The EPA compiled a list of 1,084 chemicals with unique CASRNs reported as used in the hydraulic fracturing process between 2005 and 2013 (full list, methodology, and details on sources in Appendix H).[1] These chemicals fall into different chemical classes and include 455 organic chemicals, 258 inorganic chemicals, and 361 organic mixtures or polymers. The chemical classes of commonly used hydraulic fracturing chemicals include but are not limited to:

- Acids (e.g., hydrochloric acid, peroxydisulfuric acid, acetic acid, citric acid);
- Alcohols (e.g., methanol, isopropanol, ethylene glycol, propargyl alcohol, ethanol);
- Aromatic hydrocarbons (e.g., benzene, naphthalene, heavy aromatic petroleum solvent naphtha);
- Bases (e.g., sodium hydroxide, potassium hydroxide);
- Hydrocarbon mixtures (e.g., petroleum distillates);
- Polysaccharides (e.g., guar gum);
- Surfactants (e.g., poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy, 2-butoxyethanol); and
- Salts (e.g., sodium chlorite, dipotassium carbonate).

Further details on these chemicals and their associated hazards are presented in Chapter 9.

All of the sources of information used to compile the list of chemicals found in hydraulic fracturing fluids (Appendix H) relied on reported use of those chemicals. In some cases, analysis of produced water samples by advanced analytical methods could provide information on suspected hydraulic fracturing additives, but other sources for the chemicals need careful consideration (Hoelzer et al., 2016). These sources include chemicals originating from components of the well, lab contamination, or subsurface reaction. We limit our discussion of hydraulic fracturing fluid chemicals to those directly reported as used.

An additional complication in providing an assessment on the use of chemicals in hydraulic fracturing is that companies can withhold reporting chemicals to the FracFocus registry by claiming that a chemical is Confidential Business Information (CBI). The use of CBI is to protect proprietary information, such as trade secrets. Details on CBI are provided in Text Box 5-2.

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[1] The EPA used eight different sources to identify chemicals used in hydraulic fracturing fluids. This included the EPA FracFocus report (U.S. EPA, 2015a) and seven other sources (U.S. EPA, 2013a; Colborn et al., 2011; House of Representatives, 2011; NYSDEC, 2011; PA DEP, 2010a; U.S. EPA, 2004a; Material Safety Data Sheets).

### Text Box 5-2. Confidential Business Information (CBI).

This assessment relies in large part upon information provided to the EPA or to other organizations. The submitters (e.g., businesses that operate wells or perform hydraulic fracturing services) may view some of the information as confidential business information (CBI) and accordingly asserted CBI claims to protect it. Information deemed to be CBI may include trade secrets or other proprietary business information entitled to confidential treatment under Exemption 4 of the Freedom of Information Act (FOIA) and other applicable laws. The FOIA and EPA's CBI regulations may allow for information claimed as CBI provided to the EPA to be withheld from the public, including in this document. In practical terms, when a well operator claims CBI for a specific chemical, they do not report the name or CASRN for that chemical in the disclosure submitted to the FracFocus registry (see Text Box 5-1 for information on FracFocus).

The EPA evaluated data from FracFocus, a national hydraulic fracturing chemical registry used and relied upon by some states, industry groups, and non-governmental organizations, as described in Text Box 5-1. A company submitting a disclosure to FracFocus may choose to not report the identity of a chemical it considers CBI. More than 70% of disclosures contained at least one chemical claimed as CBI and 11% of all chemicals were claimed as CBI. Of the disclosures containing CBI chemicals, there were an average of five CBI chemicals per disclosure (U.S. EPA, 2015a). Rates of withholding chemical information (designating a chemical as CBI) have increased from 11% in the 2011 to early 2013 time period of the EPA report, to 16.5% across the 2011 to early 2015 time period in another study using FracFocus data, with 92% of FracFocus 2.0 disclosures including at least one chemical claimed as CBI (Konschnik and Dayalu, 2016). When a chemical is claimed as CBI, there is no public means of accessing information on these chemicals (e.g., CASRN, name). Sometimes a CBI entry will provide the chemical family (Appendix H).

Consistent with the EPA's *Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources* (U.S. EPA, 2011d), data were submitted by nine service companies to the EPA regarding chemicals used in hydraulic fracturing from 2005 to 2009. These data were separate from the EPA FracFocus 1.0 project database. The data were submitted directly to the EPA, with the actual names and CASRNs of any chemicals the company considered CBI. This included a total of 381 CBI chemicals, with a mean of 42 CBI chemicals per company and a range of 7 to 213 (U.S. EPA, 2013a). Of these 381 chemicals, some companies only provided a generic chemical name and no CASRN, some provided neither a chemical name or CASRN, while others provided a CASRN and a specific chemical name. This resulted in 80 CASRNs/chemical names on this CBI list. Table H-3 lists generic chemical names, which may have been designed to mask CBI chemical names given to the EPA. The EPA does not know if the 381 chemicals represent 381 unique chemicals or if there are duplicates on this list.

The prevalence of CBI claims in the EPA FracFocus 1.0 project database limits completeness of the data set and introduces uncertainty. Ideally, all data would be available on all chemicals to do a full assessment.

### 5.4.1 National Frequency of Use of Hydraulic Fracturing Chemicals

A total of 692 chemicals were identified in the EPA FracFocus 1.0 project database that were reported as used in hydraulic fracturing from January 1, 2011, to February 28, 2013. This information comes from a total of 35,957 disclosures with chemical data in the database (U.S. EPA, 2015a).[1]

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[1] Chemicals may be pure chemicals (e.g., methanol) or chemical mixtures (e.g., hydrotreated light petroleum distillates), and they each have a single CASRN. Of these 692 chemicals, 598 had valid fluid and additive concentrations (34,675 disclosures). Sixteen chemicals were removed, because they were minerals listed as being used as proppants. This left a total of 582 chemicals (34,344 disclosures).

Table 5-3 presents the 35 chemicals (5% of all chemicals identified in the EPA's study) that were reported as ingredients in additives in at least 10% of the EPA FracFocus 1.0 project database disclosures for all states reporting to FracFocus 1.0 during this time (U.S. EPA, 2015c). This table also includes the top four additives in which the given chemical was reported as an ingredient.

**Table 5-3. Chemicals identified in the EPA FracFocus 1.0 project database in 10% or more disclosures, with the percent of disclosures for which each chemical is reported as an ingredient in an additive and the top four reported additives for which the chemical is used.** If a chemical is reported to be used in less than four additives, the table presents all additives (U.S. EPA, 2015c).

| No. | Chemical name[a] | CASRN | Percent of disclosures[b] | Additives in which chemical is used (four most common, EPA FracFocus 1.0 project database)[c] |
|---|---|---|---|---|
| 1 | Methanol | 67-56-1 | 72% | Corrosion inhibitors, surfactants, non-emulsifiers, scale control |
| 2 | Hydrotreated light petroleum distillates[d] | 64742-47-8 | 65% | Friction reducers, gelling agents and gel stabilizers, crosslinkers and related additives, viscosifiers |
| 3 | Hydrochloric acid | 7647-01-0 | 65% | Acids, solvents, scale control, clean perforations |
| 4 | Water[e] | 7732-18-5 | 48% | Acids, biocides, clay control, scale control |
| 5 | Isopropanol | 67-63-0 | 47% | Corrosion inhibitors, non-emulsifiers, surfactants, biocides |
| 6 | Ethylene glycol | 107-21-1 | 46% | Crosslinkers and related additives, scale control, corrosion inhibitors, friction reducers |
| 7 | Peroxydisulfuric acid, diammonium salt | 7727-54-0 | 44% | Breakers and breaker catalysts, oxidizer, stabilizers, clean perforations |
| 8 | Sodium hydroxide | 1310-73-2 | 39% | Crosslinkers and related additives, biocides, pH control, scale control |
| 9 | Guar gum | 9000-30-0 | 37% | Gelling agents and gel stabilizers, viscosifiers, clean perforations, breakers and breaker catalysts |
| 10 | Quartz[e] | 14808-60-7 | 36% | Breakers and breaker catalysts, gelling agents and gel stabilizers, scale control, crosslinkers and related additives |
| 11 | Glutaraldehyde | 111-30-8 | 34% | Biocides, surfactants, crosslinkers and related additives, sealers |
| 12 | Propargyl alcohol | 107-19-7 | 33% | Corrosion inhibitors, inhibitors, acid inhibitors, base fluid |
| 13 | Potassium hydroxide | 1310-58-3 | 29% | Crosslinkers and related additives, pH control, friction reducers, gelling agents and gel stabilizers |

| No. | Chemical name[a] | CASRN | Percent of disclosures[b] | Additives in which chemical is used (four most common, EPA FracFocus 1.0 project database)[c] |
|---|---|---|---|---|
| 14 | Ethanol | 64-17-5 | 29% | Surfactants, biocides, corrosion inhibitors, fluid foaming agents and energizers |
| 15 | Acetic acid | 64-19-7 | 24% | pH control, iron control agents, acids, gelling agents and stabilizers |
| 16 | Citric acid | 77-92-9 | 24% | Iron control agents, scale control, gelling agents and gel stabilizers, pH control |
| 17 | 2-Butoxyethanol | 111-76-2 | 21% | Surfactants, corrosion inhibitors, non-emulsifiers, fluid foaming agents and energizers |
| 18 | Sodium chloride | 7647-14-5 | 21% | Breakers/breaker catalysts, friction reducers, scale control, clay control |
| 19 | Solvent naphtha, petroleum, heavy arom.[f] | 64742-94-5 | 21% | Surfactants, non-emulsifiers, inhibitors, corrosion inhibitors |
| 20 | Naphthalene | 91-20-3 | 19% | Surfactants, non-emulsifiers, corrosion inhibitors, inhibitors |
| 21 | 2,2-Dibromo-3-nitrilopropionamide | 10222-01-2 | 16% | Biocides, clean perforations, breakers and breaker catalysts, non-emulsifiers |
| 22 | Phenolic resin | 9003-35-4 | 14% | Proppants, biocides, clean perforations, base fluid |
| 23 | Choline chloride | 67-48-1 | 14% | Clay control, clean perforations, base fluid, biocides |
| 24 | Methenamine | 100-97-0 | 14% | Proppants, crosslinkers and related additives, biocides, base fluid |
| 25 | Carbonic acid, dipotassium salt | 584-08-7 | 13% | pH control, proppants, acids, surfactants |
| 26 | 1,2,4-Trimethylbenzene | 95-63-6 | 13% | Surfactants, non-emulsifiers, corrosion inhibitors, inhibitors |
| 27 | Quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl, chlorides[g] | 68424-85-1 | 12% | Biocides, non-emulsifiers, corrosion inhibitors, scale control |
| 28 | Poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy (mixture)[h] | 127087-87-0 | 12% | Surfactants, friction reducers, non-emulsifiers, inhibitors |
| 29 | Formic acid | 64-18-6 | 12% | Corrosion inhibitors, acids, inhibitors, pH control |

| No. | Chemical name[a] | CASRN | Percent of disclosures[b] | Additives in which chemical is used (four most common, EPA FracFocus 1.0 project database)[c] |
|---|---|---|---|---|
| 30 | Sodium chlorite | 7758-19-2 | 11% | Breakers/breaker catalysts, biocides, oxidizer, proppants |
| 31 | Nonyl phenol ethoxylate | 9016-45-9 | 11% | Non-emulsifiers, resin curing agents, activators, friction reducers |
| 32 | Tetrakis(hydroxymethyl) phosphonium sulfate | 55566-30-8 | 11% | biocides, scale control, clay control |
| 33 | Polyethylene glycol | 25322-68-3 | 11% | Biocides, non-emulsifiers, surfactants, clay control |
| 34 | Ammonium chloride | 12125-02-9 | 10% | Friction reducers, crosslinkers and related additives, scale control, clay control |
| 35 | Sodium persulfate | 7775-27-1 | 10% | Breakers and breaker catalysts, oxidizer, pH control |

[a] Chemical refers to chemical substances with a single CASRN; these may be pure chemicals (e.g., methanol) or chemical mixtures (e.g., hydrotreated light petroleum distillates). Chemical names are sometimes different between FracFocus 1.0 and Appendix H, though they will have the same CASRN.

[b] Analysis considered 34,675 disclosures and 676,376 ingredient records that met selected quality assurance criteria, including: completely parsed; unique combination of fracture date and API well number; fracture date between January 1, 2011, and February 28, 2013; valid CASRN; and valid concentrations. Disclosures that did not meet quality assurance criteria (3,855) or other, query-specific criteria were excluded from analysis.

[c] Analysis considered 32,885 disclosures and 615,436 ingredient records that met selected quality assurance criteria, including: completely parsed; unique combination of fracture date and API well number; fracture date between January 1, 2011, and February 28, 2013; valid CASRN; valid concentrations; and valid purpose. Disclosures that did not meet quality assurance criteria (5,645) or other, query-specific criteria were excluded from analysis.

[d] Hydrotreated light petroleum distillates (CASRN 64742-47-8) is a mixture of hydrocarbons, in the C9 to C16 range.

[e] Quartz (CASRN 14808-60-7), the proppant most commonly reported, and water were also reported as an ingredient in other additives (U.S. EPA, 2015a).

[f] Heavy aromatic solvent naphtha (petroleum) (CASRN 64742-94-5) is mixture of aromatic hydrocarbons in the C9 to C16 range.

[g] Quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl, chlorides (CASRN 68424-85-1) is a mixture of benzalkonium chloride with carbon chains between 12 and 16.

[h] Poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy (mixture) (CASRN 127087-87-0) is mixture with varying length ethoxy links.

There is no single chemical used in all hydraulic fracturing fluids across the United States. Methanol is the most commonly used chemical, reported at 72.1% of wells in the EPA FracFocus 1.0 project database and is associated with 33 types of additives, including corrosion inhibitors, surfactants, non-emulsifiers, and scale control (U.S. EPA, 2015c).[1] Table 5-3 also shows the variability in different chemicals included in the EPA FracFocus 1.0 project database. The percentage of disclosures reporting a given chemical suggests the likelihood of that chemical's use at a site. Only three chemicals (methanol, hydrotreated light petroleum distillates, and hydrochloric acid) were used at more than half of the sites nationwide, and only 12 were used at more than one-third.

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[1] The number of additives may be an overestimate due to parsing issues. The true number of additives may be smaller.

In addition to providing information on frequency of use, the EPA FracFocus 1.0 project database provides the maximum concentration by mass of a given chemical in an additive. For example, methanol is the most frequently reported chemical. The median value for the maximum mass concentration reported for an additive in FracFocus disclosures is 30%, with a range of 0.44% to 100% (5th to 95th percentile).[1] Thus, methanol is generally used as part of a mixture of chemicals in the hydraulic fracturing fluid (typically at a concentration around 30% by mass). Other times, methanol is used as an additive in its pure form (concentration 100%). Therefore, methanol will sometimes be stored on-site in a mixture of chemicals and other times as pure methanol. This wide range of possible concentrations of methanol further complicates assessing the potential impact of spills, as the properties of the fluid will depend on the different chemicals present and on their concentrations. For all chemicals, spills of a highly concentrated chemical can have different potential impacts than spills of dilute mixtures. For more discussion on fluid and additive chemical composition, see Section 5.4.5.

A more recent study of FracFocus 2.0 data evaluated disclosures dating from March 9, 2011 to April 13, 2015 (96,449 disclosures) and reported 981 unique chemicals used in hydraulic fracturing (Dayalu and Konschnik, 2016; Konschnik and Dayalu, 2016). The earlier, EPA study (covering the 2011 to early 2013 time period) found 692 chemicals (U.S. EPA, 2015a). Konschnik and Dayalu (2016) identified 263 new CASRNs in addition to the 1,084 identified by the EPA (Appendix H), increasing the number of chemicals by approximately 24%. Of the new CASRNs, the only chemical reported in more than 1% of all disclosures was Alcohols, C9-11-iso-,C10-rich, ethoxylated propoxylated (CASRN 154518-36-2).

The 20 most common chemicals reported in Konschnik and Dayalu (2016) are similar to those listed in Table 5-3. There are three chemicals reported on their 20 most common list that are not included in Table 5-3. These chemicals are: sorbitan, mono-(9Z)-9-octadecenoate (CASRN 1338-43-8, reported in 29.6% disclosures (Konschnik and Dayalu, 2016) vs. 4% (U.S. EPA, 2015c), ethoxylated C12-16 alcohols (CASRN 68551-12-2, 27.9% vs. 4%), and thiourea polymer (CASRN 68527-49-1, 24.8% vs. 8%). Ammonium chloride was on each list, but disclosures increased from 10% to 30.5%. Four chemicals in Table 5-3 were not on their 20 most frequently used list: solvent naphtha, petroleum, heavy arom. (CASRN 64742-94-5), naphthalene (CASRN 91-20-3), 2,2-Dibromo-3-nitrilopropionamide (CASRN 10222-01-2), and phenolic resin (CASRN 9003-35-4).

### 5.4.2 Nationwide Oil versus Gas

Analyses based on the EPA FracFocus 1.0 project database also can elucidate the differences between the chemicals used during hydraulic fracturing for oil production and those used for gas production, providing a better understanding of potential spill impacts from each. Appendix Tables C-1 and C-2 present the chemicals reported in at least 10% of all gas (34 chemicals) and oil (39 chemicals) disclosures nationwide.

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[1] For more information on how chemicals are reported to FracFocus see www.fracfocus.org and U.S. EPA (2015a).

Many of the same chemicals are used for oil and gas, but some chemicals are used more frequently in oil production and others more frequently in gas.[1] For example, hydrochloric acid is the most commonly reported chemical for gas wells (73% of disclosures); it is the fifth most frequently reported chemical for oil wells (58% of disclosures). However, both oil and gas operators each reports using methanol in 72% of disclosures. Methanol is the most common chemical used in hydraulic fracturing fluids at oil wells and the second most common chemical in hydraulic fracturing fluids at gas wells.

### 5.4.3 State-by-State Frequency of Use of Hydraulic Fracturing Chemicals

The composition of hydraulic fracturing fluids varies from site to site. Since the impacts of hydraulic fracturing occur locally, the potential impact depends on the chemicals used locally. We investigated geographic variation of chemical use based on the frequency of chemicals reported to FracFocus and included in the EPA FracFocus 1.0 project database by state (U.S. EPA, 2015c). Appendix Table C-3 presents and ranks chemicals reported most frequently for each state (U.S. EPA, 2015c). The list of the 20 most frequently reported chemicals used in each state together include 94 unique chemicals. A total of 94 chemicals indicates some level of similarity in chemical usage among states.[2]

Methanol is reported in 19 of the 20 states (95%). Alaska is the only state in which methanol is not reported (based on the state's 20 disclosures). The percentage of disclosures reporting use of methanol ranges from 38% (Wyoming) to 100% (Alabama, Arkansas).

Ten chemicals (excluding water) are among the 20 most frequently reported in 14 of the 20 states. These chemicals are: methanol; hydrotreated light petroleum distillates; ethylene glycol; isopropanol; quartz; sodium hydroxide; ethanol; guar gum; hydrochloric acid; and peroxydisulfuric acid, diammonium salt.[3] These 10 chemicals are also the most frequently reported chemicals nationwide.

This state analysis showed that methanol is used across the contiguous U.S. (not Alaska). There are 9 other chemicals that are frequently used across the United States. Beyond those, however, there are a number of different chemicals that are used in one state more commonly than others, and many chemicals may not be used at all in other states.

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[1] This separation was done solely based on whether it was an oil or gas disclosure. The analysis did not separate out reservoir factors, such as temperature, pressure, or permeability, which may be important factors for which chemicals are used. There is no nationwide criterion to distinguish oil wells from gas wells. Production wells often produce some of both. A well identified as gas-producing in one place might be identified as oil-producing in another. This could affect the distribution of chemical use among these wells.

[2] The range of possible number of chemicals is from 20 to 400. If every state used the same 20 chemicals, there would be 20 different chemicals. If all 20 states each used 20 different chemicals, then there would be a total of 400 chemicals used.

[3] Quartz was the most commonly reported proppant and also reported as an ingredient in other additives (U.S. EPA, 2015a).

### 5.4.4 Volume of Chemical Use

Understanding the volume of chemicals used at each site is important for understanding potential impacts of chemicals as well as potential severity of impacts on drinking water resources. The chemical volume governs how much will be stored on-site, the types of containers required, the total amount that could spill, and how much could end up in a drinking water resource. While the on-site hydraulic fracturing service company has precise knowledge of the composition and volume of chemicals stored on-site, this information is not generally publicly available. We conducted a comprehensive review of publicly available sources and found two sources (OSHA, 2014a, b; Sjolander et al., 2011) that identify specific chemicals used at a hydraulic fracturing site and provide information on volumes. These are presented in Table 5-4. The volume of chemicals totaled 7,500 gal (28,000 L) and 14,700 gal (55,600 L) for the two sources, with a mean volume for an individual chemical of 1,900 gal (7,200 L) and 1,225 gal (4,637 L), respectively. The range of volumes for each chemical used is 30 to 3,690 gal (114 to 14,000 L).

**Table 5-4. Example list of chemicals and chemical volumes used in hydraulic fracturing.**
Volumes are for wells with an unknown number of stages and at least one perforation zone. Every well and fluid formulation is unique. Blank cells are data not reported.

| | | Sjolander et al. (2011)[a] | | OSHA (2014a, 2014b)[b] | |
|---|---|---|---|---|---|
| **Ingredient** | **Examples** | **Volume (gal) or mass (lb)** | **Percent overall[c]** | **Volume (gal)** | **Percent by volume** |
| Water | | 4,000,000 gal | 94.62 | 2,700,000 gal | 90 |
| Proppant | Sand | ~ 1,500,000 lb[d] | 5.26 | 285,300 gal | 9.51 |
| Acid | Hydrochloric acid or muriatic acid | 1,338 gal | 0.03 | 3,690 gal | 0.123 |
| Friction reducer | Polyacrylamide, mineral oil | 2,040 gal | 0.05 | 2,640 gal | 0.088 |
| Surfactant | Isopropanol | | | 2,550 gal | 0.085 |
| Potassium chloride | | | | 1,800 | 0.06 |
| Gelling agent | Guar gum or hydroxymethyl cellulose | -[e] | -[e] | 1,680 | 0.056 |
| Scale inhibitor | Ethylene glycol, alcohol, and sodium hydroxide | 2,040 gal | 0.05 | 1,290 | 0.043 |
| pH buffer | Carbonate | | | 330 | 0.011 |
| Preservative | Ammonium persulfate | | | 300 | 0.01 |

| | | Sjolander et al. (2011)[a] | | OSHA (2014a, 2014b)[b] | |
|---|---|---|---|---|---|
| **Ingredient** | **Examples** | **Volume (gal) or mass (lb)** | **Percent overall[c]** | **Volume (gal)** | **Percent by volume** |
| Crosslinker | Borate salts | -[e] | -[e] | 210 | 0.007 |
| Iron control | Citric acid | -[e] | -[e] | 120 | 0.004 |
| Corrosion inhibitor | n,n-Dimethyl formamide | -[e] | -[e] | 60 | 0.002 |
| Biocide / antimicrobial agent | Glutaraldehyde,<br>ethanol,<br>methanol | 2,040 gal | 0.05 | 30 | 0.001 |
| Gel-breaker | Ammonium persulfate | -[e] | -[e] | | |
| Total volume of all chemicals | | 7,458 gal | 0.18 | 14,700 | 0.49 |
| Individual chemical volume: mean (full range) | | 1,864.5 gal<br>(1,338 – 2,040 gal) | | 1,225<br>(30 – 3,690) | |

[a] Adapted from Penn State "Water Facts" publication entitled *Introduction to Hydrofracturing* (Sjolander et al., 2011). Composite from two companies: Range Resources, LLC, and Chesapeake Energy, which released in July 2010 the chemistry and volume of materials typically used in their well completions and stimulations.

[b] Adapted from a table generated by the Occupational Safety and Health Administration (OSHA) for use in a training module (OSHA, 2014a, b).

[c] As presented in Sjolander et al. (2011); does not explicitly state percent by mass or by volume.

[d] Sjolander et al. (2011) presents proppant in pounds instead of gallons.

[e] Listed as an ingredient, but no information on volume or percentage.

Because of the limited information on chemical volumes publicly available, we estimated chemical volumes used across the nation based on the information provided in the EPA FracFocus 1.0 project database. Figure 5-5 plots median estimated chemical volumes, ranked from high to low, with the range of 5th to 95th percentiles. Estimated volumes used are presented for the 74 chemicals that were reported in at least 100 disclosures in the EPA FracFocus 1.0 project database and for which density data were available. The estimated median volumes vary widely among the different chemicals, covering a range of near zero to 27,000 gal (98,000 L). The mean of the estimated median volumes was 650 gal (2,500 L), and the mean of the estimated median mass was 3,200 lb (1,500 kg) (U.S. EPA, 2015c). Mass, volume, and density data are presented in Appendix C along with the estimation methodology and assumptions used.

With the median chemical volume, we can estimate total chemical volume for all chemicals used. Based on the above mean of median chemical volumes of 650 gal (2,500 L) per chemical, and given that the median number of chemicals used at a site is 14 (U.S. EPA, 2015a), an estimated 9,100 gal (34,000 L) of chemicals may be used per well. Given that the number of chemicals per well ranges from 4 to 28 (U.S. EPA, 2015a), the total volume of chemicals per well may range from 2,600 to 18,000 gal (9,800 to 69,000 L).

Another way to estimate total volume of chemicals per well is to use the estimated median volume of 1.5 million gal (5.7 million L) of fluid used to fracture a well (U.S. EPA, 2015a) (Chapter 4) and assume that up to 2% of that volume consists of chemicals added to base fluid (Carter et al., 2013; Knappe and Fireline, 2012), resulting in up to 30,000 gal (114,000 L) of chemicals used per well.

Using the estimated volume per chemical of 650 gal (2,500 L), we can also estimate volume per additive and extrapolate to estimate on-site chemical storage. If we assume three to five chemicals per additive, then total volume per additive stored on-site would be approximately 1,900 to 3,200 gal (7,400 to 12,000 L). On-site containers generally store 20% to 100% more additive volume than ultimately used (Houston et al., 2009; Malone and Ely, 2007). This would suggest that 2,300 to 6,500 gal (8,800 to 25,000 L) per additive are stored on site.

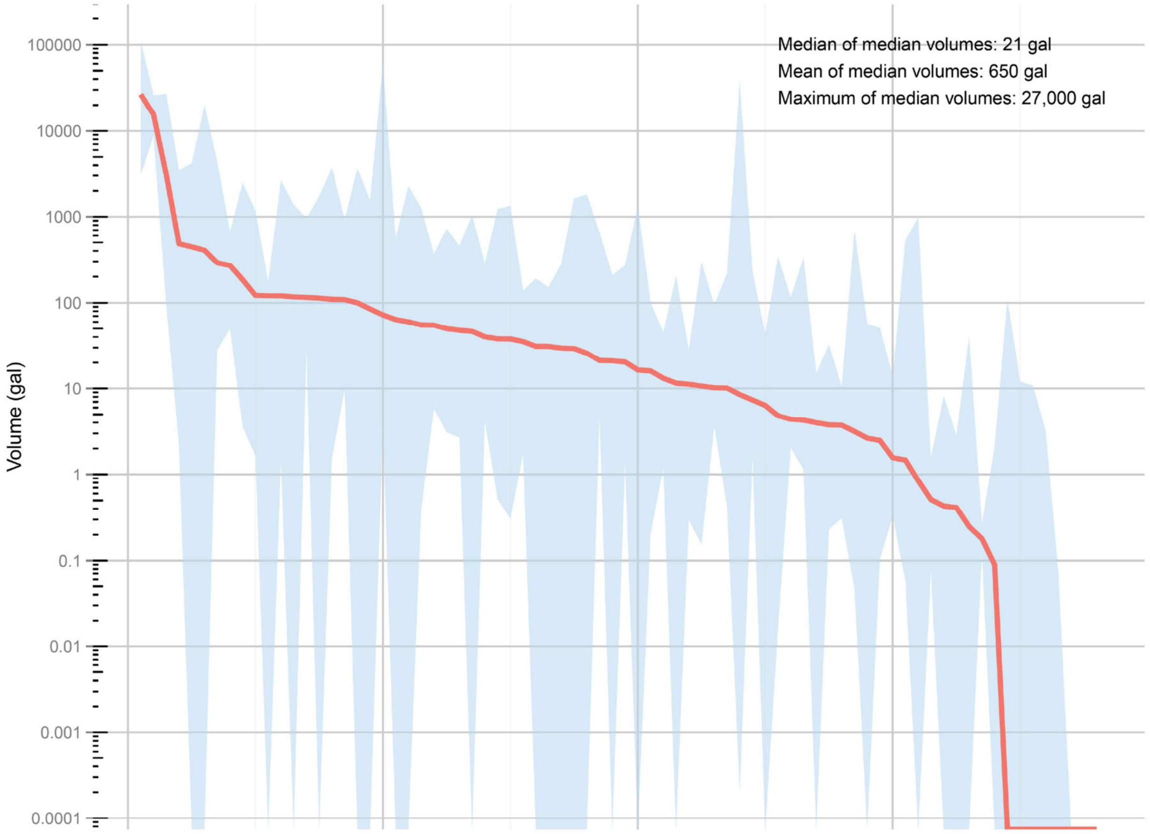

**Figure 5-5. Estimated median volumes for 74 chemicals reported in at least 100 disclosures in the FracFocus 1.0 project database for use in hydraulic fracturing from January 1, 2011 to February 28, 2013.**

Chemicals are plotted in order of largest to smallest median volume. Shaded area represents the zone of 5% and 95% confidence limits. Derived from U.S. EPA (2015c).

