

Chapter 5

Chemical Mixing

5. Chemical Mixing

5.1. Introduction

1 This chapter addresses the potential for on-site spills of chemicals used in the chemical mixing
2 process to affect the quality of drinking water resources. Chemical mixing is a complex process that
3 requires the use of specialized equipment and a range of different additives to produce the
4 hydraulic fracturing fluid that is injected into the well. The number, type, and volume of chemicals
5 used vary from well to well based on site- and company-specific factors. Spills may occur at any
6 point in the hydraulic fracturing process. Chemicals may spill from on-site storage and containment
7 units; from interconnected hoses and pipes used to transfer chemicals to and from mixing and
8 pumping units, and tanker trucks; and from the equipment used to mix and pressurize chemical
9 mixtures that are pumped down the well. The potential for a spill to affect the quality of a drinking
10 water resource is governed by three overarching factors: (1) fluid characteristics (e.g., chemical
11 composition and volume), (2) chemical management and spill characteristics, and (3) chemical fate
12 and transport (see Figure 5-1). This chapter is organized around the three factors.

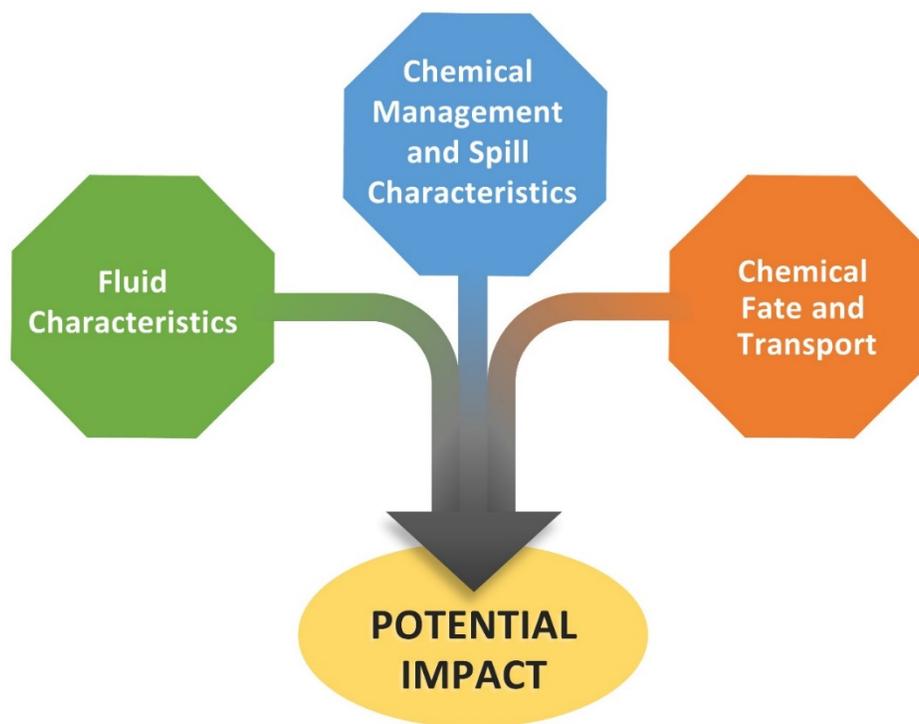


Figure 5-1. Factors governing potential impact to drinking water resources.

Factors include (1) fluid characteristics (e.g., chemical composition and volume), (2) chemical management and spill characteristics, and (3) chemical fate and transport.

1 Section 5.2 provides an introductory overview of the chemical mixing process. The number and
2 volume of chemicals used and stored on-site are affected by such variables as the type, size, and
3 goals of the operation; formation characteristics; depth of the well; the length of the horizontal leg;
4 and the number of fracturing phases and stages.

5 Section 5.3 describes the different components of the hydraulic fracturing fluid, generally
6 comprised of the base fluid, proppant, and additives, which may be either individual chemicals or
7 mixtures. The composition of the hydraulic fracturing fluid is engineered to meet specific criteria.
8 The total amount and types of additives vary according to the characteristics of the well, site
9 geology, economics, availability, and the production goals (e.g., Maule et al., 2013). Section 5.4
10 presents the wide range of different chemicals used and their classes, the most frequently used
11 chemicals nationwide and from state-to-state, and volumes used.¹ Appendix A provides a list of
12 chemicals that the EPA identified as being used in hydraulic fracturing fluids based on eight
13 sources.

