced water per 100 active wells between 2010 and 2015 (Appendix E.5). We conclude from these data that spills do occur in both the chemical mixing and produced water stages of the hydraulic fracturing water cycle, generally in the range of 1 to 10% of hydraulically fractured or active wells.

Not all spills, however, reach and therefore impact a drinking water resource. In U.S. EPA (2015m), 32 of the 457 (7%) spills characterized were reported to have reached surface water or groundwater. The California Office of Emergency Services estimated 18% of produced water spills reached waterways between January 2009 and December 2014 (CCST, 2015b). It is unclear if this estimate included groundwater, or was limited to surface water. If, however, roughly 5 to 20% of spills reach surface water or groundwater (encompassing the U.S. EPA and California estimates above), we would expect a spill to occur and reach a drinking water resource at approximately 0.05 to 2% of active or hydraulically fractured wells.[1] This estimate of spills reaching drinking water resources would be broadly consistent with estimates from the limited number of published studies addressing this topic (e.g., Brantley et al., 2014; Gross et al., 2013).[2] If a 0.05 to 2% frequency rate is applied to the estimates of approximately 275,000 to 370,000 new wells hydraulically fractured nationally between 2000 and part of 2013 and 2000 and part of 2014, respectively (Chapter 3), we would expect roughly 140 to 7,400 spills to reach a drinking water resource during this almost 14-to-15 year time-period. This would be approximately 10 to 500 spills per year reaching a drinking water resource, dividing by the respective time periods. This large range reflects the high uncertainty of these estimates and the lack of data on this topic.

Despite the data limitations and uncertainties surrounding estimates of spills, we can with more certainty identify factors likely affecting the frequency of spills reaching drinking water resources. These factors include spill characteristics, encompassing the volume of the chemical spilled; factors related to the environmental fate and transport of the spill, such as properties of the chemical spilled and characteristics of the site where the spill occurred; and finally, factors related to spill prevention and response.

Everything else being equal, a larger volume spill will be more likely to reach a drinking water resource than a smaller spill (U.S. EPA, 2015m). On-site spills in the chemical mixing and produced water handling stages are typically in the hundreds of gallons (U.S. EPA, 2015m). Larger spills, though less common, do occur. Well blowouts, pipeline leaks, and impoundment failures are sources of some of the largest individual spill volumes. Well blowouts were responsible for the

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[1] Estimated by multiplying the 1 to 10% spill rate for active or hydraulically fractured wells by 5% to 20% for spills reaching drinking water, and then reconverting to a percentage by multiplying by 100.

[2] Brantley et al. (2014) estimated approximately 0.4 to 0.8 spills per 100 hydraulically fractured wells reached surface water in Pennsylvania between 2008 to September 2013. These were spills of 400 gal (1,514 L) or more, containing hydraulic fracturing chemicals, fluids, or produced water. This might be an underestimate of spills reaching surface water since spill volumes were limited to only 400 gal (1,514 L) or more. In estimate of the frequency of spills reaching groundwater, Gross et al. (2013) examined oil and produced water spills between July 2010 and July 2011 in Weld County, Colorado. They counted 77 such spills reaching groundwater, approximately 0.4% of the nearly 18,000 active wells in the county.

highest volume spills on average in 2015 in North Dakota. In Bradford County, Pennsylvania, a well blowout resulted in a spill of approximately 10,000 gal (38,000 L) of produced water into a tributary of Towanda Creek, a state designated trout fishery. The largest volume spill identified in this assessment occurred in North Dakota, where approximately 2.9 million gal (11 million L) of produced water spilled from a broken pipeline and impacted surface water and groundwater. Though relatively rare compared to smaller volume spills, these types of spills are more likely to reach—and therefore impact—a drinking water resource because they are of larger volumes.

By this same principle, produced water spills are more likely to impact drinking water resources than chemical mixing spills. In an analysis of on-site spills, the median volume of produced water spills was approximately twice as large as that in the chemical mixing stage (990 versus 420 gal, or 3,750 versus 1,590 L; U.S. EPA (2015m)). Additionally, offsite, large pipeline spills of produced water can occur. It is possible that spills of produced water are larger, in part, because they are less likely to be stopped as quickly as spills in the chemical mixing stage. Spills in the chemical mixing stage are likely to occur when people are on-site, and so the spills can be quickly addressed. In contrast, spills of produced water may occur when no one is on-site or, in the case of pipelines, near the off-site location of the spill. This may delay a response, allowing larger volumes to spill, increasing the likelihood of the spill reaching a drinking water resource.

Properties of the chemicals spilled also affect the frequency of impacts. We identified or estimated chemical and physical properties for almost half of the chemicals used in hydraulic fracturing fluids between 2006 and 2013 (455 of the 1,084 chemicals). These were individual organic chemicals, not inorganic chemicals, polymers, or mixtures. Volatility, solubility, and hydrophobicity/hydrophilicity are three properties, among others, affecting whether a spill reaches a drinking water resource (hydrophobic chemicals tend to repel or fail to mix with water, while hydrophilic chemicals tend to mix with water). The vast majority of organic chemicals in hydraulic fracturing fluid do not readily volatilize or evaporate, meaning these chemicals tend to remain in water if spilled. These chemicals also vary widely in their solubility and hydrophobicity/hydrophilicity, defying a general characterization. Nevertheless, of the 20 chemicals most frequently used according to our analysis of FracFocus, most are highly soluble and hydrophilic, meaning they will be mobile if spilled (Chapter 5). For example, methanol, isopropanol, and ethylene glycol are all likely to travel quickly through the environment. Thus, these chemicals may more frequently reach drinking water because of two unrelated, yet compounding factors: relatively high frequency of use in hydraulic fracturing operations and relatively high mobility in the environment.

Site characteristics are also an important factor determining whether a spill reaches a drinking water resource (Figure 10-2). Site characteristics facilitating infiltration to groundwater are of particular concern, since spills into groundwater are more likely to have severe impacts than those into surface water (discussed in the severity section below). More permeable, sandier soils allow greater infiltration of spilled fluids, whereas less permeable soils with more clay content can greatly slow infiltration. More permeable rock also facilitates infiltration and movement of spills through preferential flow paths—for example, in fractured or karst bedrock. Thus, sandier soils and more permeable rock can increase the potential for spills to reach groundwater.