### 5.4.5 Chemical Composition of Hydraulic Fracturing Fluids and Additives

As the hydraulic fracturing process proceeds, the composition of the fluid injected changes over time. The overall composition of additives and hydraulic fracturing fluid may be reported by well operators to the FracFocus national registry, depending on the local disclosure requirements and operator preference. For each chemical that is injected into a well (excluding CBI chemicals), the maximum concentration in the resulting overall fluid and in each additive is given as maximum percent by mass. Based on this information, we calculated the median chemical composition reported in at least 10% of the disclosures in the EPA FracFocus 1.0 project database (Table 5-3) and a range based on the 5th and 95th percentile. Table 5-5 shows that some chemicals may be used in their pure form (100% of mass in a given additive). These chemicals include: methanol, hydrochloric acid, water, isopropanol, guar gum, citric acid, 2,2-Dibromo-3-nitrilopropionamide, tetrakis(hydroxymethyl) phosphonium sulfate, and sodium persulfate.

Chemicals may be stored in their concentrated, pure form, resulting in the potential for spills of concentrated volumes of these chemicals, which may increase the severity of impacts if they reach a drinking water resource. Once chemicals are mixed with the base fluid to form the hydraulic fracturing fluid, the chemical is diluted to much lower concentrations, which has the potential for a less severe impact. However, a larger volume of spill could occur with smaller concentrations. The larger volume may increase the potential for a spill reaching a drinking water resource, albeit at a lower concentration. There is the further complication of the hazard of the associated chemicals, since a smaller mass of a more hazardous chemical may be of more concern than a larger mass of a less hazardous chemical (as discussed in Chapter 9). It is therefore impossible to make a general statement without more detail on the spill characteristics, including the hazard, concentration, and volume.

Appendix Table C-6 provides mean, median, 5th and 95th percentile mass (kg) estimates for all reported chemicals in 100 or more disclosures in the EPA FracFocus 1.0 project database where density information was available.

**Table 5-5. Fluid and additive composition by maximum mass percent.**

Median, 5th and 95th percentile maximum concentration in hydraulic fracturing fluid and in additive (percent by mass) for the chemicals identified in the EPA FracFocus 1.0 project database in 10% or more disclosures. See Table 5-3 for percentage of disclosures and the common additives for which these chemicals are used. Analysis considered 34,675 disclosures and 676,376 ingredient records that met selected quality assurance criteria, including: completely parsed; unique combination of fracture date and API well number; fracture date between January 1, 2011, and February 28, 2013; valid CASRN; and valid concentrations. Disclosures that did not meet quality assurance criteria (3,855) or other, query-specific criteria were excluded from analysis.

| EPA-standardized chemical name | CASRN | Maximum concentration in hydraulic fracturing fluid (percent by mass) | | | Maximum concentration in additive (percent by mass) | | |
|---|---|---|---|---|---|---|---|
| | | Median | 5th Percentile | 95th Percentile | Median | 5th Percentile | 95th Percentile |
| Methanol | 67-56-1 | 0.0092 | 0.00011 | 0.12 | 30 | 0.44 | 100 |
| Distillates, petroleum, hydrotreated light | 64742-47-8 | 0.025 | 0.0013 | 0.35 | 30 | 0.70 | 70 |
| Hydrochloric acid | 7647-01-0 | 0.15 | 0.0083 | 1.3 | 15 | 2.8 | 60 |

| EPA-standardized chemical name | CASRN | Maximum concentration in hydraulic fracturing fluid (percent by mass) | | | Maximum concentration in additive (percent by mass) | | |
|---|---|---|---|---|---|---|---|
| | | Median | 5th Percentile | 95th Percentile | Median | 5th Percentile | 95th Percentile |
| Water | 7732-18-5 | 0.53 | 0.00065 | 82 | 65 | 5.0 | 100 |
| Isopropanol | 67-63-0 | 0.0038 | 0.000020 | 0.15 | 20 | 0.30 | 100 |
| Ethylene glycol | 107-21-1 | 0.016 | 0.00027 | 0.11 | 30 | 0.59 | 60 |
| Peroxydisulfuric acid, diammonium salt | 7727-54-0 | 0.0069 | 0.00010 | 0.064 | 100 | 0.11 | 100 |
| Sodium hydroxide | 1310-73-2 | 0.0092 | 0.000040 | 0.077 | 10 | 0.085 | 52 |
| Guar gum | 9000-30-0 | 0.16 | 0.0019 | 0.42 | 50 | 1.6 | 100 |
| Quartz | 14808-60-7 | 0.0033 | 0.000030 | 12 | 2.0 | 0.10 | 97 |
| Glutaraldehyde | 111-30-8 | 0.0072 | 0.00039 | 0.023 | 27 | 0.040 | 60 |
| Propargyl alcohol | 107-19-7 | 0.00015 | 0.000010 | 0.0028 | 8.0 | 0.0032 | 30 |
| Potassium hydroxide | 1310-58-3 | 0.0070 | 0 | 0.053 | 15 | 0.14 | 50 |
| Ethanol | 64-17-5 | 0.0034 | 0.000060 | 0.098 | 30 | 1.0 | 60 |
| Acetic acid | 64-19-7 | 0.0033 | 0 | 0.037 | 50 | 1.0 | 90 |
| Citric acid | 77-92-9 | 0.0027 | 0.000060 | 0.017 | 60 | 7.0 | 100 |
| 2-Butoxyethanol | 111-76-2 | 0.0047 | 0 | 0.14 | 10 | 0.29 | 60 |
| Sodium chloride | 7647-14-5 | 0.0083 | 0 | 0.14 | 30 | 0.020 | 50 |
| Solvent naphtha, petroleum, heavy arom. | 64742-94-5 | 0.0051 | 0.000020 | 0.035 | 10 | 0.00052 | 30 |
| Naphthalene | 91-20-3 | 0.0014 | 0 | 0.0055 | 5.0 | 0.0023 | 5.0 |
| 2,2-Dibromo-3-nitrilopropionamide | 10222-01-2 | 0.0018 | 0.000010 | 0.022 | 98 | 10 | 100 |
| Phenolic resin | 9003-35-4 | 0.12 | 0.0046 | 1.1 | 5.0 | 0.80 | 20 |
| Choline chloride | 67-48-1 | 0.062 | 0.00068 | 0.14 | 75 | 0.75 | 80 |
| Methenamine | 100-97-0 | 0.010 | 0 | 0.21 | 1.0 | 0 | 2.0 |
| Carbonic acid, dipotassium salt | 584-08-7 | 0.039 | 0 | 0.15 | 60 | 30 | 60 |
| 1,2,4-Trimethylbenzene | 95-63-6 | 0.00067 | 0 | 0.0068 | 1.0 | 0.010 | 20 |

| EPA-standardized chemical name | CASRN | Maximum concentration in hydraulic fracturing fluid (percent by mass) | | | Maximum concentration in additive (percent by mass) | | |
|---|---|---|---|---|---|---|---|
| | | Median | 5th Percentile | 95th Percentile | Median | 5th Percentile | 95th Percentile |
| Quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl, chlorides | 68424-85-1 | 0.0019 | 0 | 0.0041 | 7.0 | 3.0 | 10 |
| Poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy (mixture) | 127087-87-0 | 0.0025 | 0.000010 | 0.0089 | 5.0 | 5.0 | 10 |
| Formic acid | 64-18-6 | 0.0021 | 0 | 0.030 | 60 | 0.11 | 98 |
| Sodium chlorite | 7758-19-2 | 0.0040 | 0.00018 | 0.037 | 10 | 5.0 | 30 |
| Nonyl phenol ethoxylate | 9016-45-9 | 0.0088 | 0.000030 | 0.085 | 10 | 5.0 | 54 |
| Tetrakis(hydroxymethyl) phosphonium sulfate | 55566-30-8 | 0.011 | 0.00025 | 0.065 | 60 | 0.029 | 100 |
| Polyethylene glycol | 25322-68-3 | 0.0035 | 0.000010 | 0.038 | 20 | 0.0071 | 70 |
| Ammonium chloride | 12125-02-9 | 0.0025 | 0.00029 | 0.022 | 10 | 1.5 | 30 |
| Sodium persulfate | 7775-27-1 | 0.0017 | 0.000020 | 0.022 | 100 | 100 | 100 |

## 5.5 Chemical Management and Spill Potential

This section provides a description of the primary equipment used in the chemical mixing and well injection processes, along with a discussion of the spill vulnerabilities specific to each piece of equipment. Equipment breakdown or failure can trigger a spill itself, and it can also lead to a suspension of activity and the disconnection and reconnection of various pipes, hoses, and containers. Each manipulation of equipment poses additional potential for a spill. The EPA found that 31% of chemical spills on or near the well pad related to hydraulic fracturing resulted from equipment failure (U.S. EPA, 2015m). When possible, we describe documented spills, associated with or attributed to specific pieces of equipment, in text boxes in the relevant subsections.

Equipment used in hydraulic fracturing operations typically consists of chemical storage trucks, oil storage tanks/tanker trucks; a slurry blender; one or more high-pressure, high-volume fracturing pumps; the main manifold; surface lines and hoses; and a central control unit (Table 5-6). There are many potential sources for leaks and spills in this interconnected system. Furthermore, hydraulic fracturing operations are mobile and must be assembled at each well site, and each assembly and disassembly presents a potential for spills.

Equipment varies in age and technological advancement depending upon service company standards and costs associated with purchase and maintenance. Older equipment may have experienced wear and tear, which may be a factor in spills caused by equipment failure. New equipment may be more automated, potentially reducing opportunities for human error. Information detailing the extent of technological and age differences in fracturing equipment across sites and operators is limited.

**Table 5-6. Examples of typical hydraulic fracturing equipment and its function.**

| Equipment | Function |
|---|---|
| Acid transport truck | Transports acids to job sites; the truck has separate compartments for multiple acids or additives. |
| Chemical storage truck | Transports chemicals to the site in separate containment units or totes. Chemicals are typically stored on and pumped from the chemical storage truck. |
| Base fluid tanks | Stores the required volume of base fluid to be used in the hydraulic fracturing process. |
| Proppant storage units | Holds proppant and feeds it to the blender via a large conveyor belt. |
| Blender | Takes fluid (e.g., water) from the fracturing tanks and proppant (e.g., sand) from the proppant storage unit and combines them with additives before transferring the mixture to the fracturing pumps |
| High-pressure fracturing pumps | Pressurizes mixed fluids received from the blender and injected into the well. |
| Manifold trailer with hoses and pipes | Serves as a transfer station for all fluids. Includes a trailer with a system of hoses and pipes connecting the blender, the high-pressure pumps, and the fracturing wellhead. |
| Fracturing wellhead or frac head | Allows fracture equipment to be attached to the well; located at the wellhead. |
| Central control unit or frac van | Monitors the hydraulic fracturing job using pressure and rate data supplied from around the job site. |

While the primary equipment and layout are generally the same across well sites, the type, size, and number of pieces of equipment may vary depending on a number of factors (Malone and Ely, 2007):

- Size and type of the fracture treatment;
    - Length of well and number of stages;
    - Number of wells drilled per well pad;
    - Geographic location;
    - Depth below surface;
    - Length of the fractures;

- Volumes and types of additives, proppants, and fluids used; and
- Operating procedures of the well operator and service company (e.g., some companies require backup systems in case of mechanical failure, while others do not).

Figure 5-6 provides a schematic diagram of a typical layout of hydraulic fracturing equipment.

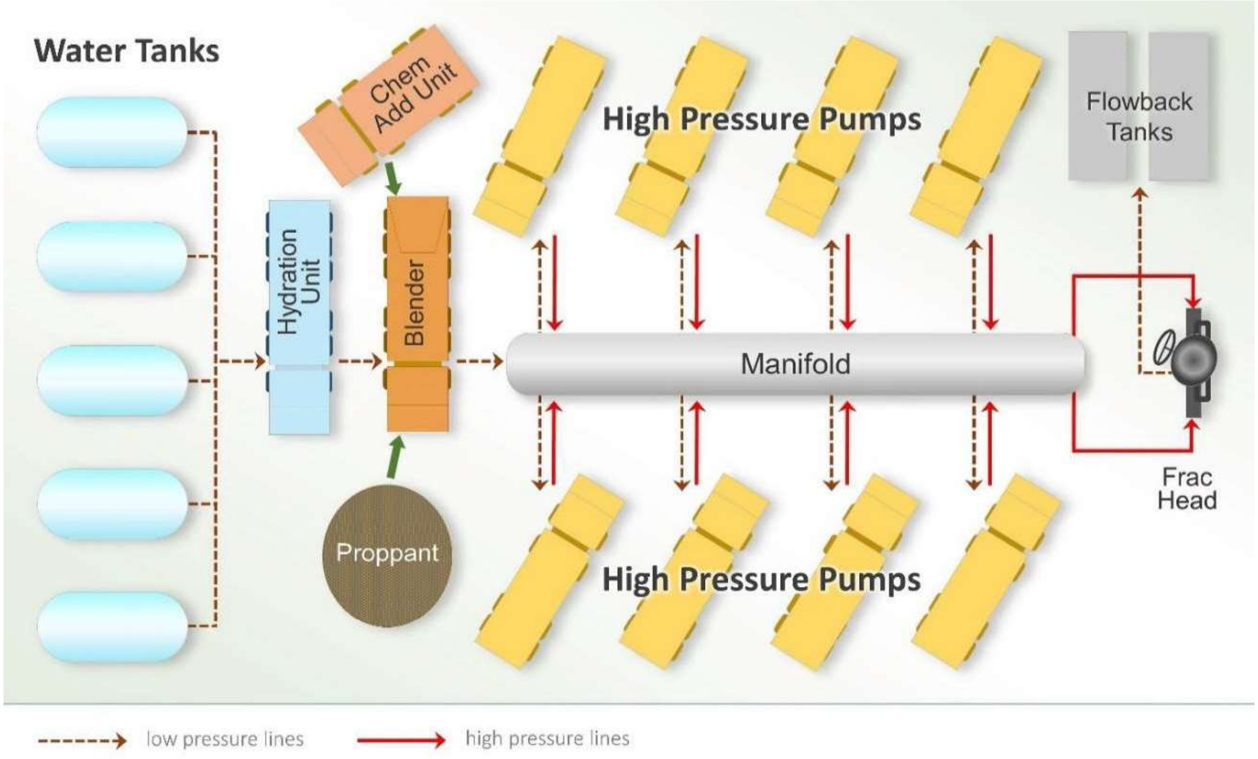

**Figure 5-6. Typical hydraulic fracturing equipment layout.**
This illustration shows how the various components of a typical hydraulic fracturing site fit together. The numbers of pumps and tanks vary from site to site. Some sites do not use a hydration unit as the gel is batch mixed prior to the treatment (Olson, 2011; BJ Services Company, 2009).

### 5.5.1 Storage

This section provides an overview of publicly available information on storage and containment of chemicals used in the hydraulic fracturing process. Most public sources provide general information on the types and sizes of containment units. While operators maintain a precise inventory of volumes of chemicals stored and used for each site, this information is typically not made public.

The volumes of each chemical used are based on the size and site-specific characteristics of each fracture treatment. Sites often store an excess of the design volume of chemicals for contingency purposes, typically 20% to 100% beyond what is necessary (Houston et al., 2009; Malone and Ely, 2007). See Text Box 5-3 for documented spills from storage units.

### Text Box 5-3. Spills from Storage Units.

Of the 151 spills of chemicals, additives, or fracturing fluid discussed and evaluated in (U.S. EPA, 2015m) (see Text Box 5-10 for more information), 54 spills were from storage units. Storage units include totes or tanks used for storing individual chemicals or additives and larger tanks containing hydraulic fracturing fluid. These spills resulted from equipment failure, failure of storage integrity, or human error. Sixteen of these spills were due to failure of container integrity, which includes holes and cracks in containers, demonstrating the importance of properly constructed and maintained storage units. The remaining spills from storage containers resulted from human error or equipment malfunctions or had an unknown cause.

### 5.5.1.1 Hydraulic Fracturing Base Fluid Storage

Base fluids used in hydraulic fracturing are typically stored on-site in large volume tanks. Non-water-based fluids may be stored in specialized containment units designed to prevent or minimize releases. For example, nitrogen and carbon dioxide must be stored in compressed gas or cryogenic liquid cylinders, as required by U.S. Department of Transportation (DOT) and OSHA regulations. Due to the large volume of base fluid storage tanks (about 21,000 gal or 80,000 L) (Halliburton, 1988), uncontrolled spills could damage other storage units and equipment, which could result in additional spills. Fresh water used as a base fluid is generally not a source of concern for spills. Reused wastewater, brine, and non-aqueous base fluids have the potential to adversely impact drinking water resources in the event of a spill. Chapter 7 discusses reusing hydraulic fracturing wastewater as a base fluid and the spill/release potential on-site from pits and impoundments.

### 5.5.1.2 Additive Storage

Additives are typically stored on-site in the containers in which they were transported and delivered. The additive trailer typically consists of a flatbed truck or van enclosure that holds a number of chemical totes, described below, and is equipped with metering pumps that feed chemicals to the blender. Depending on the size and type of the fracturing operation, there may be one or more additive trailers per site (NYSDEC, 2015; ALL Consulting, 2012). While additives constitute a relatively small portion of fluids used in a hydraulic fracturing fluid, additive volumes can range from the tens to tens of thousands of gallons.

The storage totes generally remain on the transportation trailers, but they also may be unloaded from the trailers and transferred to alternative storage areas before use. Our investigation did not find much information on how often, when, or why these transfers occur. Additional transfers and movement can increase the likelihood of a spill. See Text Box 5-4 for a documented spill from an additive storage unit.

### Text Box 5-4. Spill from Additive (Crosslinker) Storage Tote.

On Sept 19, 2009, during a tote transfer in Pennsylvania, a tote of crosslinker fell off a forklift spilling approximately 15 – 20 gal (60 – 80 L) onto the well pad. The area was scraped clean with a backhoe, and the waste was placed in a lined containment area (PA DEP, 2012, ID# 1845178).

The most commonly used chemical totes are 200 – 375 gal (760 – 1,420 L) capacity polyethylene containers that may be reinforced with steel or aluminum mesh (NYSDEC, 2015). Metal containers may also be used. The totes are typically equipped with bottom release ports, which enable direct feed of the additives to the blending equipment (NYSDEC, 2015). Spills may occur if lines are improperly connected to these ports or if the connection equipment is faulty.

**Figure 5-7. Metal and high-density polyethylene (HDPE) additive units.**
The image on the left depicts metal totes (industry source). The image on the right depicts plastic totes. Source: NYSDEC (2011).

Certain additives require specialized containment units with added spill prevention measures. For example, additives containing methanol may be subject to federal safety standards, and industry has developed guidance on methanol's safe storage and handling (Methanol Institute, 2013).

Dry additives are typically transported and stored on flatbed trucks in 50 or 55 lb (23 or 25 kg) bags, which are set on pallets containing 40 bags each (NYSDEC, 2015; UWS, 2008; Halliburton, 1988). Proppants are stored on-site in large tanks or bins with typical capacities of 350,000 to 450,000 lb (150,000 to 200,000 kg) (ALL Consulting, 2012; BJ Services Company, 2009; Halliburton, 1988).

#### 5.5.1.3 Acid Storage

Acids are generally stored on-site in the containment units in which they are transported and delivered. A typical acid transport truck holds up to 5,000 gal (19,000 L) of acid and can have multiple compartments to hold different kinds of acid (Arthur et al., 2009b). Acids such as hydrochloric acid and formic acid are corrosive and can be extremely hazardous in concentrated form. Therefore, acid transport trailers and fracture tanks must be lined with chemical-resistant coating designed to prevent leakage and must meet applicable DOT regulatory standards (pursuant to 40 Code of Federal Regulations (CFR) 173) designed to prevent or minimize spills.

Acid fracture treatments may use thousands of gallons of acid per treatment (Spellman, 2012). Given the large volumes used, failure of containment vessels during storage or failure of connections and hoses during pumping could result in high-volume acid spills. Details of a documented acid spill are presented in Text Box 5-5.

**Text Box 5-5. Spill of Acid from Storage Container.**

In July 2014, in Oklahoma, 20,000 gal (76,000 L) of hydrochloric acid spilled from a storage container when a flange malfunctioned. The acid spilled into a nearby alfalfa field, where it was contained with an emergency berm (Phillips, 2014; Wertz, 2014). There is no information on how much leached into soils or if the spill reached drinking water resources.

#### 5.5.1.4 Gel Storage

Gels can be added to hydraulic fracturing fluid using either batch or continuous (also called "on-the-fly") mixing systems. Gelling agents and gel slurries are stored differently on-site and can pose different potential spill scenarios depending on whether the site is using batch or continuous mixing processes (BJ Services Company, 2009).

In a typical batch mixing process, powdered gelling agents and related additives (e.g., buffers, surfactants, biocides) are mixed on-site with base fluid water and proppant in large tanks, typically 20,000 gal (80,000 L)(BJ Services Company, 2009; Halliburton, 1988). The number of gel slurry tanks used varies based on site-specific conditions and the size of the fracture job. These tanks can be subject to leaks or overflow during the batch mixing process and during storage prior to injection. One of the disadvantages of batch mixing is the need for multiple suction hoses to draw pre-gelled fluids from storage tanks into the blender, if used, which can increase the potential for spills. Yeager and Bailey (2013) state that a drawback of batch mixing is the "fluid spillage and location mess encountered when pre-mixing tanks," suggesting that small spills are not uncommon during batch mixing. Details of a documented gel slurry spill are presented in Text Box 5-6. Details of a documented gel slurry spill are presented in Text Box 5-6.

**Text Box 5-6. Spill of Gel Slurry during Mixing.**

On April 9, 2010, in Louisiana, a company was mixing a gel slurry for an upcoming fracture job. The tank had developed a crack, which allowed approximately 10,000 gal (38,000 L) of water mixed with 60 gal (230 L) of gel to leak out. The mixture did not reach a water receptor, and absorbents were used to clean up the gel (LDEQ, 2013).

In continuous mixing operations, powdered gels are typically replaced with liquid gel concentrates (Allen, 2013; BJ Services Company, 2009). Operators prepare dilute gelling agents as needed using specialized hydration units (BJ Services Company, 2009). Liquid gel concentrates may be stored on-site in single-purpose tanker trucks (Harms and Yeager, 1987) but are more often stored in specialized mixing and hydration units (Ayala et al., 2006). Continuous mixing requires less preparation than batch mixing but typically requires more equipment (BJ Services Company, 2009; Browne and Lukocs, 1999). This can increase the possibility for spills resulting from equipment malfunctions or human error.

### 5.5.2 Hoses and Lines

High- and low-pressure hoses and lines are used to transfer hydraulic fracturing fluids from storage units to specialized mixing and pumping equipment and ultimately to the wellhead. A discussion of the different types of hoses and lines and possible points of failure is provided below. Figure 5-8 shows an example of hoses and lines at a hydraulic fracturing site.

**Figure 5-8. Hoses and lines at a site in Arkansas.**
Photo credit: Christopher Knightes (U.S. EPA).

Suction pumps and hoses move large volumes of base fluid to the blender. Incomplete or damaged seals in inlet or outlet connections can cause fluid leaks at the connection points. Improperly fitted seals also severely limit or eliminate suction lift, which can impair the suction pump and increase spill potential. Suction hoses themselves are susceptible to leaks due to wear and tear. Equipment providers recommend hoses be closely inspected to ensure they are in good operating condition prior to use (Upstream Pumping, 2015; BJ Services Company, 2009; Malone and Ely, 2007).

Discharge hoses transfer additives from containment vessels or totes to the blender. Given the potential for concentrated chemicals to spill during transfer from storage totes to the blender, it is particularly important that these hoses are in good condition and that connector seals or washers fit properly and are undamaged. Discharge hoses are also used to carry fracturing fluid pumped from the blender via the low-pressure manifold to the high-pressure pumps. Proppant-heavy fluids are pumped through discharge hoses at relatively low rates. If a sufficient flow rate is not maintained, proppant may settle out, damaging pumps and creating a potential for spills and leaks (Upstream Pumping, 2015; BJ Services Company, 2009; Malone and Ely, 2007).

High-pressure flow lines convey pressurized fluids from the high-pressure pumps into the high-pressure manifold and from the manifold into the wellbore. High-pressure flow lines are subject to erosion caused by the high-velocity movement of abrasive, proppant-laden fluid. Curved sections of flow lines (e.g., swivel joints) where abrasive fluids are forced to turn corners are particularly subject to erosion and are more likely to develop stress cracks or other defects that can result in a leak or spill. Safety restraints are typically used to prevent movement of flow lines such as in the event of failure and to help control spills. High-pressure flow lines are pressure-tested to detect fatigue or stress cracks prior to the fracturing treatment (OSHA, 2015; BJ Services Company, 2009; Arthur et al., 2008; Malone and Ely, 2007; Halliburton, 1988).

Nineteen spills of chemicals or fracturing fluids associated with leaks from hoses or lines had a total spill volume of 12,756 gal (48,287 L), with a median volume of 420 gal (1,600 L) (U.S. EPA, 2015m).

### 5.5.3 Blender

The blender is the central piece of equipment used to create the fracturing fluid for injection. It moves, meters, and mixes precise amounts of the base fluid, additives, and proppant and pumps the mixed slurry to high-pressure pumping equipment (BJ Services Company, 2009; Malone and Ely, 2007; Halliburton, 1988) (Figure 5-6). A typical blender consists of a centrifugal suction pump for pulling base fluid, one or more chemical metering pumps to apportion the additives, one or more proportioners to measure and feed proppant, and a central agitator tank where fluid components are mixed together.

The blending process is monitored to ensure that a uniform mixture is maintained regardless of injection rates and volumes. Excessive or reduced rates of flow during treatment can cause the blender to malfunction or to shut down, which can result in spills (Malone and Ely, 2007; Halliburton, 1988). For aqueous hydraulic fracturing fluid blends, spills that occur downstream of the blender will be a dilute mixture (less than or equal to 2%) of chemicals. Details of a spill from a blender are presented in Text Box 5-7.

**Text Box 5-7. Spill of Hydraulic Fracturing Fluid from Blender.**

In May 2006, a blender malfunctioned during a fracture job in Oklahoma. Approximately 294 gal (1,110 L) of fluid spilled into a nearby wheat field. The fluid consisted of hydrochloric acid, clay stabilizer, diesel, and friction reducer. Contaminated soil was removed by the operator (OCC, 2013, ID#137000).

### 5.5.4 Manifold

A trailer-mounted manifold and pump system functions as a central transfer station for all fluids used in the hydraulic fracturing operation. The manifold is a collection of low- and high-pressure pipes equipped with multiple fittings for connector hoses. Fluids are pumped from the blender through the low-pressure manifold hoses, which distribute fluids to high-pressure pump trucks. Pressurized slurry is sent from the pump trucks through high-pressure manifold lines and into additional high pressure lines that lead to the wellhead (Malone and Ely, 2007).