14 Sections 5.5 to 5.7 discuss how chemicals are managed on-site, how spills may occur, and the
15 different approaches for addressing spills. Section 5.5 describes how the potential impact of a spill
16 on drinking water resources depends upon chemical management practices, such as storage, on-
17 site transfer, and equipment maintenance. Section 5.6 discusses spill prevention, containment, and
18 mitigation. A summary analysis of reported spills and their common causes at hydraulic fracturing
19 sites is presented in Section 5.7.

20 Section 5.8 discusses the fate and transport of spilled chemicals. Spilled chemicals may react and
21 transform into other chemicals, travel from the site of release to a nearby surface water, or leach
22 into the soils and reach ground water. Chemical fate and transport after a release depend on site
23 conditions, environmental conditions, physicochemical properties of the released chemicals, and
24 the volume of the release.

25 Section 5.9 provides an overview of on-going changes in chemical use in hydraulic fracturing, with
26 an emphasis on efforts by industry to reduce potential impacts from surface spills by using fewer
27 and safer chemicals. A synthesis and a discussion of limitations are presented in Section 5.10.

28 Factors affecting the frequency and severity of impacts to drinking water resources from surface
29 spills include size and type of operation, employee training and experience, standard operating
30 procedures, quality and maintenance of equipment, type and volume of chemical spilled,
31 environmental conditions, proximity to drinking water resources, spill prevention practices, and
32 spill mitigation measures. Due to the limitations of available data and the scope of this assessment,
33 it is not possible to provide a detailed analysis of all of the factors listed above. Data limitations also
34 preclude a quantitative analysis of the likelihood or magnitude of chemical spills or impacts. Spills
35 that occur off-site, such as those during transportation of chemicals or storage of chemicals in
36 staging areas, are out of scope. This chapter qualitatively characterizes the potential for impacts to

¹ Chemical classes are groupings of different chemicals based on similar features, such as chemical structure, use, or physical properties. Examples of chemical classes include hydrocarbons, pesticides, acids, and bases.

1 drinking water resources given the current understanding of overall operations and specific
2 components of the chemical mixing process.

5.2. Chemical Mixing Process

3 An understanding of the chemical mixing process is necessary to understand how, why, and when
4 spills that may affect drinking water resources might occur. This description provides a general
5 overview of chemical mixing in the context of the overall hydraulic fracturing process ([Carter et al.,
6 2013](#); [Knappe and Fireline, 2012](#); [Spellman, 2012](#); [Arthur et al., 2008](#)).

7 Figure 5-2 shows a hydraulic fracturing site during the chemical mixing process. The discussion
8 focuses on the types of additives used at each phase of the process. While similar processes are
9 used to fracture horizontal and vertical wells, a horizontal well treatment is described here because
10 it is likely to be more complex and because horizontal hydraulic fracturing has become more
11 prevalent over time with advances in hydraulic fracturing technology. A water-based system is
12 described because water is the most commonly used base fluid, appearing in more than 93% of
13 FracFocus disclosures between January 1, 2011 and February 28, 2012 ([U.S. EPA, 2015a](#)).



Figure 5-2. Hydraulic fracturing site showing equipment used on-site during the chemical mixing process.

Source: Industry source.

1 While the number and types of additives may widely vary, the basic chemical mixing process is
 2 similar across sites. The on-site layout of hydraulic fracturing equipment is also similar from site to
 3 site ([BJ Services Company, 2009](#)). Equipment used in the chemical mixing process typically consists
 4 of chemical storage trucks, water supply tanks, proppant supply, slurry blenders, a number of high-
 5 pressure pumps, a manifold, surface lines and hoses, and a central control unit. Detailed
 6 descriptions of specific additives and the equipment used in the process are provided in Sections
 7 5.3 and 5.5, respectively.