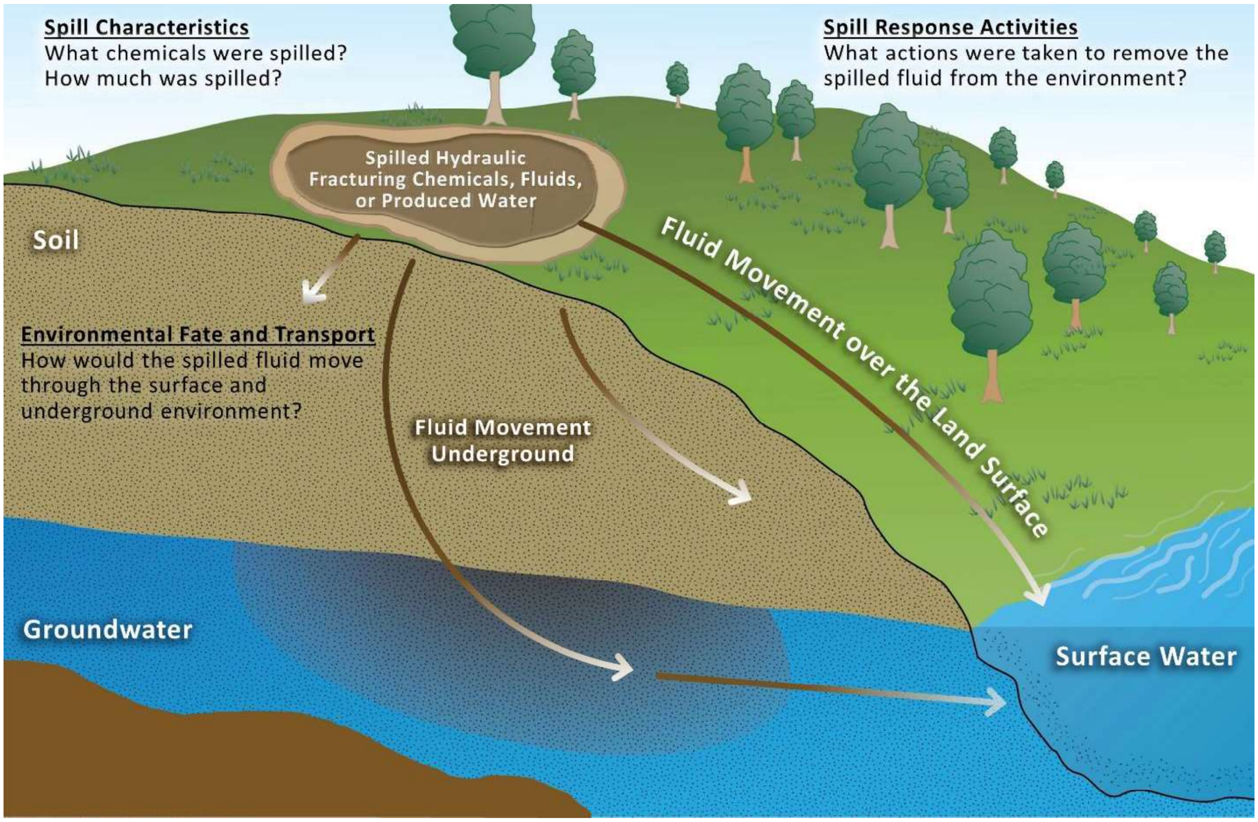

Figure 10-2. Fate and transport schematic for a spill of chemicals, hydraulic fracturing fluid, or produced water.
Schematic shows the potential paths, transport processes, and factors governing potential impacts of spills to drinking water resources.

There are spill prevention and response factors that reduce the frequency of impacts to drinking water resources from spills. Spill containment systems include primary, secondary, and emergency containment systems. Primary containment systems are the storage units, such as tanks or totes. Secondary containment systems, such as liners and berms installed during site set-up, are intended to contain spilled fluids until they can be cleaned up. Emergency containment systems, such as berms, dikes, and booms, can be implemented temporarily in response to a spill. Remediation is the action taken to clean up a spill and its affected environmental media. One of the most commonly reported remediation activities is the removal of spilled fluid and/or affected media, typically soil (U.S. EPA, 2015m). Other remediation methods include the use of absorbent material, vacuum trucks, flushing the affected area with water, and neutralizing the spilled material (U.S. EPA, 2015m). It was beyond the scope of this assessment to evaluate the implementation and efficacy of spill prevention practices and spill response activities.

10.1.2.2 Severity

In addition to frequency, there are also factors affecting the severity of an impact on a drinking water resource from a spill. For a given concentration, a larger volume spill will be more severe than a smaller spill (see frequency section above for discussion of spill volumes). In addition to volume, the concentration and toxicity of the chemicals reaching a drinking water resource affect severity, as well as site characteristics.

A spill with higher chemical concentrations will be more severe than a more dilute spill of equal volume. In the chemical mixing stage, chemicals are stored in concentrated form on-site, prior to diluting with a base fluid. Approximately 3,000 to 30,000 gal (11,000 to 114,000 L) of chemicals are used per well on average, with up to twice that amount stored on site. If multiple wells are fractured per site, tens to hundreds of thousands of gallons of chemicals are likely stored in containers at a single site during the hydraulic fracturing of these wells. These storage containers are a relatively frequent source of spills during the chemical mixing stage. Spills from these storage containers, even if low in volume, may be severe if they reach a drinking water resource because they often contain concentrated chemicals.

In the produced water handling stage, the severity of impacts from a spill also increases with higher concentrations, especially if the spill reaches groundwater (see site characteristics below). Produced water can vary substantially in chemical concentrations, including total dissolved solids (TDS), metals, radioactive isotopes, and organic chemicals. Within the Marcellus Shale, for example, produced water can range in TDS from less than 1,500 mg/L to over 300,000 mg/L (Rowan et al., 2011). By comparison, the average salinity concentration for seawater is 35,000 mg/L. The more concentrated the produced water, the more likely impacts will be severe if a spill reaches a drinking water resource. When a spilled fluid has greater concentrations of TDS than groundwater, the higher-density fluid can move downward through the groundwater resource. Depending on the flow rate and other properties of the groundwater, impacts from produced water spills can last for years.

In addition to concentration, the toxicity of chemicals affects the severity of the impact if they enter a drinking water resource. There were 37 chemicals listed in 10% or more of all FracFocus disclosures between January 1, 2011 and February 28, 2013. Of these 37 chemicals, nine had chronic oral reference values meeting the criteria used in this assessment.[1] These nine chemicals are associated with health effects including liver toxicity, kidney toxicity, developmental toxicity, reproductive toxicity, and/or carcinogenesis. Chemicals used in hydraulic fracturing fluids and detected in produced water will vary from site to site, so human health hazards are best evaluated on a site-specific basis. Nevertheless, the multi-criteria decision analysis (MCDA) presented in Chapter 9 highlighted certain chemicals that may have greater hazard potential. Propargyl alcohol, 2-butoxyethanol, and N,N-dimethylformamide are three such chemicals having relatively greater hazard potential in the MCDA based on toxicity, frequency of use in hydraulic fracturing fluids, and mobility in water.

Many of the chemicals in produced water are also known or suspected to cause cancer and/or non-cancer health effects in humans. Associated health effects include liver toxicity, kidney toxicity, neurotoxicity, reproductive and developmental toxicity, and carcinogenesis, based on the produced

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[1] The analysis of toxicity presented in Chapter 9 included chemicals regardless of accompanying concentration data in FracFocus, and therefore listed 37 chemicals that were reported in 10% or more disclosures. Comparatively, Chapter 5 listed 35 chemicals that had valid concentration data from FracFocus and were reported in 10% of more disclosures.

water chemicals having chronic oral reference values meeting the criteria used in this assessment. Benzene, pyridine, and naphthalene are three of the chemicals highlighted in the MCDA as having relatively greater hazard potential based on toxicity, measured concentrations in produced water, and mobility in water.

We did not evaluate trends in chemical use by toxicity (e.g., the trends in the use of less toxic chemicals). However, a more recent study of FracFocus data evaluated disclosures dating from March 9, 2011, to April 13, 2015 (Dayalu and Konschnik, 2016; Konschnik and Dayalu, 2016). When compared to the list of 1,084 chemicals used in hydraulic fracturing operations between 2005 and 2013 compiled for this assessment (Appendix H), an additional 263 chemicals were identified (Chapter 5). Only one of these 263 chemicals was reported in more than 1% of disclosures. This comparison of chemical lists does not address potential shifts in volumes of chemicals used, but it does suggest that a shift to new types of chemicals–less toxic or otherwise–did not occur between 2013 and early 2015.