Manifold and pump system components require varying amounts of manual assembly and undergo varying amounts of pre-testing (Malone and Ely, 2007). Improperly tested parts may be more likely to break or lose functionality, leading to a spill. In manifolds requiring more manual assembly, there may be more opportunities for human error.

### 5.5.5 High-Pressure Fracturing Pumps

High-pressure fracturing pumps take the fracturing fluid mixture from the blender, pressurize it, and propel it down the well. Typically, multiple high-pressure, high-volume fracturing pumps are needed for hydraulic fracturing (Upstream Pumping, 2015). Such pumps come in a variety of sizes. Bigger pumps move greater volumes of fluid at higher pressures; therefore, spills from these pumps can be larger. Smaller pumps can require more operators and more maintenance (BJ Services Company, 2009), and therefore have the potential for an increased frequency of spills.

The "fluid ends" of hydraulic fracturing pumps are the pump components through which fluids are moved and pressurized. Pump fluid ends must withstand high pressure and move a large volume of abrasive fluid high in solids content. These pumps have multiple parts (e.g., seals, valves, seats and springs, plungers, stay rods, studs) that can wear out under the stress of high-pressure pumping (Upstream Pumping, 2015). Given the sustained pressures involved, careful maintenance of fluid ends is necessary to prevent equipment failure (Upstream Pumping, 2015; API, 2011). Details of a documented spill from a fracture pump are presented in Text Box 5-8.

**Text Box 5-8. Spill of Fluid from Fracture Pump.**

On December 19, 2011, in Arkansas, a fluid end on a fracture pump developed a leak, spilling approximately 840 gal (3,200 L) of fracturing fluid. A vacuum truck was used to recover the spilled fluid, and all affected soils were neutralized and taken to a landfill at the end of the job, after removal of the equipment (Arkansas DEQ, 2012, ID#063012).

### 5.5.6 Surface Wellhead for Fracture Stimulation

A wellhead assembly, often referred to as a frac head or frac stack, is temporarily installed on the wellhead during the fracture treatment. The frac head assembly allows high volumes of high-pressure proppant-laden fluid to be injected into the formation (OSHA, 2015; Halliburton, 2014; Stinger Wellhead Protection, 2010). The temporary frac head is equipped with specialized isolation tools so that the wellhead is protected from the effects of pressure and abrasion.

**Figure 5-9. Multiple fracture heads.**
Source: DOE/NETL.

As with all components of hydraulic fracturing operations, repeated and prolonged stress from highly pressurized, abrasive fluids may lead to equipment damage. The presence of minute holes or cracks in the frac head may result in leaks when pressurized fluids are pumped. In addition, surface blowouts or uncontrolled fluid releases may occur at the frac head because of valve failure or failure of other components of the assembly.[1] Details of a documented frac head failure are presented in Text Box 5-9.

### Text Box 5-9. Spill from Frac Head Failure.

On March 2, 2011, in Colorado, a frac head failed during fracturing operations. Approximately 8,400 gal (32,000 L) of slickwater fracturing fluid leaked. The majority of the spill was contained on-site, though a small amount ran off into a nearby cornrow. There were 5,460 gal (20,700 L) of the fluid recovered, and saturated soils were scraped and stockpiled on the well pad. There was a net loss of 2,940 gal (11,100 L) (COGCC, 2012, ID#2524586).

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[1] A well blowout is when there is uncontrolled flow of fluids out of a well.

## 5.6 Overview of Chemical Spills Data

Spills of hydraulic fracturing fluids have occurred across the country and have affected the quality of drinking water resources (U.S. EPA, 2015m; Brantley et al., 2014; COGCC, 2014; Gradient, 2013).[1] Spills may infiltrate drinking water resources by reaching surface water or by leaching into the groundwater. Potential impacts depend upon a variety of factors including the chemical spilled, environmental conditions, and actions taken in response to the spill.

### 5.6.1 EPA Analysis of Spills Associated with Hydraulic Fracturing

The EPA used data gathered from state and industry sources to characterize hydraulic fracturing-related spills between January 2006 and April 2012 (2015m) (see Text Box 5-10 for additional information). In this study, the sources had data on over 36,000 spills. Of these spills, the EPA identified 457 spills that occurred on or near the well pad and definitively related to hydraulic fracturing. Of these 457 spills, 151 were related to the chemical mixing process – spills that consisted of chemicals, additives, or fracturing fluids. Information in the spill reports included: spill causes (e.g., human error, equipment failure), sources (e.g., storage tank, hose or line), volumes, and environmental receptors. Spill reports contain little information on chemical-specific spill composition. Spilled fluids were often described by their additive type (e.g., acids, biocides, friction reducers, cross-linkers, gels,) or as a blended hydraulic fracturing fluid. Specific chemicals mentioned in spill reports included hydrochloric acid and potassium chloride.

**Text Box 5-10. EPA Review of State and Industry Spill Data: Characterization of Hydraulic Fracturing-Related Spills.**

As part of the EPA's Study of the Potential Impacts of Hydraulic Fracturing for Oil and Gas on Drinking Water Resources, the EPA published the report titled *Review of State and Industry Spill Data: Characterization of Hydraulic Fracturing-Related Spills* (U.S. EPA, 2015m). In this document, hereafter referred to as the EPA spills report, the EPA used data gathered from state and industry sources to characterize hydraulic fracturing-related spills with respect to volumes spilled, materials spilled, sources, causes, environmental receptors, containment, and responses. For the purposes of the study, hydraulic fracturing-related spills were defined as those occurring on or near the well pad before or during the injection of hydraulic fracturing fluids or during the post-injection recovery of fluids. Because the main focus of this study is to identify hydraulic fracturing-related spills on the well pad that may reach surface or groundwater resources, the following topics were not included in the scope of this project: transportation-related spills, drilling mud spills, and spills associated with disposal through underground injection control wells.

Data on spills that occurred between January 2006 and April 2012 were obtained from nine state agencies with online spill databases or other data sources, nine hydraulic fracturing service companies, and nine oil and gas production well operators. The data sources used in this study contained over 36,000 spills. The EPA searched each spill report for keywords related to hydraulic fracturing (e.g., frac, glycol, flowback). Spill records from approximately 12,000 spills (33 percent of the total number of spills reviewed) contained insufficient information to determine whether the event was related to hydraulic fracturing.

*(Text Box 5-10 is continued on the following page.)*

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[1] In this assessment, a spill is considered to be any release of fluids. Spills can result from accidents, fluid management practices, or illegal dumping.

### Text Box 5-10 (continued). EPA Review of State and Industry Spill Data: Characterization of Hydraulic Fracturing-Related Spills.

Of the spills with sufficient information, the EPA identified approximately 24,000 spills (66%) as not related to hydraulic fracturing on or near the well pad. The remaining 457 spills (approximately 1%) occurred on or near the well pad and were definitively related to hydraulic fracturing. These 457 spills occurred in 11 different states over six years (January 2006 to April 2012). Of these 457 spills, 151 spills were chemical mixing-related and included spills of chemicals, additives, and hydraulic fracturing fluid, and 225 releases were of produced water (Chapter 7).

The EPA categorized spills according to the following causes: equipment failure, human error, failure of container integrity, other (e.g., well communication, weather, vandalism), and unknown.[1] Figure 5-10 presents the percent distribution of causes of hydraulic fracturing-related spills and for spills associated specifically with chemicals or fracturing fluid. The distributions for causes of hydraulic fracturing- and chemical mixing-related spills are similar.[2]

Spills in the EPA spills report were also categorized by the following sources: storage, equipment, well or wellhead, hose or line, and unknown. Figure 5-11 presents the percent distribution for all hydraulic fracturing- and chemical mixing-related spills associated with each source.

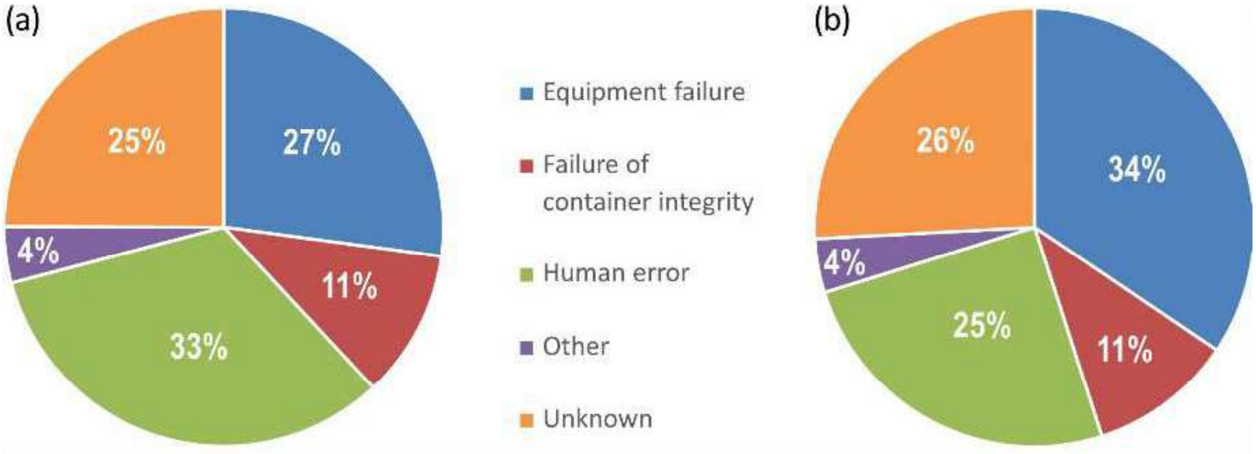

**Figure 5-10. Percent distribution of the causes of spills.**

Percent distribution by spill type for (a) 457 hydraulic fracturing-related spills (all spills) and (b) 151 chemical mixing-related spills. Data from U.S. EPA (2015m). Legend shows categories in clockwise order, from the top left of each pie chart.

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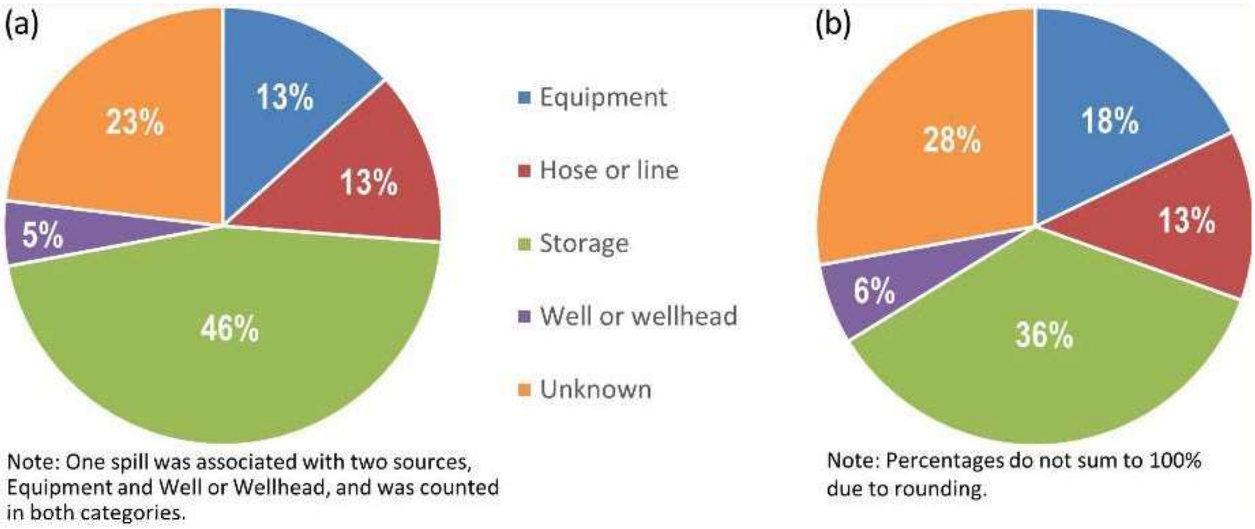
[1] Well communication is when hydraulic fracturing fluids or displaced subsurface fluids move through newly created fractures into an offset well or its fracture network (See Section 6.3.2.3 for more details),

[2] Hydraulic fracturing-related spills are spills that occur at any phase within the hydraulic fracturing water cycle. These include chemicals, additives, hydraulic fracturing fluids (chemical mixing phase); produced water; and wastewater.



Note: One spill was associated with two sources, Equipment and Well or Wellhead, and was counted in both categories.

Note: Percentages do not sum to 100% due to rounding.

**Figure 5-11. Percent distribution of the sources of spills.**
Percent distribution of spill source of (a) 457 hydraulic fracturing-related spills (all spills) and (b) 151 chemical mixing-related spills. Data from U.S. EPA (2015m). Legend shows categories in clockwise order, from the top left of each pie chart.

Figure 5-12 presents the distribution of the number of spills for different volumes for hydraulic fracturing- and chemical mixing-related spills. The spills associated with chemical mixing ranged in volume from 5 to 19,320 gal (19 to 73,130 L), with a median volume of 420 gal (1,600 L). The source of largest spills was storage containers, which released approximately 83,000 gal (314,000 L) of spilled fluid (Figure 5-13b). Spills from wells or wellheads are often associated with high spill volumes. There were no reported chemical mixing-related spills greater than 100,000 gal (380,000 L) (Figure 5-15b).

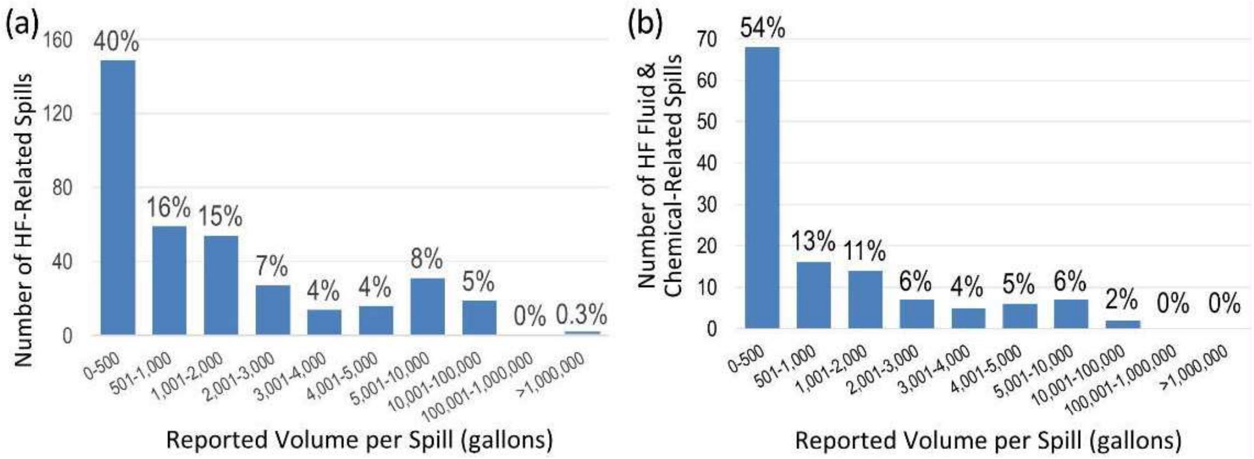


**Figure 5-12. Distribution of the number of spills for different ranges of spill volumes.**
Number of spills due to Hydraulic Fracturing related activities and distribution of spill volumes for (a) 457 hydraulic fracturing-related spills (all spills) and (b) 151 chemical mixing-related spills. A value of 0% means that there were no spills in that category. Data from U.S. EPA (2015m).

Figure 5-13 presents the total volume of spills for different sources for all hydraulic fracturing-related activity and those associated with chemicals and fracturing fluid. The reported total volume of 125 of 151 chemical or hydraulic fracturing fluid spills was approximately 184,000 gal (697,000 L). The volume was unknown for 26 of these spills.

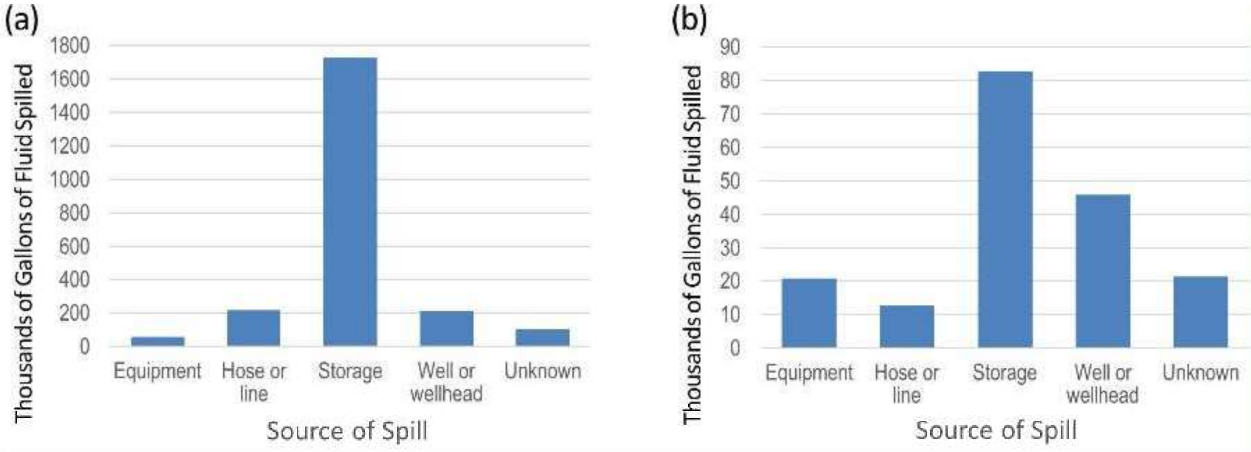


**Figure 5-13. Total volume of fluids spilled from different sources.**

Total volume of fluids spilled for (a) 457 hydraulic fracturing-related spills (all spills) and (b) 151 chemical mixing-related spills. Data from U.S. EPA (2015m).

Figure 5-14 presents the number of spills that reached environmental receptors, by receptor type, for all hydraulic fracturing-related activity (Figure 5-14a) and those associated with chemicals and fracturing fluid (Figure 5-14b). Environmental receptors (i.e., surface water, groundwater, soil) were identified in 101 of the 151 chemical mixing-related spills, or 67% of all chemical and fracturing fluid spills in the EPA's analysis (U.S. EPA, 2015m). Soil was by far the dominant environmental receptor, with 97 spills reaching soil; reported spill volumes ranged from 5 gal to 8,300 gal (19 L to 31,000 L). Thirteen spill reports indicated that the spilled fluid had reached surface water; reported spill volumes ranged from 28 gal to 7,350 gal (105 L to 27,800 L). Nine spill reports identified both soil and surface water as a receptor; spill volumes ranged from 28 gal to 2,856 gal (106 L to 10,800 L). Groundwater was not identified as a receptor from spills of chemicals or hydraulic fracturing fluid in any of the spill reports. Due to the lack of observations, it is often unclear if there was impact on groundwater. Movement through the subsurface is generally slow.[1] It may take years for a spilled fluid to reach groundwater or to reach a drinking water well. Thus, even if there is a pre-drilling characterization of groundwater chemistry in private/public wells, the time period of transport to actually detect a release at these private/public wells for contaminants that are transported at the rates of groundwater flow (see Section 5.8 for discussion on fate and transport of spilled chemicals).

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[1] For example, a groundwater flow rate of 1 foot per day (not uncommon) would mean it could take approximately 1,000 days (~3 years) to travel 1,000 ft (305 m) from the well pad. Likewise, for a groundwater travel rate of 0.1 ft (0.03m) per day, impact would not be observed for at least 10,000 days (~27 years). For a travel rate of 10 ft (3 m) per day, the time for impact would be at least 100 days (~0.3 years).

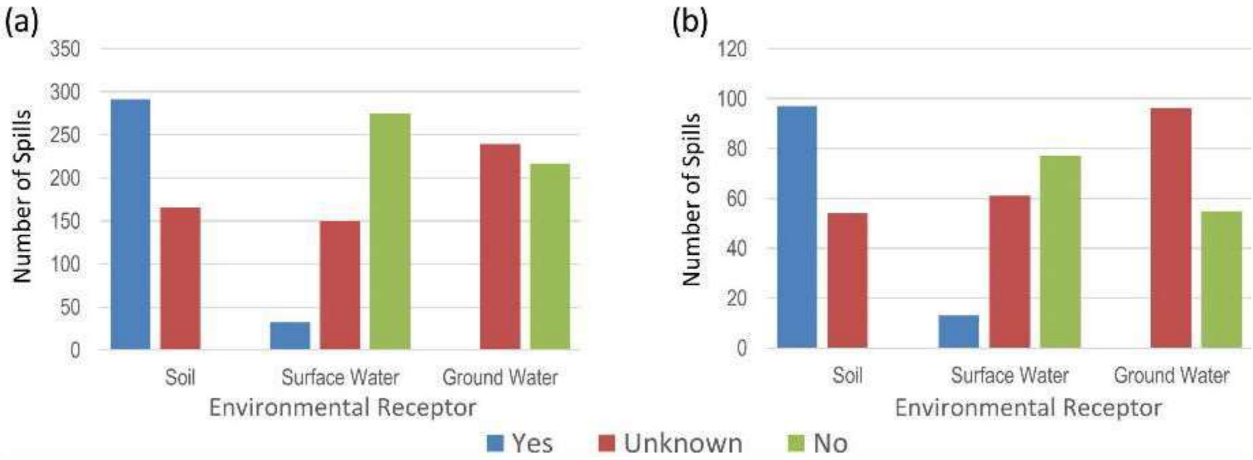

**Figure 5-14. Number of spills by environmental receptor.**

Number of hydraulic fracturing-related spills and chemical mixing-related spills that reported whether an environmental receptor was reached for (a) 457 hydraulic fracturing-related spills (all spills) and (b) 151 chemical mixing related spills. “Yes” means that the spill was reported to reach this receptor. “Unknown” refers to hydraulic fracturing related spill events for which environmental receptors were specified as unknown or not identified (positively or negatively). “No” means the spill was reported to not meet this receptor. Data from U.S. EPA (2015m).

Storage units were the predominant sources of spills that reached an environmental receptor. Six spills from storage containers reached a surface water receptor. Thirty-eight of the spills from storage units reached a soil receptor. If a spill was confined to a lined well pad, for example, it might not have reached the soil, but most incident reports did not include whether the well pad was lined or unlined. Regarding spills of hydraulic fluids and chemicals from storage containers, 16 spills were due to failure of container integrity, which includes holes and cracks in containers, and overflowing containers as a result of human error or equipment malfunctions.

### 5.6.2 Estimated Spill Rate and Other Spill Reports and Data

The rate of reported spills during the hydraulic fracturing water cycle is estimated to range from 0.4 to 12.2 reported spills for every 100 wells, based on spills data from Brantley et al. (2014), Gradient (2013), Rahm et al. (2015), U.S. EPA (2013a), and North Dakota Department of Health (2015) (Appendix E) with a median rate of 2.6 reported spills for every 100 wells. (See Appendix Section C.4 and Appendix Table C-8 for details.) The estimated rates provide an approximate estimate of the potential frequency of the number of spills at a site. It is uncertain how representative these rates are of national spill rates or rates in other states. These numbers are not specific to the chemical mixing stage.

There are an estimated 2.6 reported spills of injected fluids and chemicals per 100 wells hydraulically fractured in North Dakota, based on an analysis of the North Dakota spills database for 2015, separate from the EPA spills report. The median spill volume of injection fluid was 1750 gal (6620 L), with a range of 2.9 to 17,600 gal (11 to 66,600 L). The median spill volume of injection chemical was 44 gal (167 L), with a range of 2.1 to 126 gal (7.9 to 477 L) (see Appendix E for more information).

A study of spills reported to the Colorado Oil and Gas Conservation Commission identified 125 spills during well stimulation (i.e., a part of the life of an oil and gas well that often, but not always, includes hydraulic fracturing) between January 2010 and August 2013. Of these spills, 51% were caused by human error and 46% were due to equipment failure (COGCC, 2014).

Considine et al. (2012) identified spills related to oil and gas development in the Marcellus Shale that occurred between January 2008 and August 2011 from Notices of Violations issued by the Pennsylvania Department of Environmental Protection. The authors identified spills greater than 400 gal (1,500 L) and spills less than 400 gal (1,500 L). Among these spills, spilled fluids included hydrochloric acid, gel friction reducer, and blended hydraulic fracturing fluid. Brantley et al. (2014) identified fewer than 10 instances of spills of additives and/or hydraulic fracturing fluids greater than 400 gal (1,500 L) that reached surface waters in Pennsylvania between January 2008 and September 2013. Reported spill volumes, among these spills, ranged from 3,400 gal to 227,000 gal (13,000 L to 859,000 L).

Surface spills related to hydraulic fracturing activities are not well documented in the scientific literature. There is some evidence of spills and impacts on environmental media (e.g., U.S. EPA, 2015i; Brantley et al., 2014; Gross et al., 2013; Papoulias and Velasco, 2013). Papoulias and Velasco (2013) stated that fluid overflowed a retention pit into surface water and likely contributed to the distress and deaths of threatened blackside dace fish in Kentucky. A variety of chemicals entered the creek and significantly reduced the stream's pH and increased stream conductivity. Using data from post-spill sampling reports in Colorado, Gross et al. (2013) identified concentrations of benzene, toluene, ethylbenzene, and xylene (BTEX) in groundwater samples. They attributed this to numerous hydraulic fracturing-related spills, although not necessarily specifically related to the chemical mixing process. This work, however, demonstrate that surface spills impacted groundwater, with a frequency of < 0.5% of active wells. Drollette et al. (2015) reported that organic compounds detected in shallow aquifers were consistent with surface spills, and that diesel range compounds had elevated concentrations compared to gasoline range compounds, further suggesting evidence of feasible groundwater impact.

## 5.7 Spill Prevention, Containment, and Mitigation

Spill prevention, containment, and mitigation affect the frequency and severity of the impacts of spills. Several factors influence spill prevention, containment, and mitigation, including federal, state, and local regulations and company practices. State regulations governing spill prevention, containment, and mitigation at hydraulic fracturing facilities vary in scope and stringency (Powell, 2013; GWPC, 2009). Employee training and equipment maintenance are also factors in effective spill prevention, containment, and mitigation. Analysis of these factors was outside the scope of this assessment.

The province of New Brunswick, Canada released rules for industry on responsible environmental management of oil and natural gas activities (GNB, 2013). Hydraulic fracturing service companies themselves may develop and implement spill prevention and containment procedures. It was beyond the scope of this assessment to evaluate the efficacy of these practices or the extent to which they are implemented.

Spill containment systems include primary, secondary, and emergency containment systems. Primary containment systems are the storage units, such as tanks or totes, in which fluids are intentionally kept. 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.

The EPA investigated spill containment and mitigation measures in an analysis of spills related to hydraulic fracturing activities (U.S. EPA, 2015m). Of the approximately 25% of reports that included information on containment, the most common types of containment systems referenced in the hydraulic fracturing-related spill records included berms, booms, dikes, liners, and pits, though many of the spill reports did not indicate specific containment measures. Some spills were reported to breach the secondary containment systems. Breaches of berms and dikes were most commonly reported.

In cases where secondary containment systems were not present or were inadequate, operators sometimes built emergency containment systems. The most common were berms, dikes, and booms, but there were also instances where ditches, pits, or absorbent materials were used to contain the spilled fluid. Absorbent materials were generally used when small volumes (10 – 200 gal or 40 – 800 L) of additives or chemicals were spilled (U.S. EPA, 2015m). There was not enough information to detail the use of emergency containment systems or their effectiveness.

Remediation is the action taken to clean up a spill and its affected environmental media. The most commonly reported remediation activity, mentioned in approximately half of the hydraulic fracturing-related spill records evaluated by the EPA, was removal of spilled fluid and/or affected media, typically soil. Other remediation methods reported in U.S. EPA (2015m) included the use of absorbent material, vacuum trucks, flushing the affected area with water, and neutralizing the spilled material. Removal activities were found to occur in various combinations. For example, a spill of approximately 4,200 gal (16,000 L) of acid was cleaned up by first spreading soda ash to neutralize the acid and then removing the affected soil (U.S. EPA, 2015m).