8 The chemical mixing process begins after the drilling, casing, and cementing processes are finished
 9 and hydraulic fracturing equipment has been set up and connected to the well. The process can
 10 generally be broken down into sequential phases with specific chemicals added at each phase to
 11 achieve a specific purpose ([Knappe and Fireline, 2012](#); [Fink, 2003](#)). Phases may overlap. The
 12 process for water-based hydraulic fracturing is outlined in Figure 5-3 below.

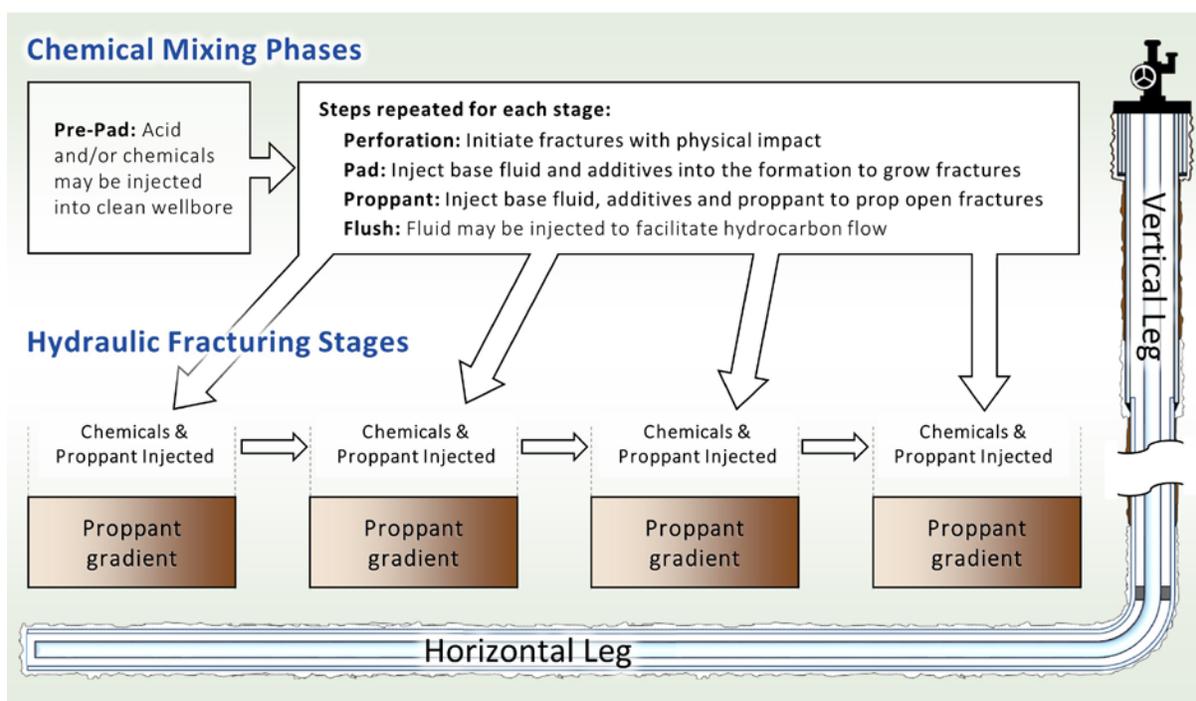


Figure 5-3. Overview of a chemical mixing process of the hydraulic fracturing water cycle.

This figure outlines the chemical mixing process for a generic water-based hydraulic fracture of a horizontal well. The chemical mixing phases outline the steps in the overall fracturing job, while the hydraulic fracturing stages outline how each section of the horizontal well would be fractured beginning with the toe of the well, shown on left-side. The proppant gradient represents how the proppant size may change within each stage of fracturing as the fractures are elongated. The chemical mixing process is repeated depending on the number of stages used for a particular well. The number of stages is determined in part by the length of the horizontal leg. In this figure, four stages are represented, but typically, a horizontal fracturing treatment would consist of 10 to 20 stages per well ([Lowe et al., 2013](#)). Fracturing has been reported to be done in as many as 59 stages ([Pearson et al., 2013](#)).