Finally, site characteristics also affect the severity of the impact. Spills into groundwater are likely to be more severe than spills into surface water, everything else being equal. This is not to say that spills into surface water cannot be severe, especially in the immediate vicinity of the spill. For instance, a tank overflowed on a well site in Kentucky spilling fluid into a nearby stream at concentrations sufficient to kill fish in the area (Papoulias and Velasco, 2013). Chemicals can also associate with stream sediments, forming a source of long-term contamination (e.g., radium). In general, however, surface water dilutes a spilled chemical much more rapidly than groundwater. Groundwater often moves slowly between areas of recharge and discharge. Groundwater movement can be as slow as one foot per year or even one foot per decade (Alley et al., 1999). Because of this dynamic, chemicals from multiple spills can accumulate over time in groundwater. Multiple chemical mixing and produced water spills, even if individually small, may impact a groundwater resource in aggregate. Additionally, groundwater contamination may not be as readily apparent as that in surface water because of the need to install monitoring wells to detect contamination in groundwater. Lastly, groundwater can be difficult and expensive to remediate, adding to the severity of impacts if spills reach groundwater (Alley et al., 1999).

10.1.3 Well Injection

Like the water acquisition, chemical mixing, and produced water handling stages, activities in the well injection stage of the hydraulic fracturing water cycle can affect drinking water resources in some instances. The well injection stage involves the injection of hydraulic fracturing fluids through the production well and into the targeted rock formation at sufficient pressure to fracture the rock. There are two fundamental pathways outlined in this assessment by which activities in the well injection stage have the potential to affect drinking water resource quality. They are: (1) fluid (meaning, liquid or gas) movement into a drinking water resource through defects or deficiencies in the production well casing and/or cement; and (2) fluid movement into a drinking water resource through the fracture network. The fluids potentially affecting drinking water resources include hydraulic fracturing fluids, hydrocarbons (including methane gas), and naturally occurring brines. The drinking water resources impacted directly in this stage are almost always groundwater resources, rather than surface water.

Though we could not in this assessment quantify an overall frequency of groundwater quality impacts from the well injection stage, we can describe factors which make impacts more or less frequent or more or less severe, as we did for other stages. We describe these factors below, first with frequency and then severity. Within the frequency discussion, we address factors by each pathway type.

10.1.3.1 Frequency

Pathway #1: Fluid movement into a drinking water resource through defects or deficiencies in the production well casing and/or cement.

To reach and then fracture the production zone, an oil or gas well must first be drilled and constructed down through the subsurface rock formations, often containing an overlying drinking water resource. Since the well passes through the drinking water resource, this means defects or deficiencies in the production well can lead to unintended movement of fluid into the drinking water resource. This can occur regardless of the vertical separation between the drinking water and the production zone.

The relatively brief hydraulic fracturing phase will likely impose the highest stresses to which the well will be exposed during its entire life. If the well cannot withstand the stresses experienced during hydraulic fracturing, the casing or cement can fail, resulting in the loss of mechanical integrity and the unintended movement of fluids into the surrounding environment.

A few studies have estimated rates of mechanical integrity failure of production wells resulting in the loss of *all* barriers protecting the groundwater or in contamination of groundwater in areas with hydraulic fracturing activity (Table 10-1). The estimates are all approximately equal to or less than 1% of wells drilled or hydraulically fractured over varying time frames. For most of these estimates, it is not possible to tell whether failures occurred during hydraulic fracturing or at some other point in the well's life, with the exception of the EPA's Well File Review (U.S. EPA, 2015n). If the failure rate from the Well File Review (0.5%) is applied to the estimates of 275,000 to 370,000 new wells hydraulically fractured nationally between 2000 and part of 2013 and 2000 and part of 2014, respectively (Chapter 3), we would expect roughly 1,370 to 1,850 mechanical integrity failures during this time-period (almost 14 to 15 years). Dividing by each time period yields approximately 100 to 125 mechanical integrity failures per year on average, resulting in the loss of all barriers protecting the groundwater during hydraulic fracturing. These estimates also have a high degree of uncertainty like the spills estimates. This not only stems from the lack of certainty about failure rates, but also uncertainties surrounding the estimates of the number of wells hydraulically fractured (Chapter 3). These are likely low estimates because they do not include mechanical integrity failures occurring outside of the hydraulic fracturing process (e.g., during the production phase), nor do they consider failures in re-fractured wells.

Table 10-1. Literature estimates of mechanical integrity failure rates resulting in contamination of groundwater or failure of all well barriers, potentially exposing the groundwater.

Citation	Mechanical Integrity Failure Rate (%)	Geographic Scope	Key Findings & Description of Mechanical Integrity Failure[a,b]
Fleckenstein et al. (2015)	0.06	Colorado-Wattenberg Field	An overall catastrophic failure rate of 0.06% was found for 16,828 wells studied (out of 17,948 total wells) drilled in the Wattenberg Field between 1970 and 2013. The timing of the failures was unknown, but most of the failures occurred in the older wells. The Wattenberg Formation is 4,400 ft (1,300m) below surface and typically is hydraulically fractured. A catastrophic failure was considered to have occurred when there was contamination of drinking water aquifers (i.e., the presence of thermogenic gas in a drinking water well) and evidence of a well defect such as exposed intermediate gas formations or casing leaks.
Considine et al. (2012)	0.06	Pennsylvania	Two wells were cited between 2008 and 2011 by PA DEP for causing methane migration into an aquifer. In this same time period, 3,533 wells were drilled.
Brantley et al. (2014)	0.12–1.1	Pennsylvania	Based on positive determination letters (PDLs) for violations that occurred between 2008 and 2012, Brantley et al. estimated between 7 and 64 problematic unconventional wells contaminated 85 properties. Since PDLs are tied to drinking water wells and not gas wells, Brantley et al. made assumptions about how many unconventional gas wells were represented by each PDL. This equates to problematic unconventional gas wells compromising approximately 0.1 to 1% of the 6,061 wells spudded between 2008 and 2012.[c] Not all of these PDLs may be due to mechanical integrity failures–they could also be due to other causes, such as spills, or methane migration from natural or other anthropogenic sources.
Vidic et al. (2013)	0.25	Pennsylvania	Of the 6,466 wells studied, 16 received notices regarding contamination of groundwater with gas or other fluids from the PA DEP associated with incidents that occurred between 2008 and 2013.

Citation	Mechanical Integrity Failure Rate (%)	Geographic Scope	Key Findings & Description of Mechanical Integrity Failure[a,b]
U.S. EPA (2016c)	0.5	National	In an estimated 0.5% of the approximately 28,500 hydraulic fracturing jobs surveyed, a failure occurred during hydraulic fracturing, such that there was no additional barrier between the annular space with fluid and the protected drinking water resource. While it could not definitively be determined whether fluid movement into the protected drinking water resource occurred, in these cases, all of the protective barriers intended to prevent such fluid migration had failed, leaving the groundwater source vulnerable to contamination.

[a] Note: While some information is available on the age of the wells studied, it is unclear whether the failure occurred during the hydraulic fracturing event, with the exception of the U.S. EPA (2016c) study. In that study, the failures occurred during hydraulic fracturing.

[b] While the Pennsylvania studies did not specifically identify whether the wells were involved in hydraulic fracturing operations, a significant portion of Pennsylvania's recent oil and gas activity is in the Marcellus Shale; therefore, many of the wells in these studies were most likely used for hydraulic fracturing.

[c] Spudding refers to starting the well drilling process by removing rock, dirt, and other sedimentary material with the drill bit (U.S. EPA, 2013f).