## 5.8 Fate and Transport of Spilled Chemicals

The fate and transport of chemicals in the environment is complex. Due to the complexities of the processes and the site-specific and chemical-specific nature of spills, it is difficult to develop a full assessment of their fate and transport. The potential for hydraulic fracturing chemicals and fluids to reach drinking water resources is further complicated by the fact that these chemicals are typically present as mixtures, and unlike many organic contaminant mixtures (e.g., gasoline, diesels, PCBs, PAHs), hydraulic fracturing fluid chemicals are present as complex mixtures of chemicals covering a range of chemical classes with varying properties, often in aqueous solutions.

In this section, we provide a general overview of fate and transport of hydraulic fracturing-related chemicals spilled in the environment to give the reader a general understanding of the potential pathways and processes with which these chemicals can impact drinking water resources (Figure 5-15). We also include a discussion of the physicochemical properties of the organic chemicals used in hydraulic fracturing fluids, because these properties directly affect the transport of chemicals in the environment. This presentation is not meant to be exhaustive.

A chemical spill has the potential to migrate to and have an impact on drinking water resources. Once spilled, there are different paths that chemicals can travel and different processes they can undergo. Chemicals can react and transform into other chemicals, volatilize, travel to surface water, leach into and partition to soils, and/or reach groundwater. The potential path and the severity of the impact of a spill depend on different factors, including site conditions; the length of the path to a drinking water resource; the type and characteristics of the drinking water resource (stream, lake, aquifer); environmental conditions; climate; weather; chemical properties, constituents, and concentrations; and the volume of the release. The point in the chemical mixing stage where the spill occurs affects potential impact. If the spill occurs before chemicals are mixed into the base fluid, the chemicals will be in a more concentrated form. If the hydraulic fracturing fluid spills, then the chemicals will be diluted by the base fluid and can feasibly be present in lower concentrations. There can also be effects on persistence and mobility due to interactions among the chemicals present. The total mass of spilled chemical can therefore be dependent on what stage in the process a spill occurs.

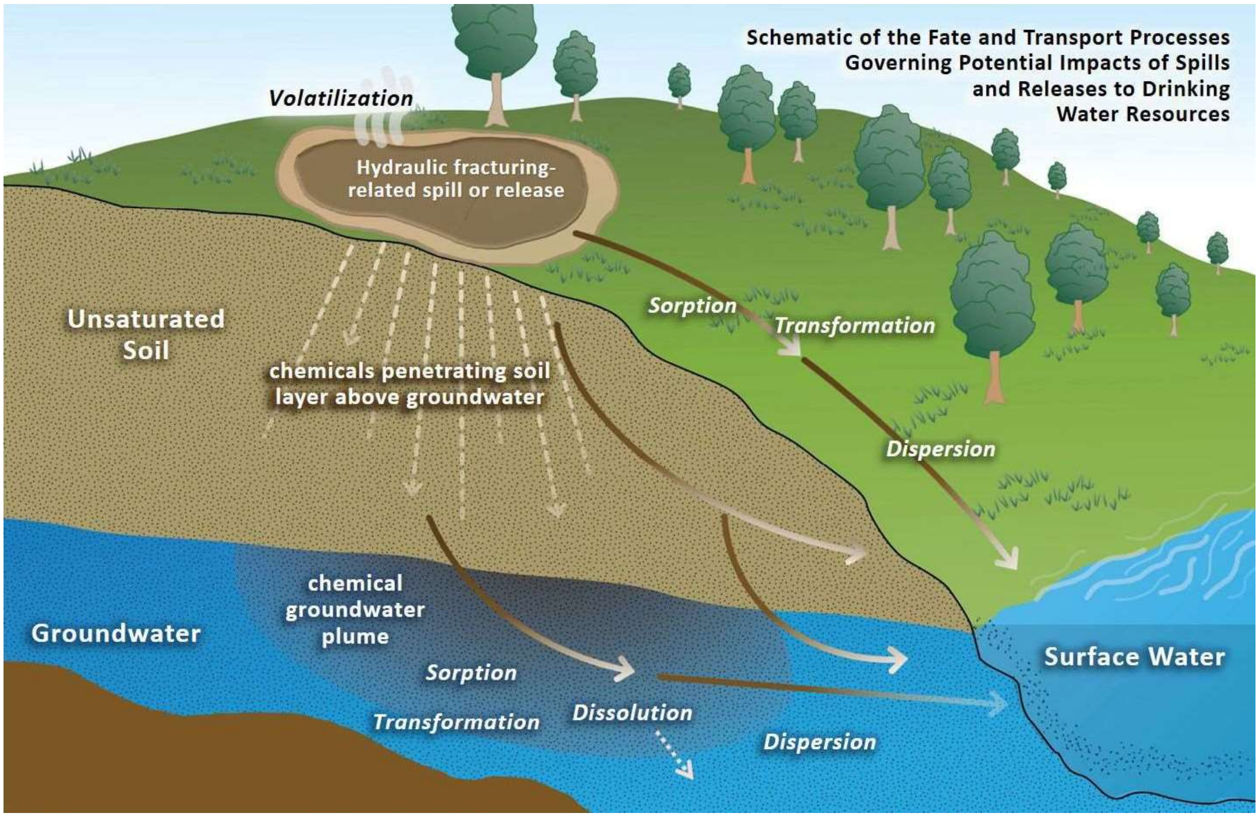

**Figure 5-15. Fate and transport schematic for a spilled hydraulic fracturing fluid.**
Schematic shows the potential paths and governing processes by which spilled chemicals can lead to potential impacts on drinking water resources.

For inorganic chemicals, the properties and processes governing fate and transport depend on pH, oxidation state, presence of iron oxides, soil organic matter, cation exchange capacity, and major ion chemistry (U.S. EPA, 1996).[1] Transport of these chemicals into groundwater depends on the nature of groundwater flow and flow through the unsaturated zone above the water table.[2] Potential transformations of inorganic chemicals differ from those of organic chemicals. Some inorganic anions (i.e., nitrate, chloride, and bromide) move with their carrier liquid and are affected mostly by physical transport mechanisms. For many inorganic chemicals, transport is driven by the physical flow processes (advection and dispersion), sorption, and precipitation. The relative role of each of these depends on both chemical and environmental characteristics.[3,4]

Determining the fate and transport of organic chemicals and mixtures is a complex problem, because of the many processes and different environmental media (air, soil, water). Unlike inorganic chemicals, organic chemicals degrade, which can affect their movement and potential impact. Schwarzenbach et al. (2002) formalized a general framework for organic chemical transport, where transport and transformation depend on both the nature of the chemical and the properties of the environment. The fate and transport of organic chemicals in soils has been presented in the literature (e.g., Bouchard et al., 2011; Rivett et al., 2011; Abriola and Pinder, 1985a, b) and in textbooks (e.g., Domenico and Schwartz, 1997; Schnoor, 1996; Freeze and Cherry, 1979b).

### 5.8.1 Potential Paths

Chemicals and hydraulic fracturing fluids that are released into the environment may travel along different potential paths, as detailed in Figure 5-15. Liquids can flow overland to nearby surface water or infiltrate the subsurface, where they may eventually reach the underlying groundwater or travel laterally to reach surface water. Movement can occur quickly or be delayed and have a later or longer-term impact. Surface and groundwater gain or lose flow to each other (Chapter 2), and can transport chemicals in the process. A dry chemical (e.g., gelling agents, biocides, friction reducers) released to the environment can remain where it is spilled. Any spill that is not removed could act as a long-term source of contamination. Wind could cause the chemical to disperse and rain could mobilize soluble chemicals. Dissolved chemicals can infiltrate into soil or flow overland. Insoluble chemicals and those sorbed to soil particles could be mobilized by rain events via runoff and erosion.

#### 5.8.1.1 Movement across the Land Surface

In low permeability soils, there may be little infiltration and greater overland flow. Higher permeability soils will allow fluid to penetrate into the soil layer. In either case, some of the

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[1] Cation exchange capacity is the total amount of cations (positively charged ions) that a soil can hold. For example, when metal ions like $Ca^{2+}$ and $Na^{+}$ pass through the soil, they adhere and remain attached to the soil.

[2] The unsaturated zone is also referred to as the vadose zone. Meaning "dry," the vadose zone is the soil zone above the water table that is only partially filled by water.

[3] Advection is a mechanism for moving chemicals in flowing water, where a chemical moves along with the flow of the water itself.

[4] Sorption is the general term used to describe the partitioning of a chemical between soil and water and depends on the nature of the solids and the properties of the chemical.

chemicals in the fluid can sorb to the soil particles and the vegetation, and then these chemicals can be mobilized during precipitation, runoff, or erosion. As precipitation percolates through the soil, it can dissolve stored chemicals, which can then migrate toward groundwater. The type of release is also important. If the spill is a slow leak, then the liquid may pond and the affected area will expand slowly with greater potential for infiltration. If a more rapid release occurs, like a blowout or tank failure, then momentum can result in greater overland movement and less soil infiltration during the event, with greater potential to reach a nearby surface water.

#### 5.8.1.2 Movement through the Subsurface

The unsaturated and saturated zones are the two zones of soils below the ground surface. Movement through the unsaturated zone is driven by the depth of ponding of the spilled fluid, gravity, and capillary properties of the subsurface.[1] In fractured rock or highly permeable soils, fluids can move quickly through the subsurface. In low permeability soil, the movement of the fluid may be slower. However, the presence of preferential pathways (e.g., fractures, heterogeneities, root holes, and burrows) can result in faster movement than the overall permeability would suggest.

As chemicals pass through the subsurface, some can sorb to soil or remain in the open spaces between soil particles, effectively slowing their movement. Chemicals can be mobilized during future precipitation events, resulting in infiltration towards groundwater or movement through the unsaturated zone towards surface water.

Fluids that move through the subsurface into the saturated zone will move in the direction of the flowing groundwater. Generally, fluids travel farther in systems with high groundwater flow rates and high recharge (e.g., sandy aquifers in humid climates) than in systems with low flow and low recharge. Chemicals can sorb to suspended soil particles, complex with naturally occurring chemicals (e.g., dissolved organic carbon), or associate with colloids and be transported with the flowing water.[2] These mechanisms can mobilize sparingly soluble chemicals that would otherwise be immobile.

### 5.8.2 Physicochemical Properties of Organic Hydraulic Fracturing Chemicals

Three physicochemical properties are useful to describe the movement of organic chemicals in the environment: (1) $K_{\mathrm{ow}}$, the octanol-water partition coefficient, (2) the aqueous solubility, and (3) the Henry's law constant.[3] These properties describe whether a chemical will sorb to soil and organic

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[1] Capillarity occurs because of the forces of attraction of water molecules to themselves (cohesion) and to other solid substances such as soils (adhesion).

[2] Complexation is a reaction between two chemicals that form a new complex, either through covalent bonding or ionic forces. This often results in one chemical solubilizing the other.

[3] The octanol-water partition coefficient ($K_{ow}$) represents the ratio of the solubility of a compound in octanol (a nonpolar solvent) to its solubility in water (a polar solvent) in a mixture of the two. The higher the $K_{ow}$, the more nonpolar the compound.

matter or stay in water ($K_{ow}$), how much of a chemical may dissolve in water (aqueous solubility), and whether a chemical will tend to remain in the water or volatilize (Henry's law constant).[1]

The $K_{ow}$ measures the relative hydrophobicity (chemicals that prefer to be in oil, log $K_{ow} > 0$) and hydrophilicity (chemicals that prefer to be in water, log $K_{ow} < 0$) of a chemical. Aqueous solubility is the maximum amount of a chemical that will dissolve in water in the presence of a pure chemical; solubility generally serves as an upper bound on possible concentrations. The Henry's law constant is the ratio of the concentration of a chemical in air (or vapor pressure) to the concentration of that chemical in water.

Estimates and measured values for physicochemical properties were obtained by using the Estimation Program Interface (EPI) Suite 4.1, as described in Appendix C.[2] Of the 1,084 chemicals the EPA listed as used in hydraulic fracturing (Appendix H), EPI Suite™ has estimated properties for 455 organic chemicals (42% of all chemicals) with structures that are considered suitably representative of the substance to compute properties within the constraints of EPI Suite™ software. Only uniquely defined organic desalted structures were submitted for property calculation. Figure 5-16 presents histograms of all 455 of the organic chemicals, sorted by four physicochemical parameters: measured log $K_{ow}$ ($n$ = 195), estimated log $K_{ow}$ (n=455), estimated log of the aqueous solubility ($n$ = 455), and estimated log of Henry's law constant (at 77°F or 25°C, $n$ = 449). Property estimation methods are limited in their ability to predict physicochemical properties. Chemicals that are different than the chemicals used to develop the estimation techniques may have more error associated with their predictions. These figures enable comparison of physicochemical properties across the organic chemicals for which we have values. These figures show how the physicochemical properties are distributed and which chemicals have higher values compared to others with lower values. Limitations in knowing what chemicals are present (e.g., CBI) further hinders our ability to know the physicochemical properties of these chemicals and their potential to move through the environment and impact drinking water resources. These estimates are solely for the organic chemicals for which EPI Suite™ could be used. This does not provide information on the 258 inorganic chemicals or the 361 organic mixtures or polymers. This limits our ability to make a full assessment on the physicochemical properties of all chemicals, yet provides insight into the properties of the organic chemicals used.

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[1] We present the physicochemical parameter values using $\log_{10}$ because of the wide range of values that these parameters cover.

[2] EPI Suite™, version 4.1, http://www.epa.gov/opptintr/exposure/pubs/episuite.htm (U.S. EPA, 2012c). The EPI (Estimation Programs Interface) Suite™ is a Windows®-based suite of physicochemical property and environmental fate estimation programs developed by the EPA Office of Pollution Prevention and Toxics and Syracuse Research Corporation. EPI Suite™ provides estimates of physicochemical properties for organic chemicals and has a database of measured values for physicochemical properties when available. EPI Suite™ cannot estimate parameters for inorganic chemicals.

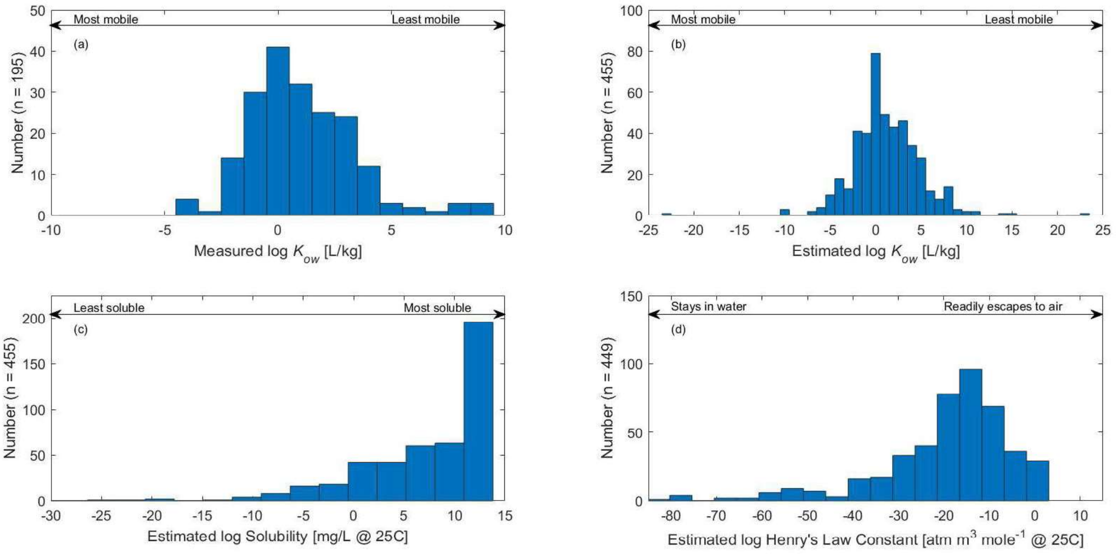

**Figure 5-16. Histograms of physicochemical properties of organic chemicals used in the hydraulic fracturing process.**

Physicochemical properties as given by EPI Suite™ (a) measured values of log $K_{ow}$, (b) estimated log $K_{ow}$, (c) estimated log Solubility, and (d) estimated log Henry's law constant.

We used EPI Suite™ to determine the physicochemical properties for 19 CBI chemicals used in hydraulic fracturing fluids. These chemicals were submitted to the EPA by nine service companies from 2005 to 2009 (see Text Box 5-3 for discussion on CBI).[1] The CBI chemical physicochemical properties are plotted as histograms in Appendix Figure C-1. The values of the physicochemical properties of known and CBI chemicals are similar, covering similar ranges and centered on similar values, suggesting that even though these chemicals are not publicly known, their physicochemical properties are not appreciably different from the known chemicals. This suggests that their fate and transport would not be appreciably different than the chemicals that are publicly known.

### 5.8.3 Mobility of Organic Hydraulic Fracturing Chemicals

Figure 5-16 shows the distribution of log $K_{ow}$, solubility, and Henry's Law constant for organic chemicals used in hydraulic fracturing fluids. These figures suggest that the organic chemicals used in hydraulic fracturing cover a wide range of physicochemical properties. For example, many chemicals are centered around log $K_{ow} = 0$, which indicates that these chemicals are likely to associate roughly equally with organic or aqueous phases. Many chemicals have log $K_{ow} > 0$, indicating less mobility, which may cause these chemicals to serve as later-term or long-term sources of impact on drinking water. Solubilities range from fully miscible to sparingly soluble. Many chemicals have log Henry's law constants less than 0, indicating that most are not highly volatile. Volatilization may not serve as a dominant loss process for hydraulic fracturing chemicals.

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[1] Well operators may specify certain ingredients as confidential business information (CBI) and not disclose the chemicals used to FracFocus. The CASRNs of a range of CBI chemicals were provided to the EPA by nine service companies.

The 20 chemicals with the smallest $K_{ow}$ (most mobile) may have greater potential to cause immediate impacts on drinking water resources (Appendix Table C-10). Most of these chemicals were infrequently reported in disclosures (≤2% of wells) in the EPA FracFocus 1.0 project database (U.S. EPA, 2015a). Choline chloride (14% of wells), used for clay control, and tetrakis(hydroxymethyl)-phosphonium sulfate (11% of wells), a biocide, were more commonly reported. The 20 chemicals with the largest $K_{ow}$ (least mobile) may have a greater potential to serve as long-term sources of contamination (Appendix Table C-11). The estimated aqueous solubilities for some of these chemicals are extremely low, with highest solubilities of less than 10 µg/L. Seven low mobility chemicals were reported in disclosures in the EPA FracFocus 1.0 project database (U.S. EPA, 2015c). Five were reported infrequently (<1% of wells). Tri-n-butyltetradecylphosphonium chloride (6% of wells), used as a biocide, and C>10-alpha-alkenes (8% of wells), a mixture of alpha-olefins with carbon numbers greater than 10 used as a corrosion inhibitor, were more commonly reported. Sorbitan, tri-(9Z)-9-octadecenoate, a mineral oil co-emulsifier (0.05% of wells) had the highest estimated log $K_{ow}$ of 22.56.[1]

Table 5-7 shows the EPI Suite™ estimated physicochemical property values of the 20 chemicals most frequently reported nationwide in disclosures along with estimated mean and median volumes based on disclosures in the EPA FracFocus 1.0 project database (U.S. EPA, 2015c). Most have log $K_{ow} < 1$, meaning that they are generally hydrophilic and will associate with water. These chemicals also have very high solubilities, so they will be mobile in the environment, transport with water, and can occur at high concentrations. These chemicals have the potential for faster impacts on drinking water resources.

Naphthalene (CASRN 91-20-3) has a measured log $K_{ow} = 3.3$ with an estimated solubility of 142.1 mg/L, which means it will be less mobile in the environment. Naphthalene will sorb to particles and move slowly through the environment and has the potential to act as a long-term source of contamination.[2] All of these chemicals have low Henry's law constants, so they tend not to volatilize. We also include ranges of similar physicochemical properties for two chemicals that are organic mixtures: distillates, petroleum, hydrotreated light (CASRN 64742-47-8) and solvent naphtha, petroleum, heavy arom. (CASRN 64742-94-5). Both of these are complex organic mixtures, and thus EPI Suite™ cannot estimate their properties. However, the Total Petroleum Hydrocarbon Work Group has provided regressions to relate physicochemical properties to the number of carbons for aliphatic and aromatic hydrocarbons (Gustafson et al., 1997), which shows that they have low solubilities and large log $K_{ow}$.

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[1] Sorbitan, tri-(9Z)-9-octadecenoate, CASRN 26266-58-0, is soluble in hydrocarbons and insoluble in water, listed as an effective coupling agent and co-emulsifier for mineral oil (Santa Cruz Biotechnology, 2015; ChemicalBook, 2010).

[2] Chemicals can have the potential to be long-term sources of contamination when they move slowly through the environment. In this discussion, we are not accounting for biodegradation or other transformation processes, which may reduce the persistence of certain chemicals in the environment. Under certain conditions, for example, naphthalene is biodegradable, which can reduce or remove it from the environment, and thus may not be a long-term source of contamination.

**Table 5-7. The 20 chemicals reported most frequently nationwide for hydraulic fracturing based on the EPA FracFocus 1.0 project database, with EPI Suite™ physicochemical parameters where available, and estimated mean and median volumes of those chemicals where density was available.**

Excludes water, sodium chloride, and quartz. NA means that the physicochemical parameter is not provided by EPI Suite™ or the volume could not be estimated due to missing data. For organic salts, parameters are estimated using the desalted form. Analysis considered 34,675 disclosures and 676,376 ingredient records that met selected quality assurance criteria, including: completely parsed; unique combination of fracture date and API well number; fracture date between January 1, 2011, and February 28, 2013; valid CASRN; and valid concentrations. Disclosures that did not meet quality assurance criteria (3,855) or other, query-specific criteria were excluded from analysis.

| Rank | Chemical name | CASRN | Number of wells using chemical (% of wells) | Log $K_{ow}$ (unitless) | | Water solubility estimate from log $K_{ow}$ (mg/L @ 25ºC) | Henry's Law Constant (atm $m^3$/mole @ 25ºC) | | | Estimated volume, per disclosure (gal) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Estimated | Measured | | Estimated, bond method | Estimated, group method 25 | Measured | Mean | Median |
| 1 | Methanol | 67-56-1 | 24,753 (72%) | -0.63 | -0.77 | $1.00 \times 10^{6}$ | $4.27 \times 10^{-6}$ | $3.62 \times 10^{-6}$ | $4.55 \times 10^{-6}$ | 1,218 | 110 |
| 2 | Distillates, petroleum, hydrotreated light[a,b] | 64742-47-8 | 22,463 (65%) | log $K_{oc}$ = 4.5 to 6.7 | NA | 0.00035 to 0.12 | 55 to 69 $cm^3/cm^3$ | NA | NA | NA | NA |
| 3 | Hydrochloric acid | 7647-01-0 | 22,380 (65%) | NA | NA | NA | NA | NA | NA | 28,320 | 3,110 |
| 4 | Isopropanol | 67-63-0 | 16,039 (47%) | 0.28 | 0.05 | $4.024 \times 10^{5}$ | $7.52 \times 10^{-6}$ | $1.14 \times 10^{-5}$ | $8.10 \times 10^{-6}$ | 2,095 | 55 |
| 5 | Ethylene glycol | 107-21-1 | 15,800 (46%) | -1.2 | -1.36 | $1.00 \times 10^{6}$ | $1.31 \times 10^{-7}$ | $5.60 \times 10^{-11}$ | $6.00 \times 10^{-8}$ | 614 | 184 |
| 6 | Peroxydisulfuric acid, diammonium salt | 7727-54-0 | 14,968 (44%) | NA | NA | NA | NA | NA | NA | NA | NA |
| 7 | Sodium hydroxide | 1310-73-2 | 13,265 (39%) | NA | NA | NA | NA | NA | NA | 551 | 38 |
| 8 | Guar gum | 9000-30-0 | 12,696 (37%) | NA | NA | NA | NA | NA | NA | NA | NA |
| 9 | Glutaraldehyde | 111-30-8 | 11,562 (34%) | -0.18 | NA | $1.672 \times 10^{5}$ | $1.10 \times 10^{-7}$ | $2.39 \times 10^{-8}$ | NA | 1,313 | 122 |
| 10 | Propargyl alcohol | 107-19-7 | 11,410 (33%) | -0.42 | -0.38 | $9.355 \times 10^{5}$ | $5.88 \times 10^{-7}$ | NA | $1.15 \times 10^{-6}$ | 183 | 2 |
| 11 | Potassium hydroxide | 1310-58-3 | 10,049 (29%) | NA | NA | NA | NA | NA | NA | NA | NA |
| 12 | Ethanol | 64-17-5 | 9,861 (29%) | -0.14 | -0.31 | $7.921 \times 10^{5}$ | $5.67 \times 10^{-6}$ | $4.88 \times 10^{-6}$ | 5.00E-06 | 831 | 121 |
| 13 | Acetic acid | 64-19-7 | 8,186 (24%) | 0.09 | -0.17 | $4.759 \times 10^{5}$ | $5.48 \times 10^{-7}$ | $2.94 \times 10^{-7}$ | $1.00 \times 10^{-7}$ | 646 | 47 |
| 14 | Citric acid | 77-92-9 | 8,142 (24%) | -1.67 | -1.64 | $1.00 \times 10^{6}$ | $8.33 \times 10^{-18}$ | NA | $4.33 \times 10^{-14}$ | 163 | 20 |

| | | | | Log $K_{ow}$ (unitless) | | | Henry's Law Constant (atm m$^3$/mole @ 25ºC) | | | Estimated volume, per disclosure (gal) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Rank** | **Chemical name** | **CASRN** | **Number of wells using chemical (% of wells)** | **Estimated** | **Measured** | **Water solubility estimate from log $K_{ow}$ (mg/L @ 25ºC)** | **Estimated, bond method** | **Estimated, group method 25** | **Measured** | **Mean** | **Median** |
| 15 | 2-Butoxyethanol | 111-76-2 | 7,347 (21%) | 0.57 | 0.83 | $6.447 \times 10^4$ | $9.79 \times 10^{-8}$ | $2.08 \times 10^{-8}$ | $1.60 \times 10^{-6}$ | 385 | 26 |
| 16 | Solvent naphtha, petroleum, heavy arom.[b,c] | 64742-94-5 | 7,108 (21%) | log $K_{oc}$ = 3.2 to 2.7 | NA | 5.8 to 65 | 0.028 to 0.39 cm$^3$/cm$^3$ | NA | NA | NA | NA |
| 17 | Naphthalene | 91-20-3 | 6,354 (19%) | 3.17 | 3.3 | $1.421 \times 10^2$ | $5.26 \times 10^{-4}$ | $3.7 \times 10^{-4}$ | $4.4 \times 10^{-4}$ | 72 | 12 |
| 18 | 2,2-Dibromo-3-nitrilopropionamide | 10222-01-2 | 5,656 (16%) | 1.01 | 0.82 | $2.841 \times 10^3$ | $6.16 \times 10^{-14}$ | NA | $1.91 \times 10^{-8}$ | 183 | 5 |
| 19 | Phenolic resin | 9003-35-4 | 4,961 (14%) | NA | NA | NA | NA | NA | NA | NA | NA |
| 20 | Choline chloride | 67-48-1 | 4,741 (14%) | -5.16 | NA | $1.00 \times 10^6$ | $2.03 \times 10^{-16}$ | NA | NA | 2,131 | 290 |

[a] Hydrotreated light petroleum distillates (CASRN 64742-47-8) is a mixture of hydrocarbons in the C9 to C16 range.

[b] Physicochemical parameters are estimated using Gustafson et al. (1997). Parameters are presented as log $K_{oc}$ (soil organic carbon-water partition coefficient), solubility (mg/L), and Henry's Law Constant (cm$^3$/cm$^3$).

[c] Heavy aromatic solvent naphtha (petroleum) (CASRN 64742-94-5) is mixture of aromatic hydrocarbons in the C9 to C16 range.

For the top 20 chemicals, many chemicals have high solubilities and negative or almost zero log $K_{ow}$ (e.g., methanol, isopropanol, ethylene glycol). These chemicals are likely to travel quickly through the environment and could result in an immediate impact. Three chemicals, with larger log $K_{ow}$ and smaller solubilities (distillates, petroleum, hydrotreated light; solvent naphtha, petroleum, heavy arom.; and naphthalene) may result in more severe impacts. These chemicals could associate with the soil particles, releasing into the groundwater at low concentrations slowly over time, and thus serve as long-term sources of contamination.