1 The first phase of the process consists of the cleaning and preparation of the well. The fluid used in
2 this phase is often referred to as the pre-pad fluid or pre-pad volume. Acid is typically the first
3 chemical introduced. Acid, with a concentration of 3%–28% (typically hydrochloric acid, HCl), is
4 used to adjust pH, clean any cement left inside the well from cementing the casing, and dissolve any
5 pieces of rock that may remain in the well and could block the perforations. Acid is typically
6 pumped directly from acid storage tanks or tanker trucks, without being mixed with other
7 additives. The first, or pre-pad, phase may also involve mixing and injection of additional chemicals
8 to facilitate the flow of fracturing fluid introduced in the next phase of the process. These additives
9 may include biocides, corrosion inhibitors, friction reducers, and scale inhibitors ([Carter et al.,
10 2013](#); [King, 2012](#); [Knappe and Fireline, 2012](#); [Spellman, 2012](#); [Arthur et al., 2008](#)).

11 In the second phase, a hydraulic fracturing fluid, typically referred to as the pad or pad volume, is
12 mixed, blended, and pumped down the wellbore to create fractures in the formation. The pad is a
13 mixture of base fluid, typically water, and additives. The pad is designed to create, elongate, and
14 enlarge fractures along the natural channels of the formation when injected under high pressure
15 ([Gupta and Valkó, 2007](#)). A typical pad consists of, at minimum, a mixture of water and friction
16 reducer. The operator may also add other additives (see [U.S. EPA \(2015a\)](#) and Table 5-1) used to
17 facilitate flow and kill bacteria ([Carter et al., 2013](#); [King, 2012](#); [Knappe and Fireline, 2012](#);
18 [Spellman, 2012](#); [Arthur et al., 2008](#)). The pad is pumped into the formation through perforations in
19 the well casing (see Text Box 5-1).

Text Box 5-1. Perforation.

20 Prior to the injection of the pad, the well casing is typically perforated to provide openings through which the
21 pad fluid can enter the formation. A perforating gun is typically used to create small holes in the section of the
22 wellbore being fractured. The perforating gun is lowered into position in the horizontal portion of the well.
23 An electrical current is used to set off small explosive charges in the gun, which creates holes through the well
24 casing and out a short, controlled distance into the formation ([Gupta and Valkó, 2007](#)).

25 In the third phase, proppant, typically sand, is mixed into the hydraulic fracturing fluid. The
26 proppant volume, as a proportion of the injected fluid, is increased gradually until the desired
27 concentration in the fractures is achieved. Gelling agents, if used, are also mixed in with the
28 proppant and base fluid in this phase to increase the viscosity and carry the proppant. Additional
29 chemicals may be added to gelled fluids, initially to maintain viscosity and later to break the gel
30 down into a more readily removable fluid. ([Carter et al., 2013](#); [King, 2012](#); [Knappe and Fireline,
31 2012](#); [Spellman, 2012](#); [Arthur et al., 2008](#)).

32 A final flush or clean-up phase may be conducted after the stage is fractured, with the primary
33 purpose of maximizing well productivity. The flush is a mixture of water and chemicals that work to
34 aid the placement of the proppant, clean out the chemicals injected in previous phases, and prevent
35 microbial growth in the fractures ([Knappe and Fireline, 2012](#); [Fink, 2003](#)).

36 The second, third, and fourth phases are repeated multiple times in a horizontal well, as the
37 horizontal section, or leg, of the wellbore is typically fractured in multiple segments referred to as

1 stages. For each stage, the well is typically perforated and fractured beginning at the end, or toe, of
2 the wellbore and proceeding backwards toward the vertical section. Each fractured stage is isolated
3 before the next stage is fractured. The number of stages corresponds directly to the number of
4 times the chemical mixing process is repeated at the site surface (see Figure 5-3). The number of
5 stages depends upon the length of the leg ([Carter et al., 2013](#); [King, 2012](#); [Knappe and Fireline,
6 2012](#); [Spellman, 2012](#); [Arthur et al., 2008](#)).

7 The number of stages per well can vary, with several sources suggesting between 10 and 20 is
8 typical ([GNB, 2015](#); [Lowe et al., 2013](#)).¹ The full range reported in the literature is much wider, with
9 one source documenting between 1 and 59 stages per well ([Pearson et al., 2013](#)) and others
10 reporting values within this range ([NETL, 2013](#); [STO, 2013](#); [Allison et al., 2009](#)). It also appears that
11 the number of stages per well has increased over time. For instance, in the Williston Basin the
12 average number of stages per horizontal well rose from approximately 10 in 2008 to 30 in 2012
13 ([Pearson et al., 2013](#)).