Not all wells are equally likely to lose mechanical integrity; instead, there are factors that make some wells more likely to experience a mechanical integrity failure than others. Well design and construction are two such factors. First, a primary element of well design is the placement of at least one additional layer of casing (besides the production casing) from the surface through the lowest depth of the drinking water resource. This additional casing provides redundancy if the production casing fails. In a study of 731 saltwater injection wells in the Williston Basin in North Dakota, Michie and Koch (1991) found the risk of aquifer contamination from leaks into the drinking water resource was 7 in 1,000,000 injection wells if a surface casing, in addition to the production casing, was set deep enough to cover the drinking water resource. The risk increased to 6,000 per 1,000,000 wells (or 6 in 1,000) if this additional casing was not set deeper than the bottom of the drinking water resource.

Second, fully cementing casing(s) through the entire drinking water resource affects the frequency of impacts. Uncemented sections of surface casing increase the frequency of fluid leaks from the well that can reach groundwater (Fleckenstein et al., 2015; Watson and Bachu, 2009). The EPA's Well File Review estimated that a portion of the protected groundwater resource identified by well operators was uncemented in 3% of the wells surveyed (U.S. EPA, 2015n). With approximately 25,000 to 30,000 new wells hydraulically fractured a year (Chapter 3), this percentage means 750 to 900 of the wells used in hydraulic fracturing operations annually might lack this protection. Adding re-fractured wells would increase the estimate of wells lacking this protection. Knowing the depth of the groundwater resource at the point of drilling and then setting and cementing casings below the lowest part of the drinking water resource can reduce the frequency or likelihood of an impact.

Third, the well's casing, cement, and components need to be designed and constructed to withstand the stresses applied to the well during hydraulic fracturing. In an example of inadequate well construction, hydraulic fracturing of a gas well with insufficient and improperly placed cement in Bainbridge Township, Ohio led to gas contamination of 26 domestic water supply wells and an explosion in the basement of one of the nearby homes. This was due in part to a failure to cement through the over-pressured gas formations and proceeding with the fracturing operation without adequate cement (ODNR, 2008). In another case, casings at an oil well near Killdeer, North Dakota, ruptured in 2010 following a pressure spike during hydraulic fracturing, allowing fluids to escape to the surface. Brine and tert-butyl alcohol were detected in two nearby water wells. Following an analysis of potential sources, the only potential source consistent with the conditions observed in the two impacted water wells was the ruptured well (U.S. EPA, 2015i).

In addition to well design and construction, the degradation or corrosion of well components can also increase the frequency of impacts to drinking water quality. Older wells exhibit more integrity problems as cement and casings age. The EPA's Well File Review estimated at least 10% of the wells represented in the national survey were greater than five years old at the time of hydraulic fracturing. Hydraulic fracturing or re-fracturing older wells has the potential to increase the frequency of casing or cement failures allowing unintended fluid migration into drinking water resources.

Confirming well mechanical integrity can reduce the frequency of water quality impacts. Pressure testing the casing used for hydraulic fracturing prior to the job can help detect problematic casing—and provide an opportunity to make needed repairs if necessary. Monitoring the annular space behind the casing used for hydraulic fracturing during the hydraulic fracturing job can detect well component failure in real time and signal for an immediate shut down. Based on the EPA's Well File Review study, casing pressure testing occurred at slightly less than 60% of the approximately 28,500 hydraulic fracturing jobs represented in that time frame (primarily 2009-2010) and annulus monitoring took place during slightly more than 50% of these same jobs, implying these activities did not always occur (U.S. EPA, 2016c). It is unclear whether the frequency of these practices have changed since this time period.

Pathway #2: Fluid movement into a drinking water resource through the fracture network.

The other potential pathway for fluid movement into a drinking water resource is through the fracture network. This could occur indirectly if the fracture network extends to a nearby well or its fracture network, or to another permeable subsurface feature, such as natural fractures or faults, which then allow the fluid to reach an underground drinking water resource. It could also occur directly by the fracture network extending out of the production zone into a drinking water resource, or hydraulic fracturing into a drinking water resource itself.[1] Key factors affecting the frequency of this pathway are the presence, distance, and condition of nearby wells; and the vertical

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[1] Hereafter, fractures extending out of the production zone are referred to as "out-of-zone" fractures, consistent with Chapter 6.

separation distance and the characteristics of the intervening rock between the production zone and the drinking water resource.

Nearby wells (often called offset wells) can be a pathway for fluid movement, with hydraulic fracturing fluid from one production well moving through the subsurface and entering another nearby oil or gas well or its fracture network. These events are commonly referred to as “well communication events” or “frac hits.” The communication event might simply be registered as an increase in pressure in the nearby well; yet there is also the possibility of damage to the nearby well or its components, causing a surface spill or a subsurface release of fluids. The EPA’s Well File Review found 1% of the wells represented in the study experienced a frac hit, and the EPA spills report identified 10 spills attributed to well communication events (U.S. EPA, 2015m, n). It is unknown whether any fluid reached a drinking water resource from these spills. Where active nearby wells exist, operators of those wells can shut them in temporarily during the nearby hydraulic fracturing to reduce the possibility of spills or damage to their wells, and therefore, the potential for drinking water resource contamination.

The distance to the nearby well can affect the frequency of these communication events. In one study, the likelihood of a frac hit was less than 10% in hydraulically fractured wells more than 4,000 ft (1,219 m) apart, while nearly 50% in wells less than 1,000 ft (300 m) apart (Ajani and Kelkar, 2012). Distance was measured from the mid-point of each horizontal lateral. Thus, the closer the nearby wells, the more likely a communication event.

If nearby wells are in good condition and can withstand an increase in pressure, then an impact is unlikely to occur. However, if the nearby well is not able to withstand the pressure of the fluid, well components may fail and allow fluid to move into a drinking water resource. Because of this, nearby older or abandoned wells are of particular concern. In older wells near a hydraulic fracturing operation, plugs and cement may have degraded over time; in some cases, abandoned wells may never have been plugged properly. This can be a significant issue in areas with legacy (i.e., historic) oil and gas exploration. A Pennsylvania Department of Environmental Protection (PA DEP) report cited three cases where migration of natural gas had been caused by well communication events via old, abandoned wells (PA DEP, 2009c). In Tioga County, Pennsylvania, following hydraulic fracturing of a shale gas well, an abandoned well nearby produced a 30 ft (9 m) geyser of brine and gas for more than a week (Dilmore et al., 2015). Various studies estimate the number of abandoned wells in the United States to be significant. For example, the Interstate Oil and Gas Compact Commission (IOGCC, 2008) estimates that approximately 1 million wells were drilled in the United States prior to a formal regulatory system, and the status and location of many of these wells are unknown. Hydraulic fracturing operators can reduce the possibility of impacts by identifying nearby wells, and if necessary, plugging or otherwise addressing deficiencies in these wells.

If nearby wells serve as a pathway, fluid movement can bypass layers of intervening rock. In the absence of this pathway, however, vertical distance and the intervening rock between the production zone and the drinking water resource are factors affecting the possible movement of fluid into a drinking water resource. The extension of fractures out of the oil and/or gas production zone can—and does—occur. Examples have been reported in Greene County, Pennsylvania (Hammack et al., 2014); at the Killdeer site in Dunn County, North Dakota (U.S. EPA, 2015i); and in other wells within the Bakken Shale (Arkadakskiy and Rostron, 2013; Arkadakskiy and Rostron, 2012; Peterman et al., 2012). In a study across several major shale formations, Davies et al. (2012) found upward vertical fracture growth was often on the order of tens-to-hundreds of feet. One percent of the fractures had a fracture height greater than 1,148 ft (350 m), and the maximum fracture height among all of the data reported was 1,929 ft (588 m). This would suggest that substantial vertical separation could preclude out-of-zone-fractures from directly reaching the drinking water resource, although these measurements were only conducted in shale formations and the extension of fractures is not the only way the drinking water resource could be contaminated from out-of-zone fractures (see below). A modeling study also suggests fractures are unlikely to extend from the production zone directly to a shallow drinking water resource in a deep Marcellus-like environment (Kim and Moridis, 2015).