Mobility of a chemical is complex, and these numbers solely represent how a chemical behaves in an infinitely dilute aqueous solution, a simplifying approximation of the real world. Many factors can affect the fate and transport of a chemical, such as the transformation process (e.g., biodegradation), the presence of other chemicals, and site and environmental conditions. We discuss these factors in the next sections.

### 5.8.4 Transformation Processes

Once a chemical is released into the environment, it can transform or degrade. Understanding the processes governing these reactions in the environment is important to assessing potential impacts. The transformation of a chemical may reduce its concentration over time. Chemicals may completely degrade before reaching a drinking water resource. Transformation processes can be biotic or abiotic and may transform a chemical into a less or more harmful chemical.

One important transformation process is biodegradation. Biodegradation is a biotic process where microorganisms transform a chemical from its original form into another chemical. For example, the general biodegradation pathway of methanol is $CH_3OH \rightarrow CH_2O \rightarrow CHOOH \rightarrow CO_2$ or methanol → formaldehyde → formic acid → carbon dioxide (Methanol Institute, 2013).[1] This pathway shows how the original chemical transforms through a series of steps until it becomes the final product, carbon dioxide. Some chemicals are readily biodegraded, while others break down slowly over time. Biodegradation is a highly site-specific process, requiring nutrients, a carbon source, water, and an energy source. A highly biodegradable chemical could be persistent if the conditions for biodegradability are not met. Conversely, a chemical could biodegrade quickly under the right conditions, affecting its potential to impact a drinking water resource. The relationship between mobility and biodegradability is complex, and a variety of factors can influence a particular chemical's movement through the environment.

Abiotic processes, such as oxidation, reduction, photochemical reactions, and hydrolysis, can transform or break apart chemicals. The typical results are products that are more polar than the

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[1] In methanol biodegradation, PQQ (pyrroloquinoline quinone) is a redox cofactor that goes from PQQ to $PQQH_2$ removing two hydrogen from methanol in the first step to form formaldehyde. Water is added to formaldehyde to provide the second oxygen to form formic acid. Nicotinamide adenine dinucleotide (NAD) is a coenzyme that takes up a hydrogen, going from NAD to $NADH^+$. This removes the hydrogen in the second and third steps, to result in carbon dioxide.

original compounds, and thus have different physicochemical properties (Schwarzenbach et al., 2002).[1]

### 5.8.5 Fate and Transport of Chemical Mixtures

Spills during the chemical mixing stage are often present as mixtures of chemicals. Additives are often mixtures of a few to several chemicals, possibly highly concentrated, and hydraulic fracturing fluids are often dilute mixtures of several additives. Chemical mixtures can act differently in the environment than individual chemicals. Individual chemicals can affect the fate and transport of other chemicals in a mixture primarily by changing their physicochemical properties and transformation rates.

Chemical mixtures can be more mobile than individual chemicals due to cosolvency, which increases solubility in the aqueous phase. Methanol and ethanol are examples of cosolvent alcohols used frequently in hydraulic fracturing fluids (U.S. EPA, 2015a). The presence of either greatly increases BTEX solubility (Rasa et al., 2013; Corseuil et al., 2011; Heermann and Powers, 1998).[2] By increasing solubility, ethanol can affect the fate and transport of other compounds. For example, BTEX has been observed to travel farther in the subsurface in the presence of ethanol (Rasa et al., 2013; Corseuil et al., 2011; Corseuil et al., 2004; Powers et al., 2001; Heermann and Powers, 1998).

The presence of surfactants lowers fluid surface tension and increases solubility of organic chemicals. Surfactants can mobilize less soluble/less mobile organic chemicals. Two common surfactants reported in disclosures in the EPA FracFocus 1.0 project database were 2-butoxyethanol (CASRN 111-76-2, 21% of disclosures) and poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy (mixture) (CASRN 127087-87-0, 20% of disclosures). Additionally, surfactants can mobilize bacteria in the subsurface, which can increase the impact of pathogens on drinking water resources (Brown and Jaffé, 2001).

When chemicals are present as mixtures, one chemical can decrease or enhance the biodegradability of another through inhibition or co-metabolism. The process of inhibition can slow biodegradation of each of the chemicals present. For example, the biodegradation of ethanol and methanol can slow the biodegradation rate of BTEX or other organic chemicals present (Rasa et al., 2013; Powers et al., 2001). Co-metabolism can increase the biodegradation rate of other chemicals. For example, when methane or propane is present with tetrachloroethylene, the enzyme produced by bacteria to degrade methane also degrades tetrachloroethylene (e.g., Alvarez-Cohen and Speitel, 2001 and references therein). For the purposes of chemicals used in hydraulic fracturing, the presence of other chemicals in additives and hydraulic fracturing fluids could result in increased or decreased biodegradation if the chemicals are spilled.

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[1] A polar molecule is a molecule with a slightly positive charge at one part of the molecule and a slightly negative charge on another. The water molecule, $H_2O$, is an example of a polar molecule, where the molecule is slightly positive around the hydrogen atoms and negative around the oxygen atom.

[2] BTEX is an acronym for benzene, toluene, ethylbenzene, and xylenes. These chemicals are a group of single ringed aromatic hydrocarbons based on the benzene structure. These compounds are found in petroleum and are of specific importance because of their potential health effects.

### 5.8.6 Site and Environmental Conditions

Environmental conditions at and around the spill site affect the movement and transformation of chemicals. This section discusses the following: site conditions (e.g., proximity, land cover, and slope), soil conditions (e.g., permeability and porosity), and weather and climate.

The proximity of a spill to a drinking water resource, either laterally in the case of a surface water body or downward for groundwater, affects the potential for impact and its severity. Land cover will affect how readily a fluid moves over land. For example, more rugged land cover such as forest can impede flow, and an asphalt road can facilitate flow. A spill that occurs on or near a sloped site can move overland faster, increasing the potential to reach nearby surface water. Flatter surfaces result in a greater chance for infiltration to the subsurface, which could increase the potential for groundwater impact.

Soil characteristics that affect the transport and transformation of spill chemicals include soil texture (e.g., clay, silt, sand), permeability, porosity, and organic content.[1,2] Fluids will move more quickly through permeable soil (e.g., sand) than through less permeable soil (e.g., clay). A soil with a high porosity provides more volume to hold water and spilled chemicals. Another important factor for a site is the organic content, of which there are two competing types: soil organic carbon and dissolved organic carbon. Each type of carbon acts as a strong substance for chemicals to associate with. Soil organic carbon present in a solid phase, such as dead and decaying leaves and roots, is not mobile and slows the movement of chemicals through the soil. Dissolved organic carbon (DOC) moves with the water and can act as a shuttling mechanism to mobilize less soluble chemicals across the surface and through the subsurface. Chemicals may also associate and move with particulates and colloids.

Weather and climate conditions affect the fate and transport of a spilled chemical. After a spilled chemical stops moving, precipitation can remobilize the chemical. The amount, frequency, and intensity of precipitation will impact the volume, distance, and speed of chemical movement. Precipitation can carry chemicals downward or overland, and it can cause erosion, which can move sorbed chemicals overland.

### 5.8.7 Peer-Reviewed Literature on the Fate and Transport of Hydraulic Fracturing Fluid Spills

There has been limited peer-reviewed research investigating the fate and transport of chemicals spilled at hydraulic fracturing sites. Aminto and Olson (2012) modeled a hypothetical spill of 1,000 gal (3,800 L) of hydraulic fracturing fluid using equilibrium partitioning. The authors evaluated how 12 chemicals typically used for hydraulic fracturing in the Marcellus Shale would partition among different phases: air, water, soil, and biota.[3] They presented a ranking of

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[1] Permeability of a soil describes how easily a fluid can move through the soil. Under a constant pressure, a fluid will move faster in a high permeability soil than the same fluid in a low permeability soil.

[2] Porosity of a soil describes the amount of empty space for a given volume of soil. The porosity describes how much air, water, or hydraulic fluid a given volume of soil can hold.

[3] The chemicals they investigated included: sodium hydroxide, ethylene glycol, 4,4-dimethyl oxazolidine, 3,4,4-trimethyl oxazolodine, 2-amino-2-methyl-1-propanol, formamide, glutaraldehyde, benzalkonium chloride, ethanol, hydrochloric acid, methanol, and propargyl alcohol.

concentrations for each phase. In water, they showed that sodium hydroxide (a pH buffer), 4,4-dimethyl oxazolidine (a biocide), hydrochloric acid (a perforation clean-up additive), and 3,4,4-trimethyl oxazolidine (a biocide) had the highest simulated water concentrations; however, these concentrations depended on the chemicals included in the simulated mixture and the concentrations of each. Their analysis suggested that after a spill, a large fraction of the spill would volatilize and leave the soil; however, some constituents would be left behind in the water, soil, and biota compartments, which could act as long-term contamination sources. Aminto and Olson (2012) only studied this one scenario. Other scenarios could be constructed with different chemicals in different concentrations. These scenarios may result in different outcomes and impacts. Any spill would require site- and spill-specific modeling on a case-by-case basis. For this reason, we cannot make any general statement about fate and transport of hydraulic fracturing chemicals and fluids. For this reason, we cannot make any general statement about fate and transport of hydraulic fracturing chemicals and fluids.

Drollette et al. (2015) suggested a link between surface spills and groundwater contamination, possibly from hydraulic fracturing activity, because the chemicals detected were hydraulic fracturing additives. This work demonstrates the pathway for surface spills to impact groundwater sources. They detected low levels of gasoline related organic chemicals with elevated diesel range organic chemicals, which suggests that the former were degraded or volatilized, while the latter were more persistent and penetrated into the subsurface and into groundwater.

### 5.8.8 Potential and Documented Fate and Transport of Documented Spills

There is limited information on the fate and transport of hydraulic fracturing fluids and chemicals. This section highlights both potential and documented impacts for three reported spills (U.S. EPA, 2015m). In each case, we provide the documented and potential paths (surface, subsurface, or combination) and the associated fate and transport governing processes by which the spill has been documented or has the potential to have an impact on drinking water resources. The three cases involve a tank overflow with a reported surface water impact, a human error blender spill with a reported soil impact, and an equipment failure that had no reported impact. We specifically chose these three spills to highlight three different cases. One demonstrates a documented impact with a demonstrated pathway that had an observed effect on a nearby drinking water resource. The second case shows how a release can impact an environmental receptor with a pathway for potential impact on a drinking water resource, but there was no observed impact. The third example is a spill that was contained and cleaned up resulting in likely no impact. None of these chemical releases have any documented pre- or post-sampling. No information on the specific chemicals spilled or the concentrations or total mass of any chemical is provided. We cannot provide any quantitative assessment from these observed cases.

In the first documented spill, shown in Figure 5-17, a tank overflowed twice, releasing a total of 7,350 gal (980 $ft^3$, 28 $m^3$, or 27,800 L) of friction reducer and gel (PA DEP, 2012, ID#1830163).[1] The spill traveled across the land surface, crossed a road, and then continued to a nearby stream. The

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[1] We provide the total volume of the spill in gallons as well as cubic length (cubic feet and cubic meters), because it may be a little harder to visualize how far a volume of 7,300 gal (28,000 L) might travel.

spill affected wetlands and a stream, where fish were reported to have been killed. The fish kill indicates an observable impact. This represents a good example for how environmental conditions can affect the severity and timing of impact, due to the slope of the lands surface, the permeability of the soil, and the proximity to surface water. We are not aware of any measurements performed for soils, groundwater, surface water, sediments, or fish tissue. Based on the publicly available information, we do not know what chemicals were in the friction reducer and gel, which limits further assessment.

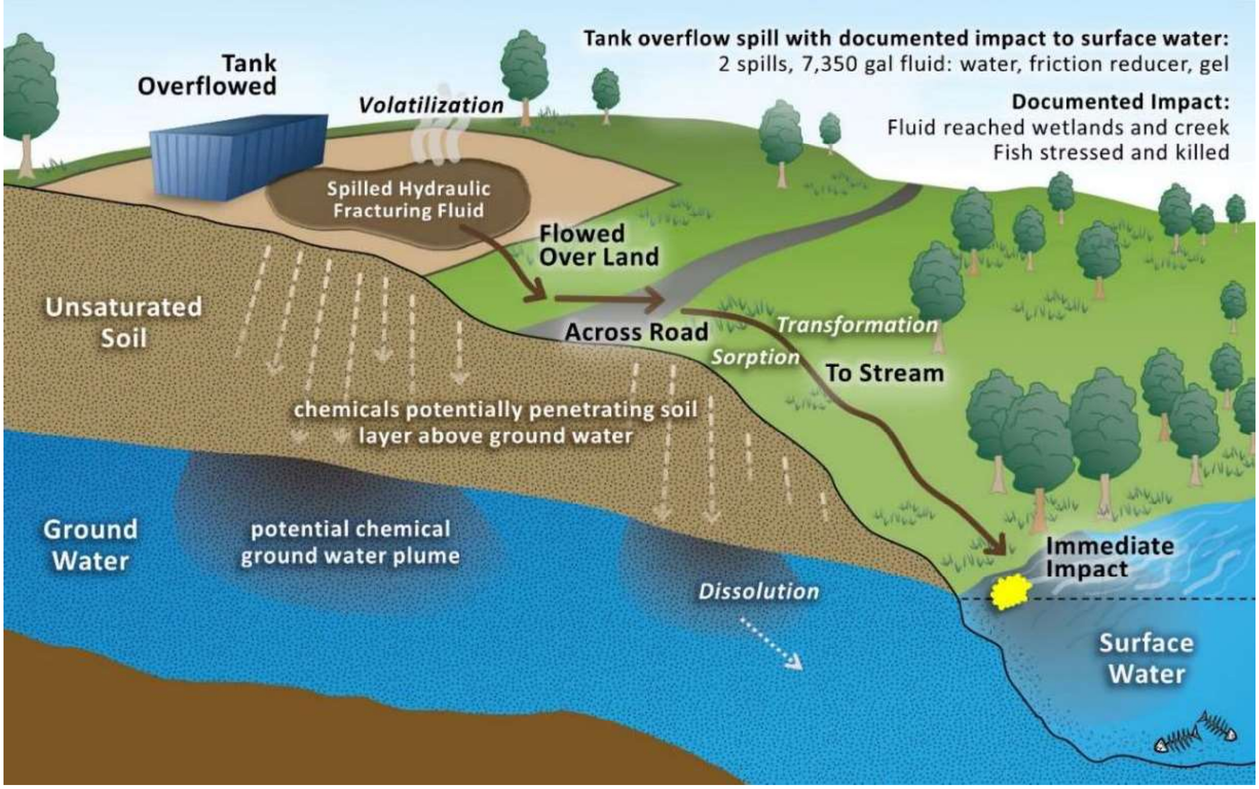

**Figure 5-17. Fate and Transport Spill Example: Case 1.**
Spills information from PA DEP (2012, ID#1830163).

For this first spill, the documented path was overland flow from the tank to the stream with a documented, immediate impact. There are also other potential paths for potential impacts on drinking water resources. The spilled chemicals could have penetrated into the soils or sorbed to soils and vegetation as the fluid moved across the ground towards the stream. Chemicals could then be mobilized during later precipitation, runoff, or erosion events. Chemicals that infiltrated the subsurface could serve as long-term sources, travel laterally across the unsaturated zone, or continue downwards to groundwater. Some chemicals could be lost to transformation processes. The absence of reported soil or groundwater sampling data prevents the ability to know if these potential paths occurred or not.

The second documented spill, shown in Figure 5-18, occurred when a cap was left off the blender, and 504 gal (70 $ft^3$ or 2 $m^3$) of biocide and hydraulic fracturing fluid were released (COGCC, 2012, ID#2608900). In addition, 294 gal (39 $ft^3$ or 1.1 $m^3$) were retained by a dike with a lined secondary containment measure, demonstrating the partial effectiveness of this containment mechanism. The remaining 210 gal (28 $ft^3$ or 0.8 $m^3$) of fluid (biocide and water) ran off-site. Of this, 126 gal were vacuumed, leaving 84 gal. There was no documented impact on surface or groundwater. However, potential impacts potentially could have occurred.

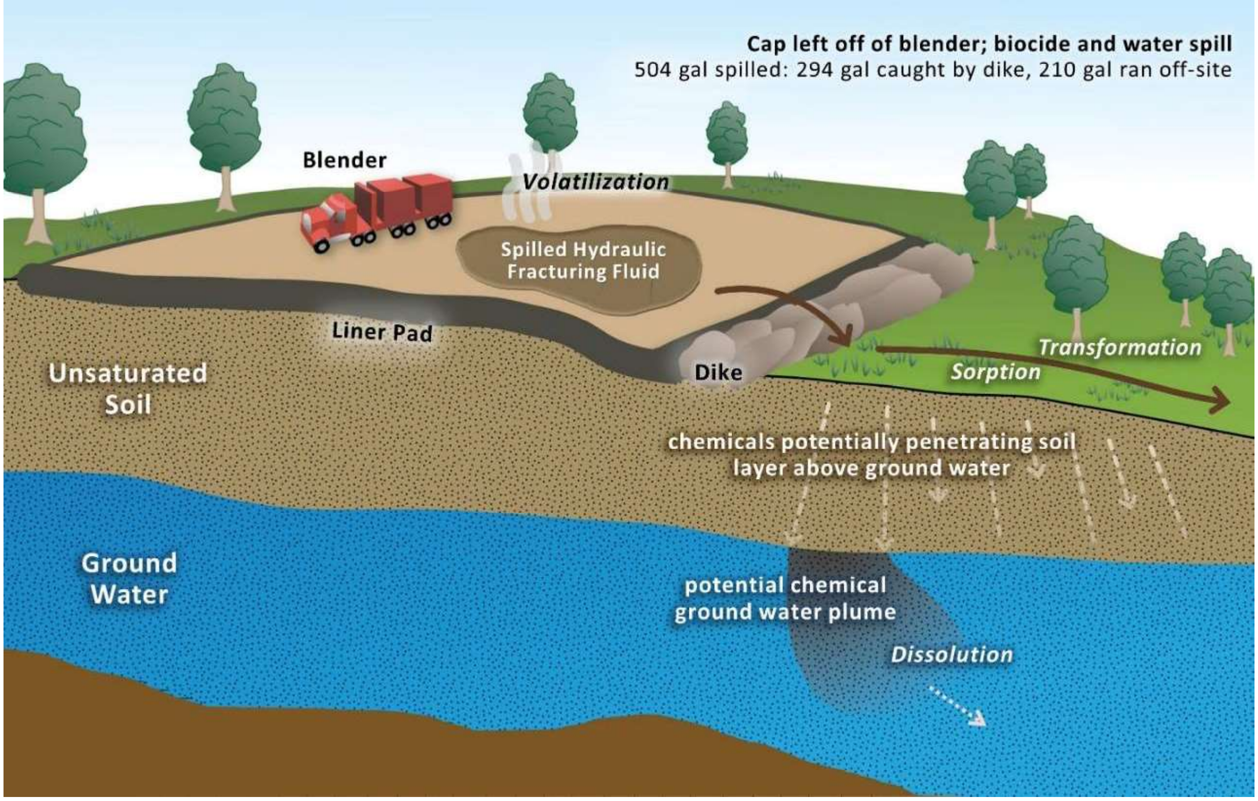

**Figure 5-18. Fate and Transport Spill Example: Case 2.**
Spills information from COGCC (2012, ID#2608900).

In this second case, the uncontained 84 gal could have infiltrated the subsurface, creating a potential path to groundwater. Highly mobile chemicals could have penetrated the soil more quickly than less mobile chemicals, which would have sorbed to soil particles. As the chemicals penetrated into the soil, some could have moved laterally in the unsaturated zone, or traveled downward to the groundwater table and moved with direction of groundwater flow. These chemicals could have served as a long-term contamination source. The chemicals also could have transformed into other chemicals with different physicochemical properties, and any volatile chemicals could have moved to the air as a loss process. As in the first case, there was no reported sampling of soil or groundwater, so there is no way to know if chemicals did or did not follow any of these pathways. We do not have any more information on the types of chemicals present or the concentrations with which they were present, which limits further assessment.

In the third documented spill, shown in Figure 5-19, 630 gal (84 $ft^3$ or 2.4 $m^3$) of crosslinker spilled onto the well pad when a hose wore off at the cuff (COGCC, 2012, ID#1395827). The spill was contained in the berm and an on-site vacuum truck was used to clean up the spill. No impact on soil or water was reported.

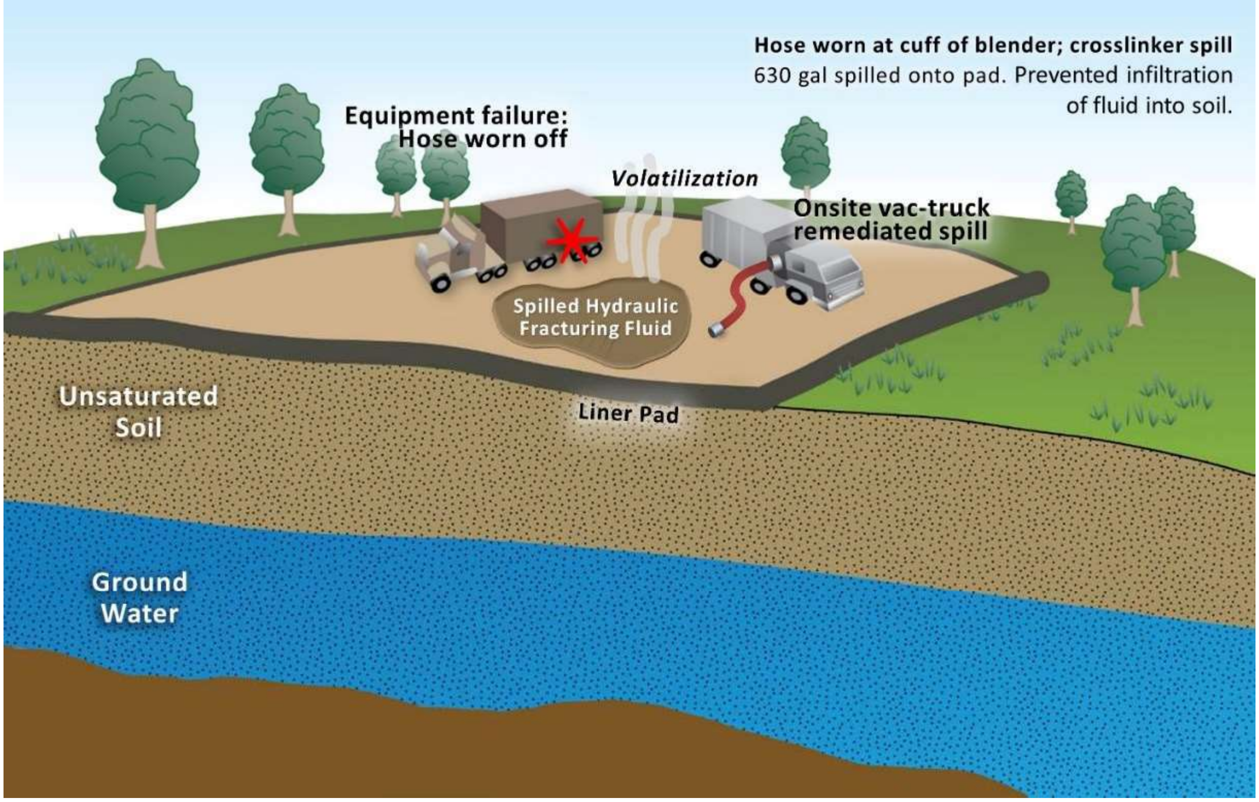

**Figure 5-19 Fate and Transport Spill Example: Case 3.**
The pad may or may not have had a liner. Spills information from COGCC (2012, ID#1395827).

For this third case, we do not have any information on whether the well pad was lined or not. If the site had a liner, the spill could have been fully contained and cleaned up. Without a liner or if the integrity of the liner was compromised (e.g., had a tear), any residual chemical that was not effectively cleaned up could have remained in the soil. This would create potential paths similar to those above in the second case, where the chemicals could have sorbed to the soils and penetrated into the subsurface and possibly reach groundwater. There was no reported sampling of soil or groundwater to determine whether or not chemicals migrated into the soil, and we do know the types of chemicals or the concentrations of the released chemicals.

### 5.8.9 Challenges with Unmonitored and Undetected Chemicals

One of the challenges confronting a thorough assessment of the fate and transport of spilled hydraulic fracturing chemicals lies in the lack of documented observations. It is difficult to prove absence of impact, and absence of observations does not necessarily imply lack of impact. Also, we know there are over 1,000 different chemicals reported used in hydraulic fracturing (Section 5.4), and this number is increasing. For many chemicals, there is not an analytical technique available to detect them in samples taken to a laboratory. Due to the lack of information on the chemicals used on site (some of which are claimed as CBI), one would not know what chemicals to include in the lab analysis. Hydraulic fracturing chemicals are typically present as complex mixtures, which also complicates sample analysis. Chemicals can transform upon release, which can result in different chemicals in the environment than those originally released. Even if chemicals are detected on-site, it can be difficult to demonstrate a direct linkage to hydraulic fracturing operations, since many of the chemicals used in hydraulic fracturing are also used for other purposes (such as gasoline or diesel from vehicles). Since there are currently no requirements for a detection–monitoring network to assess the occurrence and extent of chemical releases from the well pad, it is not possible to conclusively assess the frequency and impact of fluid releases during the chemical mixing process.

## 5.9 Trends in the Use of Hydraulic Fracturing Chemicals

Hydraulic fracturing science and engineering continues to advance. A part of this research includes using different chemicals. This section provides an overview of the changes in chemical use, with an emphasis on efforts to reduce potential impacts from surface spills by using fewer and safer chemicals. Reasons for changing the types of chemicals used can include: improving the fracturing process, using greener/safer chemicals, and reducing overall cost.

Representatives from oil and gas companies, chemical companies, and non-profits are working on strategies to reduce the number and volume of chemicals used and to identify safer chemicals (Waldron, 2014). Southwestern Energy Company, for example, is developing an internal chemical ranking tool (SWN, 2014), and Baker Hughes is working on a hazard ranking system designed for wide-scale external use (Baker Hughes, 2014; Brannon et al., 2012; Daulton et al., 2012; Brannon et al., 2011). Environmental groups, such as the Environmental Defense Fund, are also developing hazard rating systems (Penttila et al., 2013). Typical criteria used to rank chemicals include mobility, persistence, biodegradation, bioaccumulation, toxicity, and hazard characteristics. In this assessment, toxicity and a methodology to rank chemical hazards of hydraulic fracturing chemicals is discussed in Chapter 9.

Given that human error is the cause of 25% of chemical mixing related spills and spill prevention can never be 100% effective, changes to the types of chemicals used could reduce the frequency or the severity of potential impacts. Using chemicals with specific physicochemical properties that affect the fate and transport of chemicals could reduce their potential impacts. Less mobile chemicals could make cleanup of spills easier. For example, using dry chemicals that are hydrated on-site could minimize impacts if there were a container failure. Using chemicals with lower persistence and higher biodegradability, if spill prevention and cleanup are not fully effective, would lessen the severity of potential impact. Use of less hazardous chemicals could lessen impact in cases where a spill reaches a drinking water resource.

The EPA has not conducted a comprehensive review of efforts to develop safer hydraulic fracturing chemicals. However, the following are some specific examples of efforts that companies cite as part of their efforts toward safer chemical use:

- A renewable citrus-based replacement for conventional surfactants (Fisher, 2012);

- A crosslinked gel system comprised of chemicals designated as safe food additives by the U.S. Food and Drug Administration (Holtsclaw et al., 2011);
- A polymer-free gel additive (Al-Ghazal et al., 2013);
- A dry, hydrocarbon-free powder to replace liquid gel concentrate (Weinstein et al., 2009);
- Biodegradable polymers (Irwin, 2013);
- The use of ultraviolet light to control bacteria (Rodvelt et al., 2013);
- New chelating agents that reduce the use of strong acids (LePage et al., 2013);
- Eco-friendly viscoelastic surfactant (VES) polymer-free fluid reduces fracture cleanup time with 95% retrieved fluids compared to 40 – 60% and is less toxic than polymer-based fluids (AlKhowaildi et al., 2016); and
- The recovery and reuse of produced water as hydraulic fracturing fluids, which can reduce the need to add additional chemicals (Horn et al., 2013).