Not all fracturing occurs, however, with substantial vertical separation between the production zone and the drinking water resource (Figure 10-3). The EPA's Well File Review found that 20% of wells used for hydraulic fracturing had less than 2,000 ft (600 m) between the shallowest point of fracturing and the base of the protected groundwater resource (U.S. EPA, 2015n). In coalbed methane (CBM) plays, typically shallower than shale gas plays, these separation distances can be smaller. For example, in the Raton Basin of southern Colorado and northern New Mexico, approximately 10% of CBM wells have less than 675 ft (206 m) of separation between the production zone and the depth of local water wells. In certain areas of the basin, this distance is less than 100 ft (31 m) (Watts, 2006). Many of these areas are shallower in depth, and fracture growth has been shown to be primarily horizontal, rather than vertical, at less than 2,000 ft (600 m) from the surface (Fisher and Warpinski, 2012). Nevertheless, the possibility of an out-of-zone fracture reaching a drinking water resource is more likely in a setting with less vertical separation than with more.

Even if an out-of-zone fracture does not extend into a drinking water resource, it could connect to other permeable subsurface features, such as natural fractures or faults, which could then connect to a drinking water resource. Thus, properties of the intervening rock can also make this pathway more or less frequent or likely. For instance, in the Pavillion gas field in Wyoming, there are no laterally-continuous confining layers to prevent upward movement of fluids into the groundwater (Digiulio and Jackson, 2016). While flow of subsurface fluids generally tends to be downward, local areas of upward flow have been observed (Digiulio and Jackson, 2016).

There are cases of hydraulic fracturing without vertical separation between the drinking water resource and the production zone (Figure 10-3). The co-location of the oil or gas formation with the drinking water resource is the factor affecting the frequency of an impact in these cases. Directly fracturing into a drinking water resource causes an impact because it changes the quality of the resource by introducing hydraulic fracturing fluids. The EPA's Well File Review found an estimated 0.4% of the wells represented in the study had perforations used for hydraulic fracturing shallower than the base of the protected groundwater resource, as reported by well operators (U.S. EPA, 2015n). The EPA's Well File Review did not examine these instances by formation type. This practice may be concentrated in locations in western states, especially in CBM plays. Examples include the Raton Basin in Colorado (U.S. EPA, 2015k), the San Juan Basin of Colorado and New

Mexico (U.S. EPA, 2004a), and the Powder River Basin of Montana and Wyoming (Dahm et al., 2011; ALL Consulting, 2004; U.S. EPA, 2004a). This is a concern in the short term (should there be people using these drinking water resources currently) and the long term (if drought or other conditions necessitate the future use of these drinking water resources). For the most part in this chapter, we focused on factors which can be managed, changed, or used to identify areas to target monitoring efforts. In this situation, hydraulic fracturing directly into a drinking water resource would need to cease if it was decided the resulting impacts to drinking water resource quality were unacceptable.

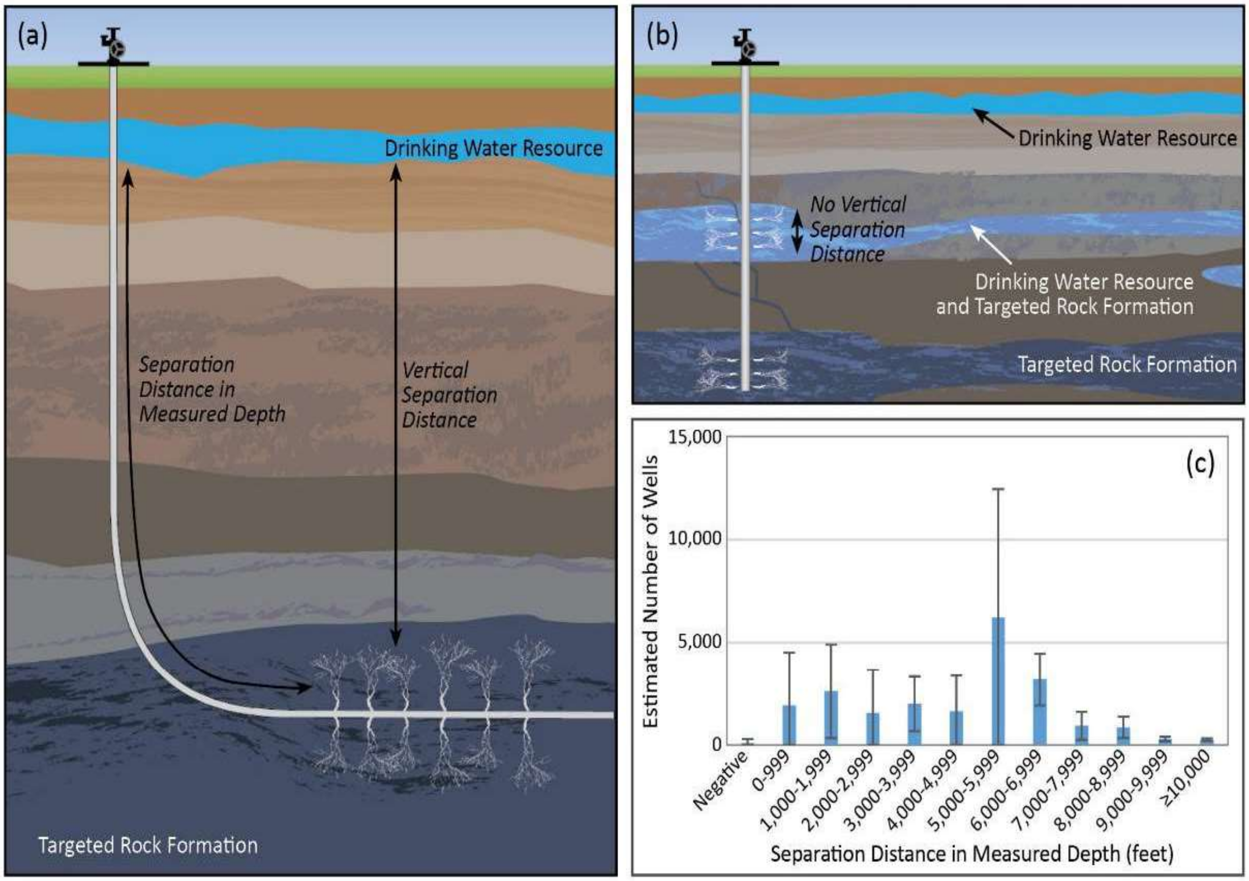

Figure 10-3. Separation in measured depth between drinking water resources and hydraulically fractured intervals in wells.

In panel (a), the oil- and gas-bearing formation (dark gray) being hydraulically fractured is much deeper than the depth where drinking water resources (light blue) exist, and hence a comparatively large separation distance exists. In panel (b), there are two oil- and gas-bearing formations (dark gray and grayish blue) being hydraulically fractured. The shallower formation has no separation distance, because the water also contained in this formation is a drinking water resource. Panel (b) also shows another subsurface drinking water zone at a shallower depth (light blue). Multiple groundwater zones of varying qualities can exist between the production zone and the surface. These two panels depict end-member cases of separation distance: from large separation distances to no separation distance. The graph in panel (c) illustrates the distribution of separation distances among the approximately 23,000 oil and gas production wells hydraulically fractured by nine service companies between 2009 and 2010 (U.S. EPA, 2015n). Error bars in the panel (c) display 95% confidence intervals.

Lastly, the presence of gas, as opposed to liquids, in the subsurface may be a factor affecting the frequency of impacts from fluid movement via defects or deficiencies in the well (pathway #1), or through the fracture network (pathway #2). The low density of gas compared to liquids makes it buoyant, which creates an upward drive toward the surface. Thus, gas found in the subsurface, such as methane, can exploit pathways in a well (such as along a well lacking mechanical integrity), or in the surrounding rock (such as induced or naturally occurring fractures). If a pathway exists and gas is present, it can reach groundwater used for drinking. Consequently, gases could be more likely to contaminate drinking water resources than liquids (Li et al., 2016a).

10.1.3.2 Severity

The well injection chapter (Chapter 6) focused primarily on the potential for impacts to occur and factors affecting frequency. By contrast, we have little-to-no information on factors affecting the severity of impacts for this stage of the hydraulic fracturing water cycle. Severity would likely be affected by the chemical composition of the fluid entering the drinking water resource; the volume of the fluid; the duration in which that volume is delivered; and the concentration of the fluid and its specific components, among other factors. Logically, the relatively simple pathway of a mechanical integrity failure might result in the highest fluid volume delivered to a drinking water resource over a short period of time—e.g., contamination of water wells in Bainbridge Township, Ohio. By contrast, fluid movement through a fracture network, then through the intervening rock, and finally into a drinking water resource may take a longer time and deliver a comparatively lower volume. Even in this case, however, the impacts could still be severe if the fluid movement was to go undetected and unaddressed.

10.1.4 Wastewater Disposal and Reuse

The last stage of the hydraulic fracturing water cycle is wastewater disposal and reuse. Produced water from hydraulically fractured oil or gas production wells is managed predominantly through disposal in underground Class II wells. Secondarily, it is disposed of via other practices, such as discharge to surface waters or disposal in pits or evaporation ponds, or reused in other hydraulic fracturing operations. Activities in the wastewater disposal and reuse stage of the hydraulic fracturing water cycle can impact drinking water resources in some instances. Two such activities are: the discharge of inadequately treated wastewater to surface water, and the storage or disposal of wastewater in unlined pits or impoundments leading to contamination of surface water or groundwater. In this section, we address factors increasing or decreasing the frequency or severity of impacts from these activities. As in the water acquisition section, we combine our discussion of frequency and severity here.

10.1.4.1 Frequency and Severity

Discharge of inadequately treated wastewater has impacted surface water. The quality of the wastewater discharged is a factor affecting the frequency and severity of impacts. This factor is a function of the chemical characteristics of the wastewater prior to treatment (i.e., the composition and concentration of chemicals in the wastewater) and the efficacy of the treatment process. The pre-2011 treatment of Marcellus wastewater in Pennsylvania illustrates this combination. In

Pennsylvania before 2011, wastewater from shale gas operations was treated at centralized waste treatment facilities (CWTs) and publicly owned treatment works (POTWs). The POTWs and some CWTs at the time were not equipped to adequately treat high TDS wastewater. This resulted in wastewater discharges containing elevated levels of TDS, including bromide and iodide, to surface waters.

The elevated levels of TDS raised concerns about the formation of disinfection byproducts (DBPs) after treatment at downstream drinking water facilities. Disinfection byproducts are formed when organic material comes in contact with disinfectants (e.g., chlorine, chloramine, chlorine dioxide or ozone). Many DBPs have long-term health effects including an increased risk of cancer, anemia, liver and kidney effects, and central nervous system effects. Of particular concern are DBPs formed in the presence of bromide or iodide, which are considered particularly toxic. Management of DBPs places a burden on downstream drinking water utilities. Concerns regarding elevated TDS (in particular high bromide) and the potential for formation of DBPs led the PA DEP to take steps in 2010 and 2011 to route Marcellus Shale wastewater away from POTWs and CWTs (that could not treat for TDS) to alternate options such as disposal via injection wells, on-site reuse, or reuse after limited treatment at CWTs. By 2014, only a small percentage (approximately less than 1%) of Marcellus wastewater went to CWTs permitted to discharge to surface waters (Figure 10-1). Additionally, the new EPA pretreatment standards prohibit oil and gas operators from sending unconventional oil and gas wastewater directly to POTWs (U.S. EPA, 2016d).

The combination of wastewater composition and inadequate treatment have also resulted in the discharge of other constituents such as barium, strontium, and radium into surface waters in Pennsylvania. Marcellus Shale wastewater contains radium, naturally occurring in the subsurface formation. Radium has been found in stream sediments at discharge points for POTWs and CWT facilities that have accepted Marcellus Shale wastewater. The ratio of radium isotopes (radium-228 to radium-226) in these sediments is consistent with ratios in Marcellus Shale wastewater (Warner et al., 2013a). Radium-226, with a half-life of approximately 1,600 years, causes long-term contamination. The practice of management of wastewaters via POTWs and CWTs without TDS removal has declined, yet it remains uncertain whether the discharge of radionuclides to surface waters from the oil and gas industry in Pennsylvania has ceased entirely (PA DEP, 2015b).

The storage or disposal of wastewater in pits or impoundments can also lead to contamination of surface water or groundwater resources. This can occur via surface spills or overflows. It can also occur via infiltration into the soil and percolation to groundwater through the pit itself. Whether the pit or impoundment is lined is an important factor affecting the frequency and severity of impacts on groundwater due to subsurface leaching. Historically, unlined pits have been used to dispose of wastewater via percolation (or evaporation). While this practice has been banned in most states, it is allowed in certain locations or instances (e.g., storage of wastewater, but not disposal) as of July 2016. Even where prohibited, unpermitted unlined disposal or storage pits exist. For example, approximately 1,000 unlined storage or disposal pits of oil and gas wastewater are located in the Central Valley Region of California (California State Water Resources Control Board, 2016; Esser et al., 2015). Of these, approximately 60% were still active as of July 2016, and roughly 20% of those pits lacked permits (CA Water Board, 2016).

Unlined pits have been shown to cause contamination of drinking water resources. The presence of BTEX (benzene, toluene, ethylbenzene, and xylenes) and other organics in groundwater are linked to pits in California and New Mexico (California Regional Water Quality Control Board Central Valley Region, 2015; Sumi, 2004; Eiceman, 1986). Groundwater impacts downgradient of an unlined pit in Oklahoma included high salinity (3500-25,600 mg/L) and the presence of volatile organic compounds (Kharaka et al., 2002). Impacts can also occur in the case of disposal of relatively low TDS wastewater (Healy et al., 2011; Healy et al., 2008). For example, a CBM wastewater impoundment in the Powder River Basin of Wyoming resulted in high concentrations of TDS, chloride, nitrate, and selenium in the groundwater (Healy et al., 2011; Healy et al., 2008). Total dissolved solids exceeded 100,000 mg/L in one groundwater sample, despite the much lower concentrations (2,300 mg/L) in the wastewater being discharged (Healy et al., 2008). Most of the solutes found in the groundwater did not originate with the CBM wastewater, but rather resulted from dissolution of previously existing salts and minerals in the subsurface. Lining pits or using closed-loop systems (i.e., tanks) can decrease the frequency of such impacts.