A review of the EPA's new chemicals program found that, from 2009 to April 2015, the Agency received pre-manufacturing notices (PMN) for about 110 chemicals that have the potential for use as additives. Examples include chemicals intended for use as clay control agents, corrosion inhibitors, gel crosslinkers, emulsifiers, foaming agents, hydrate inhibitors, scale inhibitors, and surfactants. At the time of PMN submission, these chemicals were not in commercial use in the United States. As of April 2015, the EPA had received 30 notices of commencement, indicating that some of the chemicals are now used commercially.

As different hydraulic fracturing fluids are developed, they have corresponding effects on different stages of the hydraulic fracturing water cycle. For example, in Figure 5-4(b) an example of an energized fluid uses a total water volume of 105,000 gal (397,000 L), which means less water is required in the water acquisition stage and less produced water results in less wastewater. Figure 5-4(a) shows slickwater with 4,763,000 gal (18,030,000 L) of water, yet a larger fraction of slickwater may be reused, reducing the need for more water for another frac job and requiring the treatment of less wastewater.

## 5.10 Synthesis

The chemical mixing stage includes the mixing of base fluid, proppant, and additives on the well pad to make hydraulic fracturing fluid. This chapter provided an analysis of the factors affecting potential impacts on drinking water resources during the chemical mixing stage of the hydraulic fracturing water cycle and the factors governing the frequency and severity of these impacts.

### 5.10.1 Summary of Findings

Reports have demonstrated that spills and releases of chemicals and fluids have occurred during the chemical mixing stage and have reached soils and surface water receptors. Spill reports have not documented impacts on groundwater related to the chemical mixing stage. Spill reports have little information on post-spill testing and sampling. Impacts on groundwater may remain undocumented. The potential pathway for impact on groundwater has been demonstrated and documented for chemicals spilled during other parts of the hydraulic fracture water cycle. (Evidence of groundwater impact from produced water spills is discussed Chapter 7.)

The hydraulic fracturing fluid generally consists of a base fluid (typically water), a proppant (typically sand), and additives (chemicals), although there is no standard or single composition of hydraulic fracturing fluid used. According to the analysis of the EPA FracFocus 1.0 project database, based on FracFocus disclosure data from January 2011 to February 2013, approximately 93% of hydraulic fracturing fluids use water as a base fluid. Non-aqueous fluids, such as nitrogen, carbon dioxide, and hydrocarbons, are also used as base fluids or used in combination with water as base fluids. The number of chemicals injected into a well typically ranges from 4 to 28, with a median of 14 (U.S. EPA, 2015a). In water-based hydraulic fracturing, the composition, by volume, of a typical hydraulic fracturing fluid is 90% to 97% water, 2% to 10% proppant, and 2% or less additives (Carter et al., 2013; Knappe and Fireline, 2012).

The EPA has identified 1,084 different chemicals used in chemical mixing. A recent study of FracFocus disclosure data, covering January 2011 to April 2015, has reported 263 new CASRNs, increasing the number of chemicals identified for use by approximately 24% (Konschnik and Dayalu, 2016). Hydraulic fracturing chemicals cover a wide range of chemical classes and a wide range of physicochemical properties. The chemicals include acids, aromatic hydrocarbons, bases, hydrocarbon mixtures, polymers, and surfactants. The use of 32 chemicals, excluding water, quartz, and sodium chloride, is reported in 10% or more of disclosures in the EPA FracFocus 1.0 project database. The ten most common chemicals (excluding quartz) are methanol, hydrotreated light petroleum distillates, hydrochloric acid, isopropanol, ethylene glycol, peroxydisulfuric acid diammonium salt, sodium hydroxide, guar gum, glutaraldehyde, and propargyl alcohol (U.S. EPA, 2015c). These chemicals can be present in multiple additives. Methanol, hydrotreated light petroleum distillates, and hydrochloric acid are the three chemicals reported to be used in more than half of all hydraulic fracturing jobs, with methanol being used at 72% of all sites.

An EPA analysis of spills data (January 2006 to April 2012, from nine states, nine service companies, and nine operators) identified over 36,000 spills, with 457 spills (~1%) that were on or near the well pad and definitively associated with hydraulic fracturing. Of these spills, 151 were of chemicals or hydraulic fracturing fluid and thus assumed to be associated with the chemical mixing stage. Chemical spills during the chemical mixing stage were primarily caused by equipment failure (34%), followed by human error (25%), although 26% spills had an unknown source. The remaining spills were caused by a failure of container integrity, weather, vandalism, and well communication. Reported spills covered a large range of volumes, from 5 to 19,320 gal (19 to 73,130 L), with a median of 420 gal (1,600 L) (U.S. EPA, 2015m).

The rate of reported spills during the hydraulic fracturing water cycle is estimated to range from 0.4 to 12.2 reported spills for every 100 wells, based on spills data from North Dakota, Pennsylvania, and Colorado, with a median rate of 2.6 reported spills for every 100 wells (See Appendix C). The estimated rates provide an approximate estimate of the potential frequency of the number of spills at a site. It is uncertain how representative these rates are of national spill rates or rates in other states. These numbers are not specific to the chemical mixing stage. In 2015, there are 2.6 reported spills occurring during the chemical mixing stage per 100 wells hydraulically fractured in North Dakota.

The total volume of chemicals used on site are estimated to range from 2,600 to 30,000 gal (9,800 to 114,000L). An estimate for the mean volume for any chemical used on-site is 650 gal (2,500 L) with a mean mass of 1500 kg (3,200 lb). An estimate of 2,300 to 6,500 gal (8,800 to 25,000 L) of additives are stored on site, typically in multiple totes of 200 to 375 gal (760 to 1,420 L). These volumes provide insight on how much potentially could spill at any given hydraulic fracturing site and what the volume of a spill might be depending on where/when it occurs during the chemical mixing process.

The potential of spills to reach drinking water resources depends on site and chemical properties. The fate and transport of spilled hydraulic fracturing chemicals is complex, particularly because chemicals are generally present as diverse, complex mixtures. There are different pathways for a spill to reach ground and surface water and to serve as a long term source. Roughly 40% of hydraulic fracturing chemicals are organic chemicals, which have physicochemical properties that cover the parameter space, from fully miscible to insoluble and from highly hydrophobic to highly hydrophilic. Of the 20 most frequently used chemicals used at hydraulic fracturing sites, three chemicals have low mobility: hydrotreated light petroleum distillates, heavy aromatic petroleum solvent naphtha, and naphthalene. These chemicals have the potential to act as long term sources of contamination if spilled on-site.

### 5.10.2 Factors Affecting the Frequency or Severity of Impacts

The specific factors that have the potential to affect the frequency and severity of impacts include the size and type of the fracturing operation; volume, mass, and concentration of chemicals spilled; type of chemicals and their properties; combination of chemicals spilled; environmental conditions; proximity to drinking water resources; employee training and experience; quality and maintenance of equipment; and spill containment and mitigation.

The size and type of a fracturing operation, including the number of wellheads, the depth of the well, the length of the leg(s), and the number of stages and phases, affect the potential frequency and severity spills. Larger operations can require larger volumes of chemicals, more storage containers, more equipment, and additional transfers between different pieces of equipment. Larger storage containers increase the maximum volume of a spill or leak from a storage container. Additional transfers between equipment increase the possibility of human error and potential frequency of spills.

The volume, mass, and concentration of spilled chemicals affect the frequency and severity of impacts. A larger volume increases the potential for a spill to travel a longer distance and reach a drinking water resource. The severity of the spill will be affected by the spill volume, the total mass of chemicals released, and the concentration with which it reaches the drinking water resource.

The type of chemicals spilled affects how the chemicals will move and transform in the environment and the type of impact it will have on a drinking water resource. More mobile chemicals move faster through the environment, which can increase the frequency of impact. More soluble chemicals can reach a drinking water resource at higher concentrations, thereby increasing the potential severity of an impact. Less mobile chemicals will move more slowly, and can have delayed and longer-term impacts at lower concentrations. The potential severity of impact is affected by how the chemical adversely impacts water quality. Some chemicals can have severe impacts at low concentrations, while some chemicals can have minimal impacts even at high concentrations. Water quality impacts can range from aesthetic effects (e.g., taste, smell) to adverse health effects.

The environmental conditions at and around the spill site affect the fate and transport of a given chemical and thus affect the frequency of impacts as well as potential severity. Conditions include soil properties, climate, weather, and terrain. Permeable soils allow for rapid transport of the spilled fluid through the subsurface and to groundwater. The presence of preferential flow paths (e.g., fractures, animal burrows) may provide rapid transport through the subsurface in what might appear to have low permeability. The presence of complexing agents and colloids may further increase transport of less soluble chemicals. Precipitation can re-mobilize trapped chemicals and move them over land or through the subsurface.

The proximity of a spill to drinking water resources affects the frequency and severity of impact. The closer a spill is to a drinking water resource, the higher the potential to reach it. As a fluid moves toward a drinking water resource, it can decrease in concentration, which can reduce the severity of an impact. The characteristics of the drinking water resource will also influence the severity of the impact of a spill. For example, a slow release into a fast moving stream will result in large dilution and lower concentrations of chemicals (less severe impact). The transport of a chemical to groundwater may have a more severe impact, as there may be less dispersion of the chemical (higher concentrations in the groundwater, more severe impact) and the chemical could serve as a long-term source of contamination (resulting in a chronic exposure versus an acute exposure).

Effective spill containment and mitigation measures can prevent or reduce the frequency and severity of impacts. Spill containment measures include well pad containment liners, diversion ditches, berms, dikes, overflow prevention devices, drip pans, and secondary containers. These may prevent a spill from reaching soil and water receptors. Spill mitigation, including removing contaminated soils, vacuuming up spilled fluids, and using sorbent materials can limit the severity of a spill. It is unclear how effective these practices are and to what extent they are implemented.

### 5.10.3 Uncertainties

The lack of information and the uncertainty around information having to do with the composition of additives and fracturing fluids, containment and mitigation measures in use, the proximity of chemical mixing to drinking water resources, and the fate and transport of spilled fluids limits our ability to fully assess potential impacts on drinking water resources and the factors affecting their frequency and severity.

There is no standard design for hydraulic fracturing fluids. Detailed information on the chemicals used is limited. Volumes, concentrations, and mass, as well as the identity of some of chemicals stored on-site, are generally not publicly available. The FracFocus national registry, which currently holds the most comprehensive information on water and chemicals used in hydraulic fracturing fluids, is structured so as to input chemical information as a maximum percentage of the mass of fracturing fluid and the given additive. This does not provide exact information on the volume of a chemical, the mass of a chemical, or the actual composition of an additive. The accuracy and completeness of original FracFocus disclosure information has not been verified. In applying the EPA-standardized chemical list to the ingredient records in the EPA FracFocus 1.0 project database, standardized chemical names were assigned to only 65% of the ingredient records from the more than 36,000 unique, fully parsed disclosures. The remaining ingredient records could not be assigned a standardized chemical name and were excluded from analyses (U.S. EPA, 2015a).

Operators may specify certain ingredients as confidential business information (CBI) and not disclose the chemical used. More than 70% of disclosures in the EPA FracFocus 1.0 project database contained at least one CBI chemical. Of disclosures with at least one CBI chemical, the average number of CBI chemicals per disclosure was five. Approximately 11% of all chemicals reported in the disclosures in the EPA FracFocus 1.0 project database were reported as CBI (U.S. EPA, 2015a). The rate of withholding in FracFocus 2.0 data has increased to 16.5% (Konschnik and Dayalu, 2016). No data are available in FracFocus disclosures for any chemical listed as CBI. Therefore, chemicals identified as CBI in FracFocus disclosures are not included in any of the analyses in this assessment including estimates of chemical volume, physicochemical properties, or frequency of use. It is feasible that the same chemicals are repeatedly reported as CBI. Each reported CBI chemical could also be unique, which would mean there is a very large number of chemicals that we know nothing about. This results in an unknown amount of uncertainty regarding CBI chemicals and their potential impact on drinking water resources.

Of the 1,084 hydraulic fracturing fluid chemicals identified by the EPA, 629 were inorganic chemicals, mixtures, or polymers, and thus they did not have estimated physicochemical properties reported in the EPI Suite™ database. Knowing the chemical properties of a spilled fluid is essential to predicting how and where it will travel in the environment. Although we can make some generalizations about the physicochemical properties of these chemicals and how spilled chemicals may move in the environment, the distribution of properties could change if we obtained data for all known fracturing fluid chemicals (as well as for those listed as CBI).

There has been limited research on the fate and transport of spilled chemicals on site. We have provided a limited overview discussing the processes that may be important, but the processes are complex. There is great uncertainty in how these chemicals will move in the environment. These processes are complicated by the data gaps in fluid characteristics, especially present in mixtures, and there is limited understanding on how chemicals act in mixture in the environment. Hydraulic fluid mixtures are different than other previously studied mixtures (like petroleums, coal tars, and polychlorinated biphenyls (PCBs). Those mixtures are of chemicals of similar classes, while hydraulic fracturing fluids are chemicals covering a range of different chemical classes.

There is a lack of field data at hydraulic fracturing sites. There is a lack of baseline ground and surface water quality data. This lack of data limits our ability to assess the relative change to water quality from a spill or attribute the presence of a contaminant to a specific source. There is a lack of publicly or readily accessible sampling of soils and groundwater after a fracturing job is complete. The lack of data and uncertainty on what chemicals are used for hydraulic fracturing makes it unclear what chemicals to measure. Further uncertainty lies in the limited analytical techniques for chemicals used in hydraulic fracturing.

There are uncertainties and data gaps in the current information on spills. The EPA spills report included data from January 2006 to April 2012 from nine states, nine service companies, and nine oil and gas production well operators (U.S. EPA, 2015a). This data contained over 36,000 reported spills. From this data set, only 457 were determined to be definitively associated with hydraulic fracturing and occurred on or near the well pad. With these data, it is impossible to know if all these spill reports capture all spills occurring at hydraulic fracturing sites. The available data might not extrapolate to the rest of the nation. Spill reports had limited information on spill causes, containment and mitigation measures, and sources of spills. The actual chemicals spilled, the total mass, and the composition are generally not included. There are little available data on impacts of spills, due to a lack of baseline data and incomplete documentation of follow-up actions and testing.

In general, then, we are limited in our ability to fully assess potential impacts on drinking water resources from chemical spills, based on current available information. To improve our understanding we need: more information on the chemical composition of additives and fracturing fluids and the physicochemical properties of chemicals used; baseline monitoring and field studies of spilled chemicals; ground and surface water drinking water resources located and identified, with quality conditions performed before and after hydraulic fracturing; detailed site-specific environmental conditions; more information on containment and mitigation measures and their effectiveness; and more detail on the characteristics of spills, such as the exact chemicals and the amount spilled (mass, concentration, volume).

### 5.10.4 Conclusions

This chapter discusses the factors that affect the potential for the chemical mixing stage of the hydraulic fracturing water cycle to impact drinking water resources. Reports have demonstrated that spills and releases of chemicals and fluids have occurred during the chemical mixing stage and have reached soils and surface waters with the potential to reach groundwater. The potential for spilled fluids to reach, and therefore impact, ground or surface water resources depends on the composition of the spilled fluid, spill characteristics, spill response activities, and the fate and transport of the spilled fluid. There is no standard composition for a hydraulic fracturing fluid, which consists of base fluid, proppant, and additives. The EPA identified 1,084 chemicals that have been reported to be used nationwide, and these chemicals cover a wide variety of chemical classes and physicochemical properties, and this number is increasing. These chemicals cover a range of classes and physicochemical properties. The type of fluid and the number, volume, and type of chemicals used vary from site to site. Hydraulic fracturing fluids generally consist of a mixture of chemicals, which affects the potential for a release to reach a drinking water resource and the severity of the potential impact. State and industry spill data collected and reviewed by the EPA and others indicate that small (approximately 30 gal or 100 L) and large spills (greater than 1,000 gal or 4,000 L) can reach surface water resources. While small spills have reached surface water resources (and have the potential to reach groundwater resources), large volume spills are more likely to travel longer distances and thus have a greater potential to reach ground and surface water resources. Large volume spills, particularly of concentrated additives, also have a greater potential to result in more severe impacts on drinking water resources, because they can deliver a large quantity of potentially hazardous chemicals to ground or surface water resources.

# Chapter 6. Well Injection

## Abstract

The well injection stage of the hydraulic fracturing water cycle involves the injection of hydraulic fracturing fluids through the oil and gas production well and their movement in the production zone. Subsurface pathways created during this stage—including the production well and newly created fractures—can allow hydraulic fracturing fluids or naturally occurring fluids to reach groundwater resources.

This chapter examines two types of pathways by which hydraulic fracturing fluids and liquids and/or gases that exist in the subsurface can move to, and affect the quality of, subsurface drinking water resources. First, fluids can move via pathways adjacent to or through the production well as a result of inadequate design, construction, or degradation of the casing or cement. Second, fluid movement can occur within the subsurface geologic formations via fractures extending out of oil/gas-containing formations, by intersecting abandoned or active offset wells, or via naturally occurring faults and fractures.

The primary factors that can affect the frequency or severity of impacts to drinking water associated with injection for hydraulic fracturing are: (1) the condition of the well's casing and cement and their placement relative to drinking water resources, (2) the vertical separation between the production zone and formations that contain drinking water resources, and (3) the presence/proximity and condition of wells near the hydraulic fracturing operation.

We identified two cases where hydraulic fracturing activities affected the quality of drinking water resources due to well construction issues, including inadequate cement or ruptured casing. Additionally, there are places where oil and gas reservoirs and drinking water resources co-exist in the same formation and hydraulic fracturing operations occur, which results in the introduction of hydraulic fracturing fluids into the drinking water resource. There are other cases involving the migration of stray gas where hydraulic fracturing could be a contributing cause to impacts on drinking water resources.

While there is evidence that these pathways have formed and that groundwater quality has been impacted, there are limited nationally available data on the performance of wells used in hydraulic fracturing operations, pre- and post-hydraulic fracturing groundwater quality, and the extent of the fractures that develop during hydraulic fracturing operations.

These data limits, in combination with the geologic complexity of the subsurface environment and the fact that these processes cannot be directly observed, make determining the frequency of such impacts challenging.

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# 6. Well Injection

## 6.1 Introduction

In the well injection stage of the hydraulic fracturing water cycle, hydraulic fracturing fluids (primarily water, mixed with the types of chemicals and proppant described in Chapter 5) are injected into a well under pressure.[1] These fluids flow under pressure through the well, then exit the well and move into the formation, where they create fractures in the rock. This process is also known as a fracture treatment or a type of stimulation.[2] The fractures, which typically extend hundreds of feet away from the well, are designed to remain within the production zone to access as much oil or gas as possible by using an appropriate amount of water and chemicals to complete the operation.[3]

Production wells are sited and designed primarily to optimize production of oil or gas, which requires isolating water-bearing formations from hydrocarbon-bearing formations in order to prevent the water from diluting the hydrocarbons and to protect drinking water resources.[4] However, problems with the well's components or improperly sited, designed, or executed hydraulic fracturing operations (or combinations of these) could adversely impact the quality of drinking water resources. (Note that, due to the subsurface nature of activities in the well injection stage, the drinking water resources that may be directly impacted are groundwater resources; see Chapter 2 for additional information about groundwater.[5])

The well and the geologic environment in which it is located are a closely linked system. Wells are often designed with multiple barriers (i.e., isolation afforded by the well's casing and cement and the presence of subsurface rock formations) to prevent fluid movement between oil/gas zones and drinking water resources. Therefore, this chapter discusses (1) the well (including its construction and operation) and (2) the characteristics of or features in the subsurface geologic formations that could provide or have provided pathways for migration of fluids to drinking water resources. If present, and in combination with the existence of a fluid and a physical force that moves the fluid, these pathways can lead to impacts on the quality of drinking water resources throughout the life of the well, including during and after hydraulic fracturing.[6]

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[1] A fluid is a substance that flows when exposed to an external pressure; fluids include both liquids and gases.

[2] In the oil and gas industry, "stimulation" has two meanings—it refers to (1) injecting fluids to clear the well or pore spaces near the well of drilling mud or other materials that block or inhibit optimal production (i.e., matrix treatment) and (2) injecting fluid to fracture the rock to optimize the production of oil or gas. This chapter focuses on the latter.

[3] The "production zone" (sometimes referred to as the target zone or the targeted rock formation) refers to the portion of a subsurface rock zone that contains oil or gas to be extracted (sometimes using hydraulic fracturing). "Producing formation" refers to the larger geologic unit in which the production zone occurs.

[4] A subsurface formation (or "formation") is a mappable body of rock of distinctive rock type(s) and characteristics (such as permeability and porosity) with a unique stratigraphic position.

[5] Government agencies and other organizations use a variety of terms to describe potable groundwater and groundwater resources. In this chapter, we use the general term "groundwater resources" to refer to drinking water resources that occur underground. However, other terms are used in specific contexts to reflect the language used in cited materials.

[6] The primary physical force that moves fluids within the subsurface is a difference in pressure. Fluids move from areas of higher pressure to areas of lower pressure when a pathway exists. Density-driven buoyancy may also serve as a driving force; see Section 6.3 for more information.

Fluids can move via pathways adjacent to or through the production well that are created in response to the stresses exerted during hydraulic fracturing operations if the well is not able to withstand these stresses (Section 6.2). While wells are designed and constructed to isolate fluids and maximize the production of oil and gas, inadequate construction or degradation of the casing or cement can allow fluid movement that can impact drinking water quality. Potential issues associated with wells may be related to the following:

- Inadequate or degraded casing. This may be influenced by the number of casing strings and the depths to which they are set, compatibility with the geochemistry of intersected formations, the age of the well, whether re-fracturing is performed, and other operational factors.
- Inadequate or degraded cement. This may be influenced by a lack of cement in key subsurface intervals, poor-quality cement, improperly placed cement, or degradation of cement over time.

Fluid movement can also occur via induced fractures and/or other features within subsurface formations (Section 6.3). While the hydraulic fracturing operation may be designed so that the fractures will remain within the production zone, it is possible that, in the execution of the hydraulic fracturing treatment, fractures can extend beyond their designed extent. Four scenarios associated with induced fractures may contribute to fluid migration or communication between zones:

- Flow of injected and/or displaced fluids through pore spaces in adjacent rock formations out of the production zone due to pressure differences and buoyancy effects.
- Fractures extending out of oil/gas formations into drinking water resources or zones that are in communication with drinking water resources or fracturing into zones containing drinking water resources.
- Fractures intersecting artificial structures, including active (producing) or inactive offset wells near the well that is being stimulated (i.e., well communication) or abandoned or active mines.
- Fractures intersecting geologic features that can act as pathways for fluid migration, such as existing permeable faults and fractures.

This chapter describes the conditions that can contribute to or cause the development of the pathways listed above, the evidence for the existence of these pathways, examples of impacts on the quality of drinking water resources associated with these pathways that have been documented in the literature, and the factors that can affect the frequency or severity of those impacts. (See Chapter 10 for a discussion of factors and practices that can reduce the frequency or severity of impacts to drinking water quality.)

The interplay between the well and the subsurface features is complex and not directly observable; therefore, sometimes it is not possible to identify what specific element is contributing to or is the primary cause of an impact on drinking water resources. For example, concerns have been raised regarding stray gas detected in groundwater in natural gas production areas (for additional information about stray gas, see Sections 6.2.2 and 6.3.2.4).[1] Stray gas migration is a technically complex phenomenon, because there are many potential naturally occurring or artificially created routes for migration of gas into aquifers, including along production wells and via naturally existing or induced fractures. It is also challenging to determine the source of the natural gas and whether the mobilization is related to oil or gas production activities.

Furthermore, identifying cases where contamination of drinking water resources occurs due to oil and gas production activities—including hydraulic fracturing operations—requires extensive amounts of site and operational data, collected before and after hydraulic fracturing operations. (See Section 6.4 for additional information on data limitations.) Where such data do exist and provide evidence of contamination, we present it in the following sections. We do not attempt to predict which of these pathways is most likely to occur or to lead to a drinking water impact, or the magnitude of an impact that might occur as a result of migration via any single pathway, unless the information is available and documented based on collected data. However, a qualitative assessment of the factors that can affect the frequency or severity of impacts on drinking water quality associated with the well injection stage is possible; see Section 6.4.

## 6.2 Fluid Migration Pathways Within and Along the Production Well

In this section, we discuss pathways for fluid movement along or through the production well used in the hydraulic fracturing operation. While these pathways can form during other times within the life of an oil and gas well, the repeated high pressure stresses exerted during hydraulic fracturing operations can make maintaining the mechanical integrity of the well more difficult (Council of Canadian Academies, 2014).[2] Section 6.2.1 presents the purpose of the various well components and typical well construction configurations. Section 6.2.2 describes the pathways for fluid movement that can potentially develop within the production well and wellbore and the conditions that lead to pathway development, either as a result of the original design of the well, degradation over time or use, or hydraulic fracturing operations.

While we discuss casing and cement separately, it is important to note that these are related—inadequacies in one of these components can lead to stresses on the other. For example, flaws in cement may expose the casing to corrosive fluids. Furthermore, casing and cement work together in the subsurface to form a barrier to fluid movement, and it may not be possible to distinguish whether mechanical integrity problems are related to the casing, the cement, or both. For additional information on well design and construction, see Appendix D.

### 6.2.1 Overview of Well Construction

Production wells are constructed to transport hydrocarbon resources from the reservoirs in which they are found to the surface. They are also used to isolate fluid-bearing zones (containing oil, gas,

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[1] Stray gas refers to the phenomenon of natural gas (primarily methane) migrating into shallow drinking water resources or to the surface.

[2] Mechanical integrity of a well refers to the absence of significant leakage within the injection tubing, casing, or packer (referred to as internal mechanical integrity) or outside of the casing (referred to as external mechanical integrity).

or fresh water) from each other. Multiple barriers (i.e., casing and cement) are often present, and they act together to prevent both horizontal fluid movement (in or out of the well) and vertical fluid movement (along the wellbore from deeper oil- or gas-bearing formations to drinking water resources). Proper design and construction of the casing, cement, and other well components in the context of the location of drinking water resources and maintaining mechanical integrity throughout the life of a well are necessary to prevent migration of hydraulic fracturing fluids and formation fluids into drinking water resources.

A well is a multiple-component system that typically includes casing, cement, and a completion assembly, and it may be drilled vertically, horizontally, or in a deviated orientation (Figure 6-1).[1,2] These components work together to prevent unintended fluid movement into, out of, or along the well. Due to the presence of multiple barriers within the well and the geologic system in which it is placed, the existence of a pathway for fluid movement through a component of this system does not necessarily mean that an impact on a drinking water resource has occurred or will occur.

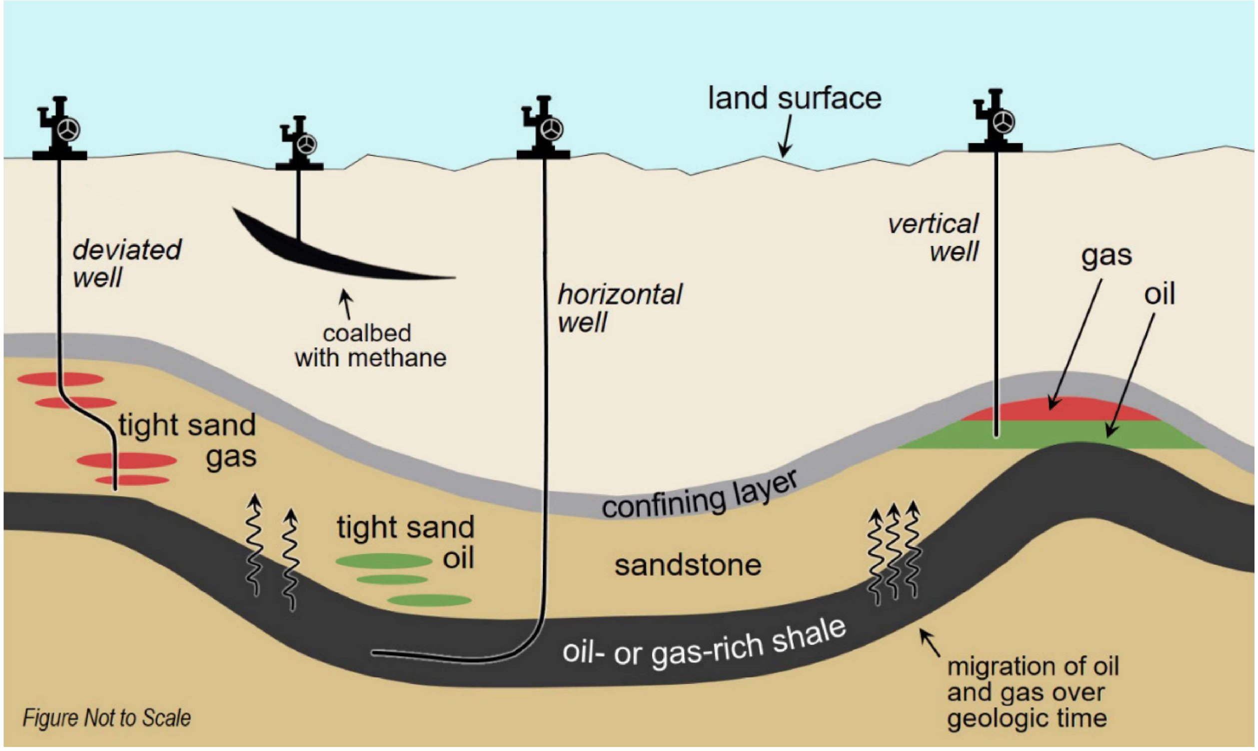

**Figure 6-1. Schematic cross-section of general types of oil and gas resources and the orientations of production wells used in hydraulic fracturing.**

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[1] Completion is a term used to describe the assembly of equipment at the bottom of the well that is needed to enable production from an oil or gas well. It can also refer to the activities and methods (including hydraulic fracturing) used to prepare a well for production following drilling.