10.1.5 Summary

In the above section, we synthesized the information in this assessment by discussing factors increasing or decreasing the frequency or severity of impacts from activities in the hydraulic fracturing water cycle. We focused particularly on factors that could be managed, changed, or used to identify locations for additional monitoring or alteration of practices. Based on the information reviewed, we conclude the following combinations of activities and factors are more likely than others to result in more frequent or more severe impacts:

- Water withdrawals for hydraulic fracturing in times or areas of low water availability, particularly in areas with limited or declining groundwater resources;
- Spills during the management of hydraulic fracturing fluids and chemicals or produced water that result in large volumes or high concentrations of chemicals reaching groundwater resources;
- Injection of hydraulic fracturing fluids into wells with inadequate mechanical integrity, allowing gases or liquids to move to groundwater resources;
- Injection of hydraulic fracturing fluids directly into groundwater resources;
- Discharge of inadequately treated hydraulic fracturing wastewater to surface water resources; and
- Disposal or storage of hydraulic fracturing wastewater in unlined pits, resulting in contamination of groundwater resources.

Conversely, the scientific literature and data provide evidence that certain factors can reduce the frequency or severity of impacts. Based on the information reviewed in this assessment, we conclude the following factors are likely to reduce the frequency or severity of impacts:

- Passby flows, or low-flow criteria, for surface water withdrawals, and the use of brackish groundwater or reused wastewater as substitutes for fresh water withdrawals;

- Implementation of spill prevention and response measures;
- Design and placement of well casing and cement able to withstand the stresses imposed by hydraulic fracturing (including identifying the depth of the drinking water resource at the point of drilling, and setting and cementing casings through the entire drinking water resource);
- Confirming mechanical integrity of oil and gas wells prior to, during, and after hydraulic fracturing, and correcting deficiencies if necessary;
- Identification of active or abandoned wells near hydraulic fracturing operations and, if necessary, adjustment of the operations to minimize well-to-well communication and/or plugging improperly abandoned wells;
- The use of treatment technologies to remove TDS, and other constituents, such as radium, when present prior to discharge; and
- Storage of wastewater in lined pits or the use of closed-loop systems instead of pits.

The above factors are not the only factors that can reduce the frequency or severity of impacts, yet are the ones most emphasized by the information reviewed for this assessment. It should be noted that the above factors reduce, but do not completely eliminate, the possibility of an impact occurring. In the case of hydraulic fracturing directly into a drinking water resource or disposal of wastewater via unlined pits, we did not identify factors which could reduce the frequency or severity of impacts, besides restricting the activity itself.

10.2 Uncertainties and Data Gaps

In this assessment, we identified impacts on drinking water resources in all stages of the hydraulic fracturing water cycle and described the factors affecting the frequency or severity of impacts. The major conclusions presented above (in Section 10.2.5) are the strongest conclusions based on data and information synthesized for the assessment.

There were also many areas within the assessment for which strong conclusions could not be reached. This was because of the lack of publicly available data and large uncertainties in available sources of information. Below, we provide perspective on what data gaps and uncertainties prevented us from drawing additional strong conclusions about the potential for impacts and/or the factors affecting the frequency or severity of impacts.

We encountered uncertainties associated with, and gaps in, aggregated, publicly accessible information about both activities in the hydraulic fracturing water cycle and groundwater data. In general, comprehensive information on the location of activities in the hydraulic fracturing water cycle is lacking, either because it is not collected, not publicly-available, or prohibitively difficult to aggregate. Thus, we lacked complete information on the geographic locations of well sites (both new and existing) where the chemical mixing, well injection, and produced water handling stages take place; the depth(s) of zones that have been hydraulically fractured in these wells; where water is being acquired (i.e., the source water) for hydraulic fracturing; and where hydraulic fracturing wastewater is treated and/or disposed. FracFocus provided data on well locations, and water and other chemicals used at those locations. However, reporting to FracFocus at the time period studied was not always required, making it difficult to determine the completeness or representativeness of the information.

In addition, there are uncertainties about where groundwater resources are located. This includes the thickness of the resource, from its top to its lowest depth, and its relation to the shallowest depth where hydraulic fracturing occurred. If comprehensive data about the locations of both drinking water resources and activities in the hydraulic fracturing water cycle were available, it would have been possible to more completely identify areas in the United States where hydraulic fracturing-related activities and drinking water resources overlap.

There are also uncertainties and data gaps related to chemicals used in hydraulic fracturing fluid and those detected in produced water. Some chemicals and chemical mixtures remain undisclosed because of confidential business information (CBI) claims. Well operators claimed at least one chemical as CBI at more than 70% of disclosures reported to FracFocus between 2011 and early 2013. Data suggests this practice is increasing. Konschnik and Dayalu (2016) reported that 92% of FracFocus disclosures submitted between approximately March 2011 and April 2015 included at least one chemical claimed as confidential. When chemicals are claimed as CBI, there is no public means of accessing information on these chemicals. Furthermore, many of the chemicals and chemical mixtures disclosed, or those detected in produced water, lack information on properties affecting their movement, persistence, and toxicity in the environment should they be spilled. Better information on these chemicals would allow for a more robust evaluation of potential human health hazards posed, and thus a better understanding about the severity of impacts should the chemicals reach drinking water resources.

In places where we know hydraulic fracturing water cycle activities have occurred, data to assess impacts are often either not collected or are not publicly available in accessible forms. Specifically, local water quality monitoring and well mechanical integrity integrity data are not consistently collected or readily available. In particular, sufficient baseline data on local water quality are needed to quantify any changes post-hydraulic fracturing. There are exceptions to this, for example, the state of California recently implemented a plan to make water quality monitoring information public (Text Box 10-1). In general, however, the limited amount of data collected before, during, and after hydraulic fracturing activities and made public, reduces the ability to determine whether hydraulic fracturing affected drinking water resources.

Text Box 10-1. Hydraulic Fracturing and Groundwater Quality Monitoring in California.

In July 2015, the California Water Resources Control Board adopted Senate Bill 4 (SB4), *Model Criteria for Groundwater Monitoring in Areas of Oil and Gas Well Stimulation*. This resolution directed the establishment of a "comprehensive regulatory groundwater monitoring and oversight program...in order to assess the potential effects of well stimulation treatment activities on the state's groundwater resources" (California State Water Resources Control Board, 2015). The adoption of SB4 concluded a multi-year process, which incorporated stakeholder engagement, review by the public, and consultation with an expert scientific panel.

(Text Box 10-1 is continued on the following page.)

Text Box 10-1 (continued). Hydraulic Fracturing and Groundwater Quality Monitoring in California.

The recommendations of the expert panel informed the creation and implementation of SB4 with respect to criteria "to be used for assessment, sampling, analytical testing, and reporting of water quality associated with oil and gas well stimulation activities" (Esser et al., 2015).

The resolution requires two different scales of groundwater monitoring for different purposes. First, it requires well-by-well (also called "area-specific") groundwater monitoring by well operators. This includes groundwater monitoring conducted for all hydraulic fracturing projects initiated after July 2015. Each oil or gas production well operator must submit a design and timeline for monitoring groundwater resources in proximity to its proposed well. The State Water Resources Control Board approves the monitoring plan before hydraulic fracturing can proceed. The groundwater monitoring plan must include:

- The installation of monitoring wells within 0.5 miles of the wellhead. At least one monitoring well must be upgradient of the production well and two monitoring wells must be downgradient. Should the production well penetrate more than one protected groundwater resource (as defined by the resolution), monitoring wells must facilitate sampling of at least one that is shallow and one that is deep.
- A monitoring timeline that includes sampling prior to production well construction and hydraulic fracturing, as well as semi-annual sampling after completion.
- A list of water quality parameters and constituents to be monitored, including TDS, specific metals, and specific organic compounds.