[2] For the purposes of this assessment, a well's orientation refers to its inclination from verticality. Wells drilled straight downward are considered to be vertical, wells drilled directionally to end up parallel to the production zone's bedding plane are considered horizontal, and directionally drilled wells that are neither vertical nor horizontal are referred to as deviated. In industry usage, a well's orientation commonly refers both to its inclination from vertical and the azimuthal (compass) direction of a directionally drilled wellbores.

Casing primarily acts as a barrier to lateral movement of fluids, and cement primarily acts as a barrier to unintended vertical movement of fluids. Together, casing and cement are important in preventing fluid movement into drinking water resources, and are the focus of this section. Figure 6-2 illustrates the configurations and types of casing and cement and other features that may occur in oil and gas production wells. The figure depicts an idealized representation of the components of a production well; it is important to note that there is a wide variety in the design of hydraulically fractured oil and gas wells in the United States (U.S. EPA, 2015n), and the descriptions in the figure or in this chapter do not represent every possible well design.

#### 6.2.1.1 Casing

Casing is steel pipe that is placed into the drilled wellbore to maintain the stability of the wellbore, to transport the hydrocarbons from the subsurface to the surface, and to prevent intrusion of other fluids into the well and wellbore (Hyne, 2012; Renpu, 2011). A long continuous section of casing is referred to as a casing string, which is composed of individual lengths of casing (known as casing joints) that are threaded together using casing collars. In different sections of the well, multiple concentric casing strings of different diameters can be used, depending on the construction of the well.

The presence of multiple layers of casing strings can isolate and protect geologic zones containing drinking water. In addition to conductor casing, which prevents the hole from collapsing during drilling, one to three other types of casing may be also present in a well. The types of casing include (from largest to smallest diameter) surface casing, intermediate casing, and production casing (GWPC, 2014; Hyne, 2012; Renpu, 2011). One or more of any of these types of casing (but not necessarily all of them) may be present in a well. Surface casing often extends from the wellhead down to the base (i.e., the bottom or lowest part) of the drinking water resource to be protected. Wells also may be constructed with production liners, which are anchored or suspended from inside the bottom of the previous casing string. Production liners serve the same purpose as production casing but extend only to the end of the previous casing, rather than all the way to the surface. Wells may also have production tubing, which is used to transport the hydrocarbons to the surface. Tie-back liners may be used to extend a production liner to the surface when downhole pressure or corrosive conditions warrant additional protection of the intermediate or production casing.

Among the wells represented by the Well File Review (described in Text Box 6-1), between one and four casing strings were present (the Well File Review did not evaluate conductor casings). A combination of surface and production casings was most often reported, followed by a combination of surface, intermediate, and production strings. All of the production wells used in hydraulic fracturing operations in the Well File Review had surface casing, while approximately 39% of the wells (an estimated 9,100 wells) had intermediate casing, and 94% (an estimated 21,900 wells) had production casing (U.S. EPA, 2015n).[1, 2]

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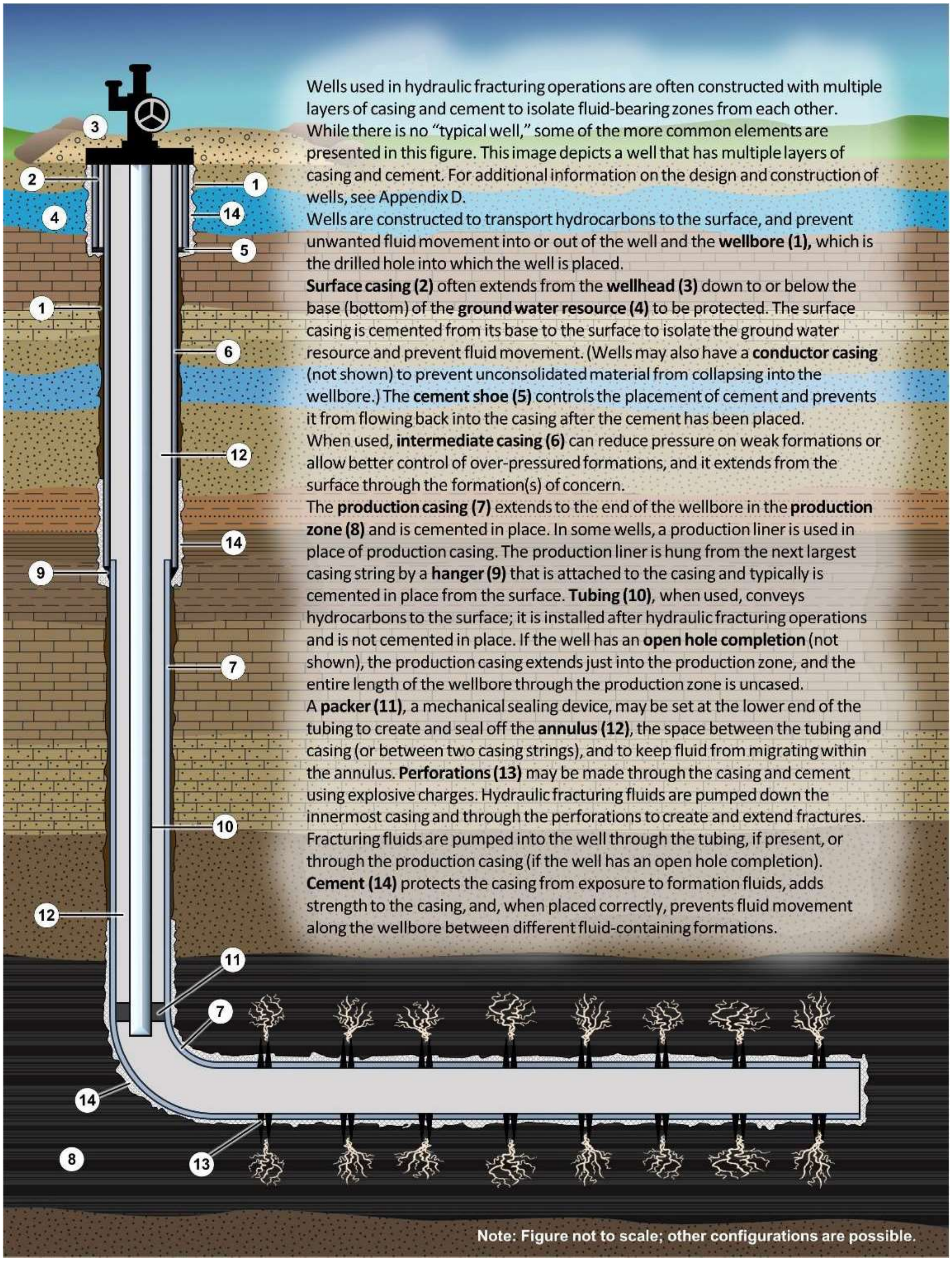
[1] 9,100 wells (95% confidence interval: 2,900 – 15,400 wells).

[2] 21,900 wells (95% confidence interval: 19,200 – 24,600 wells).



Wells used in hydraulic fracturing operations are often constructed with multiple layers of casing and cement to isolate fluid-bearing zones from each other. While there is no "typical well," some of the more common elements are presented in this figure. This image depicts a well that has multiple layers of casing and cement. For additional information on the design and construction of wells, see Appendix D.

Wells are constructed to transport hydrocarbons to the surface, and prevent unwanted fluid movement into or out of the well and the **wellbore (1),** which is the drilled hole into which the well is placed.

**Surface casing (2)** often extends from the **wellhead (3)** down to or below the base (bottom) of the **ground water resource (4)** to be protected. The surface casing is cemented from its base to the surface to isolate the ground water resource and prevent fluid movement. (Wells may also have a **conductor casing** (not shown) to prevent unconsolidated material from collapsing into the wellbore.) The **cement shoe (5)** controls the placement of cement and prevents it from flowing back into the casing after the cement has been placed.

When used, **intermediate casing (6)** can reduce pressure on weak formations or allow better control of over-pressured formations, and it extends from the surface through the formation(s) of concern.

The **production casing (7)** extends to the end of the wellbore in the **production zone (8)** and is cemented in place. In some wells, a production liner is used in place of production casing. The production liner is hung from the next largest casing string by a **hanger (9)** that is attached to the casing and typically is cemented in place from the surface. **Tubing (10)**, when used, conveys hydrocarbons to the surface; it is installed after hydraulic fracturing operations and is not cemented in place. If the well has an **open hole completion** (not shown), the production casing extends just into the production zone, and the entire length of the wellbore through the production zone is uncased.

A **packer (11)**, a mechanical sealing device, may be set at the lower end of the tubing to create and seal off the **annulus (12)**, the space between the tubing and casing (or between two casing strings), and to keep fluid from migrating within the annulus. **Perforations (13)** may be made through the casing and cement using explosive charges. Hydraulic fracturing fluids are pumped down the innermost casing and through the perforations to create and extend fractures. Fracturing fluids are pumped into the well through the tubing, if present, or through the production casing (if the well has an open hole completion).

**Cement (14)** protects the casing from exposure to formation fluids, adds strength to the casing, and, when placed correctly, prevents fluid movement along the wellbore between different fluid-containing formations.

Note: Figure not to scale; other configurations are possible.

**Figure 6-2. Overview of well construction.**

Hydraulic fracturing operations impose a variety of stresses on the well components. In order to prevent the formation of pathways to drinking water resources, the casing should be designed with sufficient strength to withstand the stresses it will encounter during the installation, cementing, hydraulic fracturing, production, and post-production phases of the life of the well. These stresses, illustrated in Figure 6-3, include burst pressure (the interior pipe pressure that will cause the casing to burst), collapse pressure (the pressure applied to the outside of the casing that will cause it to collapse), tensile stress (the stress related to stretching exerted by the weight of the casing or tubing being raised or lowered in the hole), compression and bending (the stresses that result from pushing along the axis of the casing or bending the casing), and cyclic stress (the stress caused by frequent or rapid changes in temperature or pressure). While the injection stage represents a relatively brief portion of the life of a hydraulic fracturing well (Section 3.3), injection imposes the highest stresses the well is likely to encounter.

### Text Box 6-1. The Well File Review.

The EPA conducted a survey of onshore oil and gas production wells that were hydraulically fractured by nine oil and gas service companies in the continental United States between approximately September 2009 and September 2010. This effort, known as the "Well File Review," produced two reports. The first report, *Review of Well Operator Files for Hydraulically Fractured Oil and Gas Production Wells: Well Design and Construction* (U.S. EPA, 2015n) describes well design and construction characteristics and their relationships to the location of operator-reported drinking water resources and the number and relative location of constructed barriers (i.e., casing and cement) that can block pathways for potential subsurface fluid movement. A second report, *Review of Well Operator Files for Hydraulically Fractured Oil and Gas Production Wells: Hydraulic Fracturing Operations* (U.S. EPA, 2016c) presents information on hydraulic fracturing job characteristics and the reported use of casing pressure tests, annular pressure monitoring, surface treating pressure monitoring, and microseismic monitoring conducted before or during hydraulic fracturing operations; it also explores the roles of well mechanical integrity and induced fracture growth as they relate to the potential for subsurface fluid movement to intersect protected groundwater resources.

The survey was based on a sample of 323 hydraulically fractured oil and gas production wells. Results of the research are presented as rounded estimates of the frequency of occurrence of hydraulically fractured production well design, construction, and operational characteristics with 95% confidence intervals (CIs). The results are statistically representative of an estimated 23,200 onshore oil and gas production wells hydraulically fractured in 2009 and 2010 by nine service companies where an estimated 28,500 hydraulic fracturing jobs were performed.

In addition, the casing must be resistant to corrosion from contact with the formations and any fluids that might be transported through the casing, including hydraulic fracturing fluids, brines, and oil or gas. Casing strength or corrosion resistance can be increased by using fiberglass or high-strength alloys or by increasing the thickness of the casing.

One way to ensure that the strength of the casing is sufficient to withstand the stresses imposed by hydraulic fracturing operations is to pressure test the casing. The casing can be pressurized to the pressure anticipated during hydraulic fracturing operations and shut-in periods; if the well can hold the pressure, it is considered to be leak-free and therefore should be able to withstand the pressures of hydraulic fracturing. However, if the test pressure is less than the hydraulic fracturing pressure, the casing is determined to be leak-free, but its suitability to resist the stresses associated with the planned fracturing operation is less certain.

The Well File Review (U.S. EPA, 2016c) found that pressure tests were performed prior to an estimated 15,600 of 28,500 hydraulic fracturing jobs the EPA studied, including cases where a frac string was pressure tested.[1] In 52% of those pressure tests performed (representing 28% of the hydraulic fracturing jobs studied), the well was tested to a pressure equal to or greater than the maximum pressure that occurred during the hydraulic fracturing job (U.S. EPA, 2016c).[2] Thus, in a significant number of hydraulic fracturing jobs (i.e., 72% of the wells studied), there are no data in the well files to indicate that the casing was tested in a manner that could ensure the adequacy of the casing to withstand the pressures of hydraulic fracturing. While, in some cases, casing may not have been pressure tested because a frac string was to be installed to protect the casing from the increased pressure, only 10% of fracturing jobs were conducted using a frac string.

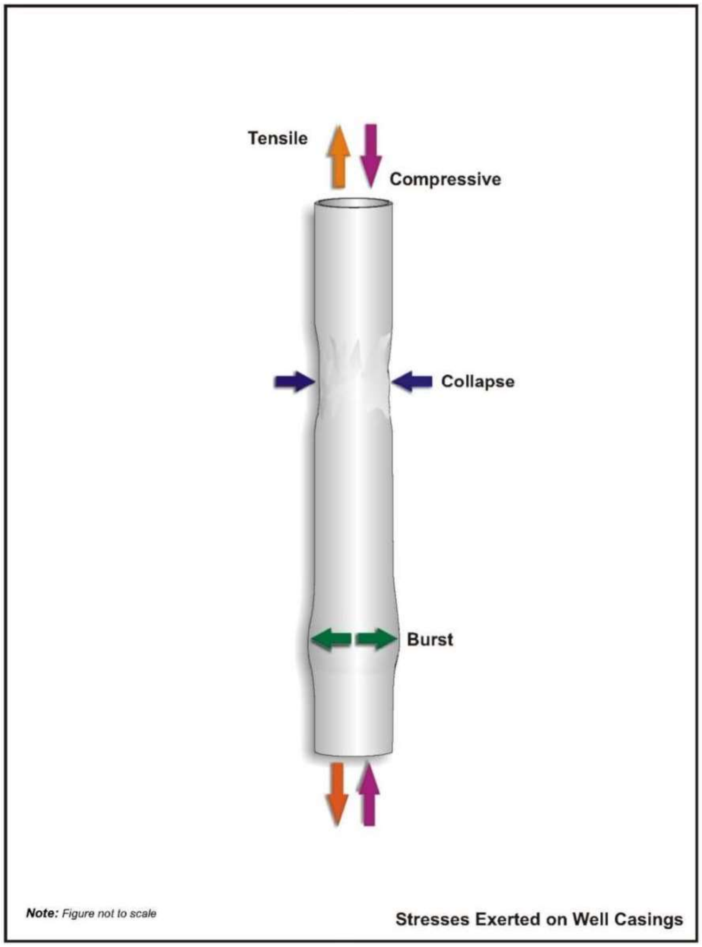


**Figure 6-3. The various stresses to which the casing will be exposed.**

In addition to the stresses illustrated, the casing will be subjected to bending and cyclic stresses. Source: U.S. EPA (2012d).

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[1] 15,600 jobs (95% confidence interval: 11,800 – 19,300 jobs).

[2] 52% of pressure tests (95% confidence interval: 20 – 82% of tests).

#### 6.2.1.2 Cement

Cement is one of the most important components of a well for providing zonal isolation and reducing impacts on drinking water. Cement in the space between the casing and formation isolates fluid-containing formations from each other, protects the casing from exposure to formation fluids, and provides additional strength to the casing. The strength of the cement and its compatibility with the formation and fluids encountered are important for maintaining mechanical integrity throughout the life of the well.

A variety of methods are available for placing the cement, evaluating the adequacy of the cementing process and the resulting cement job, and repairing any identified deficiencies. Cement is most commonly emplaced by pumping the cement down the inside of the casing to the bottom of the wellbore and then up the space between the outside of the casing and the formation (or the next largest casing string). This method is referred to as the primary cement job and can be performed as a continuous event in a single stage (i.e., "continuous cementing") or in multiple stages (i.e., "staged cementing"). Staged cementing may be used when, for example, the estimated weight and pressure associated with standard cement placement could damage weak zones in the formation (Crook, 2008).

Deficiencies in the cementing process can result from poorly centered casing, poor removal of drilling mud behind the casing, cement shrinkage, premature gelation, excessive fluid loss, improper mixing, or lost cement.[1, 2] Cement deficiencies can be reduced by proper design of the cementing process including use of casing centralizers, proper design of the cement, proper mud removal, and use of cement additives (Kirksey, 2013).[3] If any deficiencies or defects in the primary cement job are identified, remedial cementing may be performed. See Text Box 6-2 for an example of an incident where cementing issues were studied as part of an evaluation of drinking water well impacts.

**Text Box 6-2. Dimock, Pennsylvania.**

In 2009, shortly after drilling and hydraulic fracturing in the Marcellus Shale commenced in the area, residents near the township of Dimock, Pennsylvania reported that natural gas was appearing or increasing in their water wells (Hammond, 2016; PA DEP, 2009a).

Water wells in the area largely draw from the Catskill Formation and range in depth from less than 50 ft (15 m) to more than 500 ft (150 m) (Molofsky et al., 2013). In this area, the Marcellus Shale is about 7,000 ft (2,000 m) below the surface and its natural gas is extracted through vertical and horizontal wells (Hammond, 2016). Methane exists naturally in the subsurface in this part of Pennsylvania, including in the Catskill Formation and the geologic formations below it (Baldassare et al., 2014; Molofsky et al., 2013; Molofsky et al., 2011).

*(Text Box 6-2 is continued on the following page.)*

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[1] Gelation is the process in the setting of the cement where it begins to solidify and lose its ability to transmit pressure to the formation.

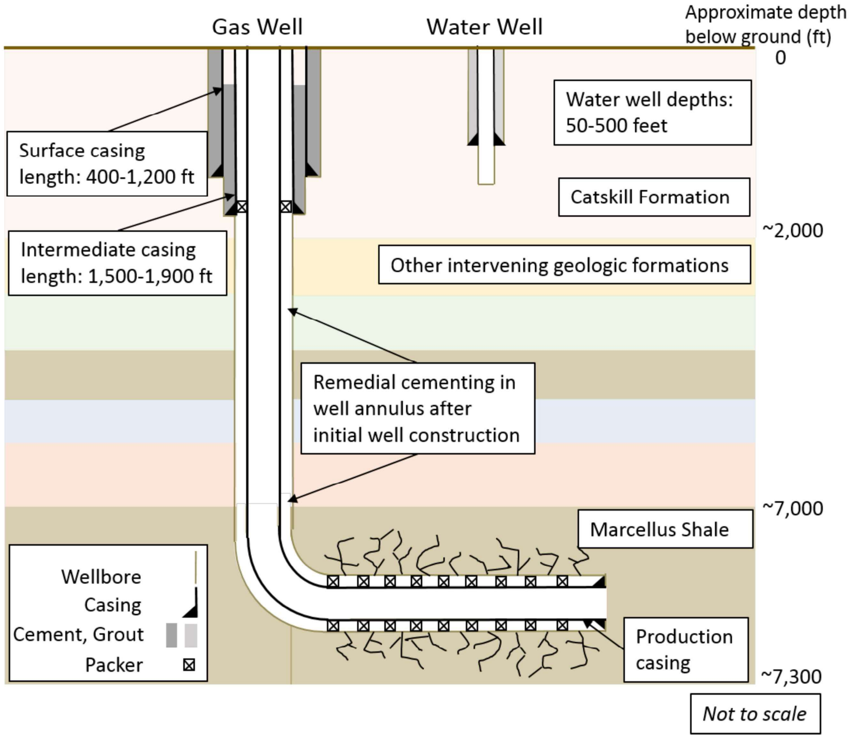
[2] Lost cement refers to a failure of the cement or the spacer fluid used to wash the drilling fluid out of the wellbore to be circulated back to the surface, indicating that the cement has escaped into the formation.

[3] Centralizers are used to keep the casing in the center of the hole and allow an even cement job.

## Text Box 6-2 (continued). Dimock, Pennsylvania.

The Pennsylvania Department of Environmental Protection (PA DEP) investigated and made a determination that 18 water wells located within a 9 mi$^2$ (23 km$^2$) area had been negatively affected as a result of natural gas extraction activities. For approximately two years, during which there was a partial ban on gas well drilling and hydraulic fracturing in the vicinity, the gas company plugged four gas wells and undertook remedial construction actions at 18 additional gas wells (including remedial cementing at several wells, adding as much as 6,300 ft (1,900 m) of cement behind the production casings) (PA DEP, 2010b, d, 2009a).

The figure below presents a simplified geologic representation of water wells and one type of horizontal gas well completed within the geologic formations in the area. The location of remedial cementing performed in some gas wells is indicated.



Several studies in this and surrounding areas have focused on the geochemistry of the groundwater, in particular on gas composition, and noble and natural gas isotopes in the water. Results are consistent with an accumulation of stray gas originating from greater depth and moving to the Catskill Formation (Jackson et al., 2013c; Molofsky et al., 2013; Molofsky et al., 2011). However, the identity of the geologic formation(s) sourcing the natural gas is not always certain and may be consistent with sourcing from either the Marcellus (as suggested by Jackson et al. (2013c)), or the intervening geologic formations (Molofsky et al., 2013).

The role of hydraulic fracturing in the migration of gas to the Catskill Formation, and the specific pathways by which this migration occurred, is even less certain. Some investigators suspect that the initial gas well construction allowed natural gases from deeper formations to move upward along uncemented wellbores (Hammond, 2016; PA DEP, 2010b, d, 2009a). However, no publicly available information exists to document whether hydraulic fracturing may have aided fluid movement along wellbores to enter drinking water resources from greater depths. Reviews of information, such as hydraulic fracturing job reports showing the intervals hydraulically fractured, injection rates, and pressure monitoring, would support an evaluation of whether hydraulic fracturing might have played a role in the migration of natural gas to drinking water wells in the area.

Among the wells represented in the Well File Review, over 90% of cemented casings were cemented using primary cementing methods. Secondary or remedial cementing was used on an estimated 8% of casings (most often on surface and production casings and less often on intermediate casings).[1] The remedial cementing techniques employed in these wells included cement squeezes, cement baskets, and pumping cement down the annulus (U.S. EPA, 2015n). See Appendix D for more information on remedial cementing techniques.

The cement does not always need to be continuous along the entire length of the well to protect drinking water resources; rather, protection of drinking water resources depends on a good cement seal across the appropriate subsurface zones, including all fresh water- and hydrocarbon-bearing zones. One study of wells in the Gulf of Mexico found that, if at least 50 ft (15 m) of high quality cement was present, pressure differentials as high as 14,000 psi (97 MPa) would not lead to breakdown in isolation between geologic zones (King and King, 2013).

Most wells have cement behind the surface casing, which is a key barrier to contamination of drinking water resources. The surface casings in nearly all of the wells used in hydraulic fracturing operations represented in the Well File Review (93% of the wells, or an estimated 21,500 wells) were fully cemented.[2,3] None of the wells studied in the Well File Review had completely uncemented surface casings.

The length and location of cement behind intermediate and production casings can vary based on the presence and locations of over-pressured formations, formations containing fluids, or geologically weak formations (i.e., those that are prone to structural failure when exposed to changes in subsurface stresses). State regulations and economics also play a role.

In the Well File Review, the intermediate casings of most of the wells studied were fully cemented, although there were relatively wide 95% confidence intervals in the results. Among production casings, about half were partially cemented, about a third were fully cemented, and the remainder were either uncemented or their cementing status was undetermined. Among the approximately 9,100 wells represented in the Well File Review that are estimated to have intermediate casing, the intermediate casing was fully cemented in an estimated approximately 7,300 wells (80%) and partially cemented in an estimated 1,700 wells (19%).[4,5] Production casings were partially cemented in 47% of the wells, or approximately 10,900 wells (U.S. EPA, 2015n).[6]

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[1] 8% of casings (95% confidence interval: 3% – 14% of casings).

[2] The Well File Review defined fully cemented casings as casings that had a continuous cement sheath from the bottom of the casing to at least the next larger and overlying casing (or the ground surface, if surface casing). Partially cemented casings were defined as casings that had some portion of the casing that was cemented from the bottom of the casing to at least the next larger and overlying casing (or ground surface), but were not fully cemented. Casings with no cement anywhere along the casing, from the bottom of the casing to at least the next larger and overlying casing (or ground surface), were defined as uncemented.

[3] 21,500 wells (95% confidence interval: 19,500 – 23,600 wells).

[4] 9,100 wells (95% confidence interval: 2,900 – 15,400 wells).

[5] 7,300 wells (95% confidence interval: 600 – 13,900 wells).

[6] 10,900 wells (95% confidence interval: 6,900 – 14,900 wells).

The Well File Review also estimated the number of wells with a continuous cement sheath along the outside of the well. An estimated 6,800 of the wells represented in the study (29%) had cement from the bottom of the well to the ground surface, and approximately 15,300 wells (66%) had one or more uncemented intervals between the bottom of the well and the surface.[1,2] In the remaining wells, the location of the top of the cement was uncertain, so no determination could be made regarding whether the well had a continuous cement sheath along the outside of the well (U.S. EPA, 2015n).

A variety of logs are available to evaluate the quality of cement behind the well casing. Among wells in the Well File Review, the most common type of cement evaluation log run was a standard acoustic cement bond log (U.S. EPA, 2015n). Standard acoustic cement bond logs are used to evaluate both the extent of the cement placed along the casing and the cement bond between the cement, casing, and wellbore. Cement bond indices calculated from standard acoustic cement bond logs on the wells in the Well File Review showed a median bond index of 0.7 just above the hydraulic fracturing zone; this value decreased to 0.4 over a measured distance of 5,000 ft (2,000 m) above the hydraulic fracturing zone (U.S. EPA, 2015n).[3] While standard acoustic cement bond logs can give an average estimate of bonding, they cannot alone indicate zonal isolation, because they may not be properly run or calibrated (Boyd et al., 2006; Smolen, 2006). One study of 28 wells found that cement bond logs failed to predict communication between formations 11% of the time (Boyd et al., 2006). In addition, they cannot discriminate between full circumferential cement coverage by weaker cement and lack of circumferential coverage by stronger cement (King and King, 2013; Smolen, 2006). A few studies have compared cement bond indices to zonal isolation, with varying results. For example, Brown et al. (1970) showed that among 16 South American wells with varying casing size and cement bond indices, a cemented 5.5 in (14 cm) diameter casing with a bond index of 0.8 along as little as 5 ft (1.5 m) can act as an effective seal. The authors also suggest that an effective seal in wells having calculated bond indices differing from 0.8 are expected to have an inverse relationship between bond index and requisite length of the cemented interval, with longer lengths needed along casing having a lower bond index. Another study recommends that wells undergoing hydraulic fracturing should have a given cement bond over an interval three times the length that would otherwise be considered adequate for zonal isolation (Fitzgerald et al., 1985). Conversely, King and King (2013) concluded field tests from wells studied by Flournoy and Feaster (1963) had effective isolation when the cement bond index ranged from 0.31 to 0.75.