The area-specific monitoring requirements also include submission of information by well operators about geologic and human-made features in the subsurface that could serve as pathways for impacts to groundwater, aspects of production well construction, and hydraulic fracturing fluid composition.

Second, a regional groundwater monitoring program will document trends in baseline water quality and locate protected groundwater state-wide. In addition to monitoring for trends in groundwater quality related to activities at well sites, it will also be designed to detect trends related to impacts from wastewater disposal practices.

All data from the monitoring programs will be publicly accessible in a state-maintained database. The database is intended to support public health, scientific, and academic needs, as well as future "investigation, assessment, and research relevant to oil and gas development impacts on groundwater quality" (Esser et al., 2015).

Together, the data and information collected and made publicly available as part of the area-specific and regional groundwater monitoring in California will help fill data gaps identified in this section of the assessment by locating groundwater resources, monitoring drinking water resources at spatial and temporal scales relevant for detecting impacts from activities in the hydraulic fracturing water cycle, and distinguishing impacts from hydraulic fracturing activities from the impacts of other potential sources.

In the cases where effects are suspected, it is often difficult to separate the potential effects of hydraulic fracturing activities from effects of broader oil and gas industry activities and other industries or causes. The use of long-lasting, mobile tracer chemicals added to hydraulic fracturing fluids to monitor for impacts has been proposed (Kurose, 2014), but has received relatively little attention in the scientific literature as of mid-2016. Instead, measured changes in water quality parameters can be associated with, but not necessarily diagnostic of, impacts from hydraulic fracturing activities. For instance, measurable changes in methane levels, TDS, ratios of geochemical constituents, and isotopic ratios might suggest impacts from hydraulic fracturing but could also be from other sources, either natural or anthropogenic. To try to assign a cause, these measurements often have to be followed with further collection of evidence supporting or refuting hydraulic fracturing activities as the cause of the changes. (See Text Box 10-2 for discussion of causal assessments.)

Text Box 10-2. Causal Assessment and Hydraulic Fracturing Water Cycle Activities.

A number of recent studies have conducted regional-scale assessments of trends in water quality in areas with hydraulic fracturing activity, showing either no trend or trends linked temporally or spatially with hydraulic fracturing (Burton et al., 2016; Hildenbrand et al., 2016; Hildenbrand et al., 2015; Siegel et al., 2015; Darrah et al., 2014; Fontenot et al., 2013; Warner et al., 2013b) Regional assessments can be important for integrating information over broader scales, and for posing hypotheses about how hydraulic fracturing water cycle activities may impact drinking water resources. Oftentimes, however, activities in the hydraulic fracturing water cycle are merely one of several possible causes of an observed change in water quality or quantity at a specific site. In this case, more thorough, site-specific investigations are often necessary. Causal assessment (also called causal analysis) involves collecting multiple kinds of evidence to determine which of several possible causes of contamination is most likely.

Causal assessment requires several steps. First, the spatial and temporal scope of the issue is defined, including a description of all the possible causes of an observed impact, in this case the change in quality or quantity of a drinking water resource. Once this is done, evidence is collected and assembled to support or refute the potential causes. Evidence indicating how a potential cause and an observed effect are related in time can help support or refute potential causes. Other kinds of evidence can also be useful in identifying a cause, including: determining whether the composition and volume of a leaked, spilled, or treated and discharged fluid are capable of causing observed impacts on water quality; and determining whether a physical pathway between a well or well site exists by measuring the mechanical integrity of hydraulically fractured wells and/or establishing the presence/absence of a contaminant plume.

Ideally, the evidence helps exclude possible causes of the reported contamination, narrowing down the list of potential causes to a single cause. Causal assessments can take a long time to complete and can require a lot of resources and expertise. In some situations, available data and resources are simply not sufficient to definitively identify the cause. Nevertheless, causal assessments conducted in a consistent and transparent way can help enable the identification of the likely cause(s) of contamination of drinking water resources.

The retrospective case studies conducted by the EPA under the Study Plan are examples of scientific investigations using a multiple lines of evidence approach consistent with the principles of causal assessment (U.S. EPA, 2015i, j, l, 2014f, g). These case studies were cited throughout this report. For instance, as noted previously, the Killdeer, North Dakota case study found that an inner string of casing burst during hydraulic fracturing of an oil well, resulting in a release of hydraulic fracturing fluids and formation fluids that impacted a groundwater resource (U.S. EPA, 2015i). Following an analysis of potential sources, the only potential source consistent with the conditions observed was the ruptured well (U.S. EPA, 2015i).

Regardless of whether a single cause can be determined, actions can still be taken to mitigate one or more potential causes of contamination. Information gained once the suspected activity has been halted or at least reduced could elucidate whether hydraulic fracturing operations are more or less likely to have been the source of the contamination.

Many members of the public are interested in understanding the national frequency of impacts to drinking water resources from activities across the entire hydraulic fracturing water cycle. Because of the significant data gaps and uncertainties in the available data, it was not possible to estimate the national frequency of impacts to drinking water resources from activities in the hydraulic fracturing water cycle collectively. We were, however, able to estimate impact frequencies in some, limited cases within the larger hydraulic fracturing water cycle (i.e., spills of hydraulic fracturing fluids or produced water, and mechanical integrity failures). These more specific estimates had a high degree of uncertainty, but were the best estimates that could be provided with the data and literature currently available.

Finally, it should be recognized that this assessment is a snapshot in time. Our understanding of the factors affecting the frequency or severity of impacts may change in the future as industry practices evolve and new information becomes available.

10.3 Use of this Assessment

This assessment contributes to the understanding of the potential impacts to drinking water resources by activities in the hydraulic fracturing water cycle and the factors influencing those impacts. The scientific information presented can be used by federal, tribal, state, and local officials; industry; and the public to better understand and address vulnerabilities of drinking water resources to activities in the hydraulic fracturing water cycle.

The uncertainties and data gaps identified throughout this assessment could be used to identify future data collection efforts. Data collection efforts could include, for example, surface water and groundwater monitoring programs in areas with hydraulically fractured oil and gas production wells; collection and the public dissemination of data on the condition of hydraulically fractured wells; or targeted research programs to better characterize the environmental fate and transport and human health hazards associated with chemicals in the hydraulic fracturing water cycle. Data collected and analyzed through new data collection efforts may identify new factors increasing or decreasing the frequency or severity of impacts.

In the near term, decision-makers could focus their attention on the combinations of activities and factors that we conclude are more likely than others to result in more frequent or more severe impacts (Section 10.2.5). By focusing attention on the above combinations, impacts to drinking water resources from activities in the hydraulic fracturing water cycle can be prevented or reduced.

Overall, the practice of hydraulic fracturing is expanding and continues to change. Oil and gas production associated with hydraulic fracturing was insignificant in 2000, but by 2015 it accounted for an estimated 51% of U.S. oil production and 67% of U.S. gas production (EIA, 2016c, d). The number of wells drilled and hydraulically fractured is likely to continue to increase in the coming decades (EIA, 2014a). The work of evaluating potential impacts from combinations of activities and factors in the hydraulic fracturing water cycle will need to keep pace with this industry and as new scientific studies are produced. This assessment provides a foundation for those efforts, while offering information to support the reduction of current vulnerabilities of drinking water resources.

Chapter 11. References

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Hyperlinks to the reference citations throughout this document will take you to the ORD National Center for Environmental Assessment HERO database (Health and Environmental Research Online) at https://hero.epa.gov/hero. HERO is a database of scientific literature used by the U.S. EPA in the process of developing selected science assessments.

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