External mechanical integrity tests (MITs), including temperature logs, noise logs, and radioactive tracer logs, are another means to evaluate the zonal isolation performance of well cement. Instead of measuring the apparent quality of the cement, external MITs measure whether there is evidence of fluid movement along the wellbore (and potentially to a drinking water resource). An external MIT conducted before the hydraulic fracturing job can allow detection of channels in the cement that could allow injected fluids to move out of the production zone. An external MIT performed

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[1] 6,800 wells (95% confidence interval: 1,600 – 11,900 wells).

[2] 15,300 wells (95% confidence interval: 10,500 – 20,100 wells).

[3] Cement bond logs are used to calculate a bond index, which varies between 0 and 1, with 1 representing the strongest bond and 0 representing the weakest bond.

after hydraulic fracturing operations can detect any fluid movement resulting from cement damage caused by the hydraulic fracturing job. It is important to note that, if a well fails an MIT, this does not mean there is a failure of the well or that drinking water resources are impacted. An MIT failure is a warning that something needs to be addressed, and a loss of mechanical integrity is an event that can result in fluid movement from the well if remediation is not performed. More details on MITs are available in Appendix D.

Monitoring the treatment pressure of the hydraulic fracturing operation can also detect problems occurring during fracturing. Sudden changes in pressure during hydraulic fracturing operations can be indicative of failures in the cement or casing. This type of monitoring is performed in nearly all hydraulic fracturing jobs: the Well File Review (U.S. EPA, 2016c) found that the treatment pressure was monitored in 97% (or 27,700) of all hydraulic fracturing jobs studied.[1]

#### 6.2.1.3 Well Orientation

A well can be drilled and constructed with any of several different orientations: vertical, horizontal, and deviated. The well's orientation can be important, because it affects the difficulty of drilling, constructing, and cementing the well. In particular, as described in Section 6.2.2, constructing and cementing horizontal wells present unique challenges (Sabins, 1990). In a vertical well, the wellbore is vertical throughout its entire length, from the wellhead at the surface to the production zone. Deviated wells are usually drilled vertically in the shallowest part of the well but are then drilled directionally, deviating from the vertical direction at some point such that the bottom of the well is at a significant lateral distance away from the point in the subsurface directly under the wellhead. In a horizontal well, the well is drilled vertically to a point known as the kickoff point, where the well turns toward the horizontal, extending into and parallel with the approximately horizontal targeted producing formation (Figure 6-2).

Among wells evaluated in the Well File Review, about 65% were vertical, 11% were horizontal, and 24% were deviated wells (U.S. EPA, 2015n).[2] This is generally consistent with information available in industry databases—of the approximately 16,000 oil and gas wells used in hydraulic fracturing operations in 2009 (one of the years for which the data for the Well File Review were collected), 39% were vertical, 33% were horizontal, and 28% were either deviated or the orientation was unknown (DrillingInfo, 2014b). See Section 3.3 for additional information on the use of horizontal wells in the United States.

#### 6.2.1.4 Well Completion

Another important aspect of well construction is the way in which the well is completed into the production zone, because the well's completion is part of the system of barriers and must be intact for the well to operate properly. A variety of completion configurations are available. The most common configuration is for casing to extend to the end of the wellbore and be cemented in place (U.S. EPA, 2015n; George et al., 2011; Renpu, 2011). In these cased and cemented completions, the

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[1] 27,700 jobs (95% confidence interval: 24,800 – 30,600 jobs).

[2] The Well File Review considered any non-horizontal well in which the well bottom was located more than 500 ft (152 m) laterally from the wellhead as being deviated.

cement provides the primary containment of fluids to the production zone. Before hydraulic fracturing begins, perforations are made through the casing and cement into the production zone. It is through the perforated casing and cement that hydraulic fracturing is conducted. In some cases, a smaller temporary casing, known as a temporary frac string, is inserted inside the production casing to protect the casing from the high pressures imposed during hydraulic fracturing operations.

A different type of a cased completion uses production casing set on formation packers, where the production casing extends through the production zone and the length of the casing extending through the drilled horizontal wellbore is left uncemented, but has a series of formation packers that swell to seal the annulus between the casing and the formation.[1] With these completions, the production zone is fractured in separate stages through ports that open between the formation packers. When formation packers are used, they provide the primary isolation of hydraulic fracturing fluids during hydraulic fracturing.

Another type of completion is an open hole completion. When open hole completions are used, the entire production zone is fractured all at once in a single stage or may be fractured in separate stages using a temporary frac string set on one or more temporary formation packers that are positioned to a different interval for each stage. If a temporary frac string is used in an open hole completion, its packer(s) provide the primary isolation of hydraulic fracturing fluids during hydraulic fracturing and if no temporary frac string is used, then the next higher casing in the well provides the primary isolation of hydraulic fracturing fluids during the treatment.

Among wells represented in the Well File Review, an estimated 6% of wells (1,500 wells) had open hole completions, 6% of wells (1,500 wells) used formation packers, and the rest were cased and cemented (U.S. EPA, 2015n).[2,3]

In some cases, wells may be re-completed after the initial construction, with re-fracturing if production has decreased (Vincent, 2011). Re-completion also may include additional perforations in the well at a different interval to produce from a new formation, lengthening the wellbore, or drilling new laterals from an existing wellbore. In 95% of the re-completions represented in the Well File Review, hydraulic fracturing occurred at shallower depths than the previous job (U.S. EPA, 2016c).[4]

### 6.2.2 Factors that can Affect Fluid Movement to Drinking Water Resources

The following sections describe the pathways for fluid movement that can develop within the production well and wellbore. We also describe the conditions leading to the development of fluid movement pathways and, where available, evidence that a pathway has allowed fluid movement to

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[1] A formation packer is a specialized casing part that has the same inner diameter as the casing but whose outer diameter expands to make contact with the formation and seal the annulus between the uncemented casing and formation, preventing migration of fluids.

[2] 1,500 wells with open hole completions (95% confidence interval: 10 – 4,800 wells).

[3] 1,500 wells using formation packers (95% confidence interval: 1,400 – 1,600 wells).

[4] 95% of jobs (95% confidence interval: 75 – 99% of jobs).

occur within the casing or cement, and—in the case of sustained casing pressure (Section 6.2.2.4)—a combination of factors within the casing and cement. (See Figure 6-4 for an illustration of potential fluid movement pathways related to casing and cement.)

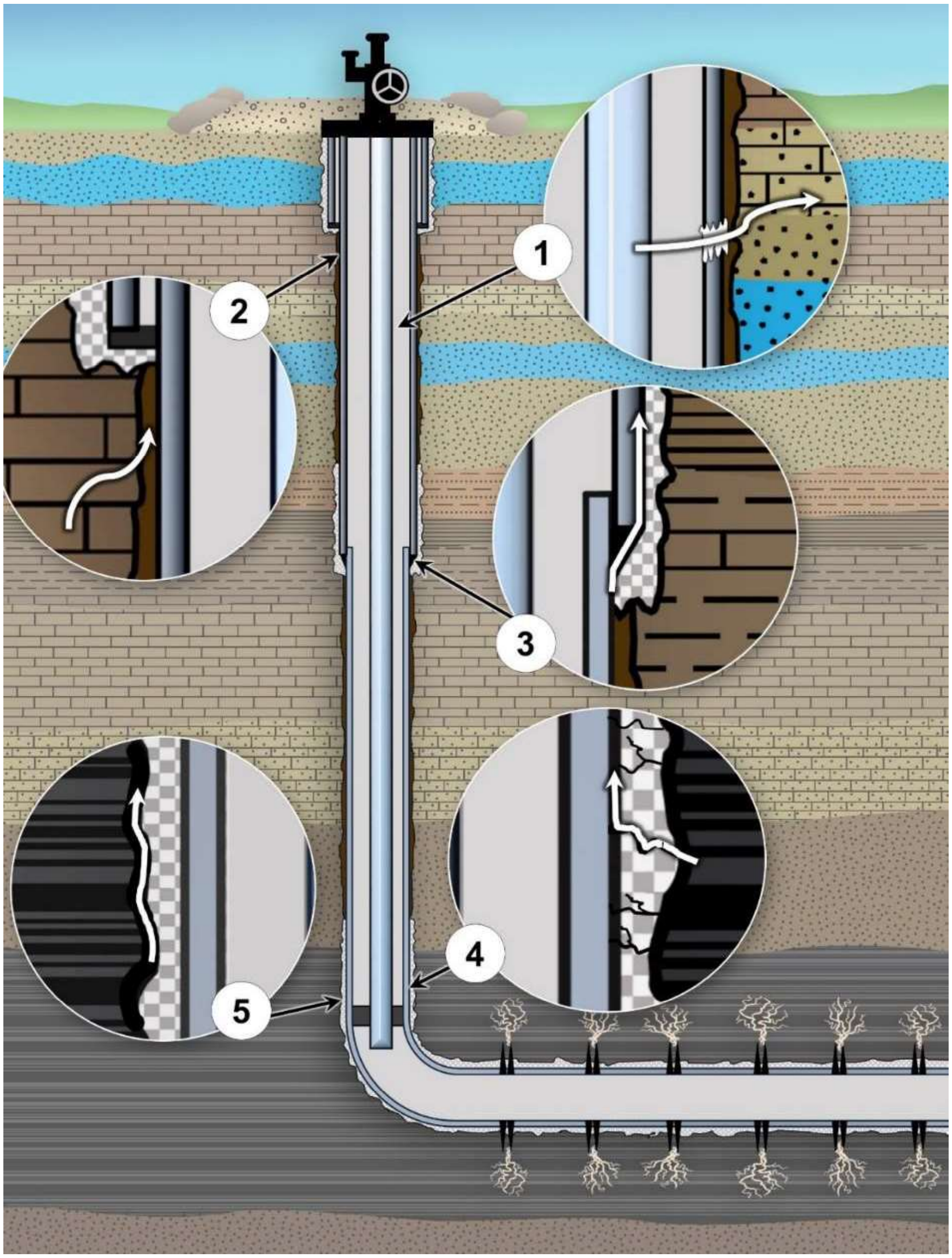

**Figure 6-4. Potential pathways for fluid movement in a cemented wellbore.**

These pathways (represented by the white arrows) include: (1) casing and tubing leak into a permeable formation, (2) migration along an uncemented annulus, (3) migration along microannuli between the casing and cement, (4) migration through poor cement, and (5) migration along microannuli between the cement and formation. Note: the figure is not to scale and is intended to provide a conceptual illustration of pathways that may develop within the well.

We describe information regarding the rate at which these pathways have been identified in hydraulic fracturing wells when it is available. Where such information does not exist, we present the results of research on oil and gas production wells in general or on injection wells, including those used for the geologic sequestration of carbon dioxide.[1] Publicly accessible information is insufficient to determine whether wells intended for hydraulic fracturing are constructed differently from production wells where no fracturing is conducted. See Chapter 10 for additional discussion of data gaps. It is not generally possible, based on the literature reviewed for this assessment, to determine the precise degree to which hydraulic fracturing created, or moved fluids along, the pathways described or whether all of the wells studied were hydraulically fractured. Nor is it generally possible to estimate the degree to which wells that were hydraulically fractured have a significantly different number of redundant barriers to protect drinking water resources than other production wells. However, given the applicability of well construction technology to address the subsurface conditions encountered in hydraulic fracturing operations and production or injection operations in general, the information presented here is considered relevant to the assessment.

#### 6.2.2.1 Pathways Related to Well Casing

High pressures associated with hydraulic fracturing operations can damage casing and lead to fluid movement that can impact drinking water quality. As noted above, the casing string through which hydraulic fracturing fluids are injected is subject to higher internal pressures during hydraulic fracturing operations than during other phases in the life of a production well. To withstand the stresses created by the high pressure of hydraulic fracturing, the well and its components must have adequate strength and elasticity. If the casing is compromised or is otherwise not strong enough to withstand these stresses (Figure 6-3), a casing failure can result. If undetected or not repaired, casing failures can serve as pathways for hydraulic fracturing fluids to leak out of the casing. Below we present data or information suggesting that pathways along the casing are present or allowing fluid movement. See Chapter 10 for more information on factors that can increase or decrease the frequency or severity of impacts to drinking water quality associated with well construction.

Hydraulic fracturing fluids or fluids present within the well casing could flow into other zones in the subsurface if there is a leak in the casing, and cement is inadequate or not present. As described below, pathways for fluid movement associated with well casing can be related to the original design or construction of the well, degradation of the casing over time, or problems that can arise through extended use as the casing succumbs to stresses.

Casing failure can also occur if the wellbore passes through a structurally weak geologic zone that shears and deforms the well casing. Such shearing is common when drilling through zones containing salt (Renpu, 2011). The changes in the pressure field in the portions of the formation near the wellbore during hydraulic fracturing can also cause mechanically weak formations to shear, potentially damaging the well's casing or cement. Palmer et al. (2005) demonstrated through modeling that hydraulic fracturing within coal that had a low unconfined compressive strength

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[1] An injection well is a well into which fluids are being injected (40 Code of Federal Regulations (CFR) 144.3).

could cause shear failure of the coalbeds surrounding the wellbore. Shearing of the coalbed layers can cause the casing to deform and potentially fail.

Corrosion in uncemented zones is the most common cause of casing failure. This can occur if uncemented sections of the casing are exposed to corrosive substances such as brine or hydrogen sulfide (Renpu, 2011). Corrosion commonly occurs at the collars that connect sections of casing or where equipment is attached to the casing. Corrosion at collars can exacerbate problems with loose or poorly designed connections, which are another common cause of casing leaks (Agbalagba et al., 2013; Brufatto et al., 2003). Watson and Bachu (2009) found that 66% of all casing corrosion occurred in uncemented well sections, as shown in Pathway 1 of Figure 6-4.

As noted above, the casing and cement work together to strengthen the well and provide zonal isolation. Uncemented casing does not necessarily lead to fluid migration. However, migration can occur if the casing in an uncemented zone fails during hydraulic fracturing operations.

Other mechanical integrity problems have been found to vary with the well environment, particularly environments with high pressures and temperatures. Wells in high pressure/high temperature environments, wells with thermal cycling, and wells in corrosive environments can have life expectancies of less than 10 years (Agbalagba et al., 2013).

The depth of the surface casing relative to the base of the drinking water resource to be protected is an important factor in protecting the drinking water resource. In a limited risk modeling study of selected injection wells in the Williston Basin, Michie and Koch (1991) found the risk of aquifer contamination from leaks from the inside of the well to the drinking water resource was seven in 1,000,000 injection wells if the surface casing was set deep enough to cover the drinking water resource, and that the risk increased to six in 1,000 wells if the surface casing was not set deeper than the bottom of the drinking water resource. An example where surface casing did not extend below drinking water resources comes from an investigation of 14 selected drinking water wells with alleged water quality problems in the Wind River and Fort Union formations near Pavillion, Wyoming (WYOGCC, 2014b). The state found that the surface casing of oil and gas wells was shallower than the depth of three of the 14 drinking water wells. Some of the oil and gas wells with shallow surface casing had elevated gas pressures in their annuli (WYOGCC, 2014b). The presence of gas in the annuli, combined with surface casing that is set above the lowest drinking water resource, could allow migration of gas into drinking water resources.

Fleckenstein et al. (2015) found that the depth of surface casing and the presence of uncemented gas zones are major factors in determining the likelihood of well failures and contamination. Their study in the Wattenberg field in Colorado classified the wells in the field into seven categories based on the depth of surface casing, the presence of cement, and the presence of intermediate gas zones above the production zone (Table 6-1). The categories were arranged in order of risk, with category 1 wells being at the highest risk of allowing fluid migration and category 7 wells being the least likely to allow migration. The overall barrier failure rate was 2.4% of all wells, and the overall catastrophic failure rate was 0.06% of all wells. A remediation effort was made in order to decrease the likelihood of fluid migration, which included the plugging of 1,103 of the 17,948 wells studied. All the wells shown in the table are vertical wells that were drilled between 1970 and 2013. Similar categories were created for the 973 horizontal wells in the field. No failures were recorded for any of the horizontal wells.

**Table 6-1. Failure rates of vertical wells in the Wattenberg field, Colorado.**
From Fleckenstein et al. (2015).

| Category and description[a, b] | Total wells | Wells with barrier failures[c] | Wells with catastrophic failures[d] |
|---|---|---|---|
| 1--Shallow surface casing and exposed (uncemented) over-pressured intermediate gas zones | 399 | 92 (23.06%) | 3 (0.75%) |
| 2 – Shallow surface casing and exposed under-pressured intermediate gas zones | 7,811 | 276 (3.53%) | 6 (0.08%) |
| 3 – Shallow surface casing but no exposed gas zones | 3,407 | 20 (0.59%) | 1 (0.03%) |
| 4 – Shallow surface casing with production casing cemented to bottom of surface casing | 1,063 | 0 (0%) | 0 (0%) |
| 5 – Deep surface casing with production casing cement below top of gas | 1,374 | 13 (0.95%) | 0 (0%) |
| 6 – Deep surface casing with production casing cement above top of gas | 2,069 | 0 (0%) | 0 (0%) |
| 7 – Deep surface casing with production casing cement to bottom of surface casing | 705 | 0 (0%) | 0 (0%) |
| Total | 16,828 | 401 (2.4%) | 10 (0.06%) |

[a] The study defined shallow surface casing as casing that did not extend below the Fox Hills Aquifer, a deep aquifer that had not been identified and protected by the state prior to 1994.

[b] Uncemented zones could be located along the intermediate or production casings.

[c] Barrier failures were considered to have occurred when there were signs of a failure, but no contamination.

[d] A catastrophic failure was considered to have occurred where 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 zone or casing leaks.

Sherwood et al. (2016) examined complaint records in the same field. They reviewed 29 Colorado Oil and Gas Commission complaint records associated with 32 incidents at 42 drinking water wells in which thermogenic methane was detected. (See Text Box 6-3 for more information on thermogenic and biogenic methane.) Of the 29 complaints, 10 were determined to be caused by oil and gas wellbore failures, one was suspected of being a wellbore failure but not confirmed, three were settled in court with documents being sealed, and the remaining 15 were unresolved.[1] If all 32 cases are assumed to be associated with an individual oil and gas well, that would result in a failure rate of 0.06% of all oil and gas wells in the basin, the same failure rate as found in the Fleckenstein et al. (2015) study. As in the Fleckenstein study, surface casing that was set too shallow and

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[1] This paper defined a wellbore failure as the failure of one or more barriers to fluid movement in the wellbore (e.g., cement, casing, etc.).

uncemented intermediate zones were the main contributing factors to wellbore failure. All 11 of the confirmed or suspected wellbore failures involved vertical wells that were drilled before 1933 and had surface casing shallower than nearby aquifers. Of these wells, seven had been hydraulically fractured. The study noted that the failure rate was fairly constant over time with about two new cases per year since 2000 and that the rate had not changed since high rates of hydraulic fracturing of horizontal wells became prevalent around 2010. This is consistent with the study's finding of no failures in horizontal wells.

During hydraulic fracturing operations in September of 2010 near Killdeer, in Dunn County, North Dakota, the production, surface, and conductor casing of the Franchuk 44-20 SWH well ruptured, causing fluids to spill to the surface (Jacob, 2011). The rupture occurred during the 5th of 23 planned stages of hydraulic fracturing when the pressure spiked to over 8,390 psi (58 MPa). Ruptures were found in two locations along the production casing—one just below the surface and one at about 55 ft (17 m) below ground surface. The surface casing ruptured in three places down to a depth of 188 ft (57 m), and the conductor casing ruptured in one place. Despite a shutdown of the pumps, the pressure was still sufficient to cause fluid to travel through the ruptured casings and to flow to the surface. Ultimately, over 166,000 gal (628,000 L) of fluids and approximately 2,860 tons (2,595 metric tons) of contaminated soil were removed from the site (Jacob, 2011).

The EPA investigated the Killdeer site as part of its Retrospective Case Study in Killdeer, North Dakota: Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources (U.S. EPA, 2015i). As part of the study, water quality samples were collected from three domestic wells, nine monitoring wells, two supply wells, one municipal well, and one state well in July 2011, October 2011, and October 2012. Two study wells installed less than 60 ft (20 m) from the production well (NDGW08 and NDGW07) had significant differences in water quality compared to the remaining study wells.[1] These two wells showed differences in ion concentrations (e.g., chloride, calcium, magnesium, sodium, strontium) and tert-butyl alcohol (TBA). The sampling identified brine contamination that was consistent with mixing of local groundwater with brine from Madison Group formations, which the well had penetrated. The TBA was consistent with degradation of tert-butyl hydroperoxide, a component of the hydraulic fracturing fluid used in the Franchuk well. Based on the analysis of potential sources of contamination, the EPA determined that the only potential sources of TBA were gasoline spills, leaky underground storage tanks, and hydraulic fracturing fluids. However, the lack of MTBE and other signature compounds associated with gasoline or fuels strongly suggests that the rupture (blowout) was the only source consistent with findings of high brine and TBA concentrations in the two wells.[2] For additional information about impacts at the Killdeer site, see Section 6.3.2.2.

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[1] Based on comparison with historical Killdeer aquifer water quality data, the remaining study wells were in general consistent with historical background data; these wells were then used for the data analysis as background wells. Comparisons of TBA between the study data and historical data could not be made since no historical data for TBA were found for the Killdeer aquifer.

[2] A well blowout is the uncontrolled flow of fluids out of a well.

Inadequate casing or cement can respond poorly when blowout preventers activate.[1] When blowout preventers are activated, they immediately stop the flow in the well, which can create a sudden pressure increase in the well. If the casing or cement are not strong enough to withstand the increased pressure when this occurs, well components can be damaged (The Royal Society and the Royal Academy of Engineering, 2012) and the potential for fluid release and migration in the subsurface increases. Blowouts can also occur during the production phase, and cause spills on the surface that can affect drinking water resources; see Section 7.4.2.2.

While well construction and hydraulic fracturing techniques continue to change, the pressure- and temperature-related stresses associated with hydraulic fracturing remain as factors that can affect the integrity of the well casing. Tian et al. (2015) investigated one such case where temperature effects led to casing damage in China. In the Changning-Weiyuan basin in China, 13 of 33 wells (39.4%) suffered casing damage, with most of the wells experiencing the damage after fracturing. The authors found that injection of the cooler hydraulic fracturing fluid led the casing temperature to drop from the formation temperature of 212°F to 64°F (100°C to 18°C) in some cases. This drop in temperature, in turn, caused pockets of high pressure fluid outside the casing to contract. If the temperature dropped below 136°F (58°C), the effect was sufficient to form a vacuum outside the casing, potentially leading to casing deformation. Areas of the casing with severe doglegs (i.e., bends in the well) and where there was a smaller space between the casing and formation were more prone to this type of damage. While the conditions in this Chinese basin may or may not represent conditions in U.S. basins, they do demonstrate that temperature changes during hydraulic fracturing can place additional stress on the well and highlight their importance as a consideration in casing design. In the case mentioned, increasing the space around the casing, decreasing dogleg angles, properly removing drilling mud, and using high strength, low elasticity cement were found to improve performance.

Sugden et al. (2013) used numerical simulation to examine a similar problem using parameters chosen to represent the Haynesville Shale. They found that injecting a fluid at 70°F (21°C) could cool the wellbore temperature from 320°F to 96°F (160°C to 36°C). The temperature change was 90% complete within the first half hour of hydraulic fracturing operations. They also found that a well with a 20 degree per 100 ft (31 m) dogleg decreased the pressure required to damage the well casing by 850 psi (5.9 MPa). The study also reported that cooling of fluids in voids in the cement can lead to contraction of the fluids. In low permeability shales, fluid cannot flow in fast enough to compensate, and the pressure in the void can drop significantly. Sugden et al. (2013) report that such cement voids can reduce the pressure needed to rupture the casing by 40%.

Emerging isotopic techniques can be used to identify the extent to which stray gas occurring in drinking water resources is linked to casing failure. (See Text Box 6-3 for more information on stray gas.) Darrah et al. (2014) used hydrocarbon and noble gas isotope data to investigate the source of gas in eight identified "contamination clusters" that occurred in the Marcellus and Barnett shales. Seven of these clusters were stripped of atmospheric gases (Argon-36 and Neon-20) and were

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[1] A blowout preventer (BOP) is casinghead equipment that prevents the uncontrolled flow of oil, gas, and mud from the well by closing around the drill pipe or sealing the hole (Oil and Gas Mineral Services, 2010). BOPs are typically a temporary component of the well, in place only during drilling and perhaps through hydraulic fracturing operations.

enriched in crustal gases, indicating the gas migrated quickly from depth without equilibrating with intervening formations. The rapid transport was interpreted to mean that the migration did not occur along natural fractures or pathways, which would have allowed equilibration to take place. Based on the isotopic results, the authors also ruled out the possibility that the gas was carried upward (relative to the surface) as the geologic formation in which it formed was uplifted over geologic time. Possible explanations for the rapid migration include transport up the well and through a leaky casing (Pathway 1 in Figure 6-4) or along uncemented or poorly cemented intervals from shallower depths (Pathways 2 through 5 in Figure 6-4). In four Marcellus Shale clusters, gas found in drinking water wells had isotopic signatures and ratios of ethane to methane that were consistent with those in the producing formation. The authors conclude that this suggests that gas migrated along poorly constructed wells from the producing formation, likely with improper, faulty, or failing production casings. In three clusters, the isotopic signatures and ethane to methane ratios were consistent with formations overlying the Marcellus. The authors suggest that this migration occurred from the shallower gas formations along uncemented or improperly cemented wellbores. In another Marcellus cluster in the study, deep gas migration was linked to a subsurface well, likely from a failed well packer.

### Text Box 6-3. Stray Gas Migration.

Stray gas refers to the phenomenon of natural gas (primarily methane) migrating into shallow drinking water resources, into water wells or other types of wells, to the surface, or to near-surface features (e.g., basements, streams, or springs). The source of the migrating gas can be natural gas reservoirs (either conventional or unconventional), or from coal mines, landfills, leaking gas wells, leaking gas pipelines, buried organic matter, or natural microbial processes (Li and Carlson, 2014; Baldassare, 2011). Although methane is not a regulated drinking water contaminant, its presence in drinking water resources can initiate chemical and biological reactions that release or mobilize other contaminants. Over time, it can promote more reducing conditions in groundwater, potentially leading to reductive dissolution of iron and manganese and the possible liberation of naturally occurring contaminants, such as arsenic, that are potentially associated with iron and manganese (U.S. EPA, 2014f). In addition, methane can accumulate to explosive levels in confined spaces (like basements or cellars) if it exsolves (degases) from groundwater into those spaces. (See Section 9.5.5 for information about the hazards associated with methane exposure.)

Detectable levels of dissolved natural gas exist in some aquifers, even in the absence of human activity (Gorody, 2012). In northern Pennsylvania and New York, low levels of methane are frequently found in water wells in baseline studies, prior to commercial oil or gas development (Christian et al., 2016; Kappel, 2013; Kappel and Nystrom, 2012); for example, one USGS study detected methane in 80% of sampled wells in Pike County, Pennsylvania (Senior, 2014). The origin of methane in groundwater can be either thermogenic (produced by high temperatures and pressures in deeper formations, such as the gas found in the Marcellus Shale) or biogenic (produced in shallower formations by bacterial activity in anaerobic conditions).

Gas occurrence is linked to local and regional geologic characteristics. In some cases, thermogenic methane occurs naturally in shallow formations because the formation itself was uplifted (relative to the surface) over geologic time. In other cases, it has migrated there via one or more pathways. For example, Brantley et al. (2014) suggest that northern Pennsylvania's glacial history can help explain why stray gas is more common

*(Text Box 6-3 is continued on the following page.)*