14 In each of these phases, water is the primary component of the hydraulic fracturing fluid, though
15 the exact composition of the fluid injected into the well changes over the duration of each stage. In
16 water-based hydraulic fracturing, water typically comprises between 90% and 94% of the
17 hydraulic fracturing fluid, proppant comprises 5% to 9%, and additives comprise the remainder,
18 typically 2% or less ([Carter et al., 2013](#); [Knappe and Fireline, 2012](#); [SWN, 2011](#)). The exception to
19 this typical fluid composition may be when a concentrated acid is used in the initial cleaning phase
20 of the fracturing process.

5.3. Overview of Hydraulic Fracturing Fluids

21 Hydraulic fracturing fluids are formulated to perform specific functions: create and extend the
22 fracture, transport proppant, and place the proppant in the fractures ([Montgomery, 2013](#);
23 [Spellman, 2012](#); [Gupta and Valkó, 2007](#)). The hydraulic fracturing fluid generally consists of three
24 parts: (1) the base fluid, which is the largest constituent by volume, (2) the additives, which can be
25 a single chemical or a mixture of chemicals, and (3) the proppant. Additives are chosen to serve a
26 specific purpose in the hydraulic fracturing fluid (e.g., friction reducer, gelling agent, crosslinker,
27 biocide) ([Spellman, 2012](#)). Throughout this chapter, “chemical” is used to refer to individual
28 chemical compounds (e.g., methanol). Proppants are small particles, usually sand, mixed with
29 fracturing fluid to hold fractures open so that the target hydrocarbons can flow from the formation
30 through the fractures and up the wellbore. The combination of chemicals, and the mixing and
31 injection process, varies based on a number of factors as discussed below. The chemical
32 combination determines the amount and what type of equipment is required for storage and,
33 therefore, contributes to the determination of the potential for spills and impacts of those spills.

34 The particular composition of hydraulic fracturing fluids is selected by a design engineer based on
35 empirical experience, the formation, economics, goals of the fracturing process, availability of the

¹ The number of stages has been reported to be 6 to 9 in the Huron in 2009 ([Allison et al., 2009](#)), 25 and up in the Marcellus ([NETL, 2013](#)), and up to 40 by [STO \(2013\)](#).

1 desired chemicals, and preference of the service company or operator ([Montgomery, 2013](#); [ALL](#)
2 [Consulting, 2012](#); [Klein et al., 2012](#); [Ely, 1989](#)). No single set of specific chemicals is used at every
3 site. Multiple types of fracturing fluids may be appropriate for a given site and any given type of
4 fluid may be appropriate at multiple sites. For the same type of fluid formulation, there can be
5 differences in the additives, chemicals, and concentrations selected. There are broad criteria for
6 hydraulic fracturing fluid selection based on the fracturing temperatures, formation permeability,
7 fracturing pressures, and formation water sensitivity, as shown in Figure 5-4 ([Gupta and Valkó,](#)
8 [2007](#); [Elbel and Britt, 2000](#)). One of the most important properties in designing a hydraulic
9 fracturing fluid is the viscosity ([Montgomery, 2013](#)).¹

10 Figure 5-4 provides a general overview of which fluids can be used in different situations. As an
11 example, crosslinked fluids with 25% nitrogen foam (titanate or zirconate crosslink + 25% N₂) can
12 be used in both gas and oil wells with high temperatures with variation in water sensitivity.

¹ Viscosity is a measure of the internal friction of fluid that provides resistance to shear within the fluid, informally referred to as how “thick” a fluid is. For example, custard is thick and has a high viscosity, while water is runny with a low viscosity. Sufficient viscosity is needed to create a fracture and transport proppant ([Gupta and Valkó, 2007](#)). In lower-viscosity fluids, proppant is transported by turbulent flow and requires more hydraulic fracturing fluid. Higher-viscosity fluids allows the fluid to carry more proppant, requiring less fluid but necessitating the reduction of viscosity after the proppant is placed ([Rickman et al., 2008](#); [Gupta and Valkó, 2007](#)).

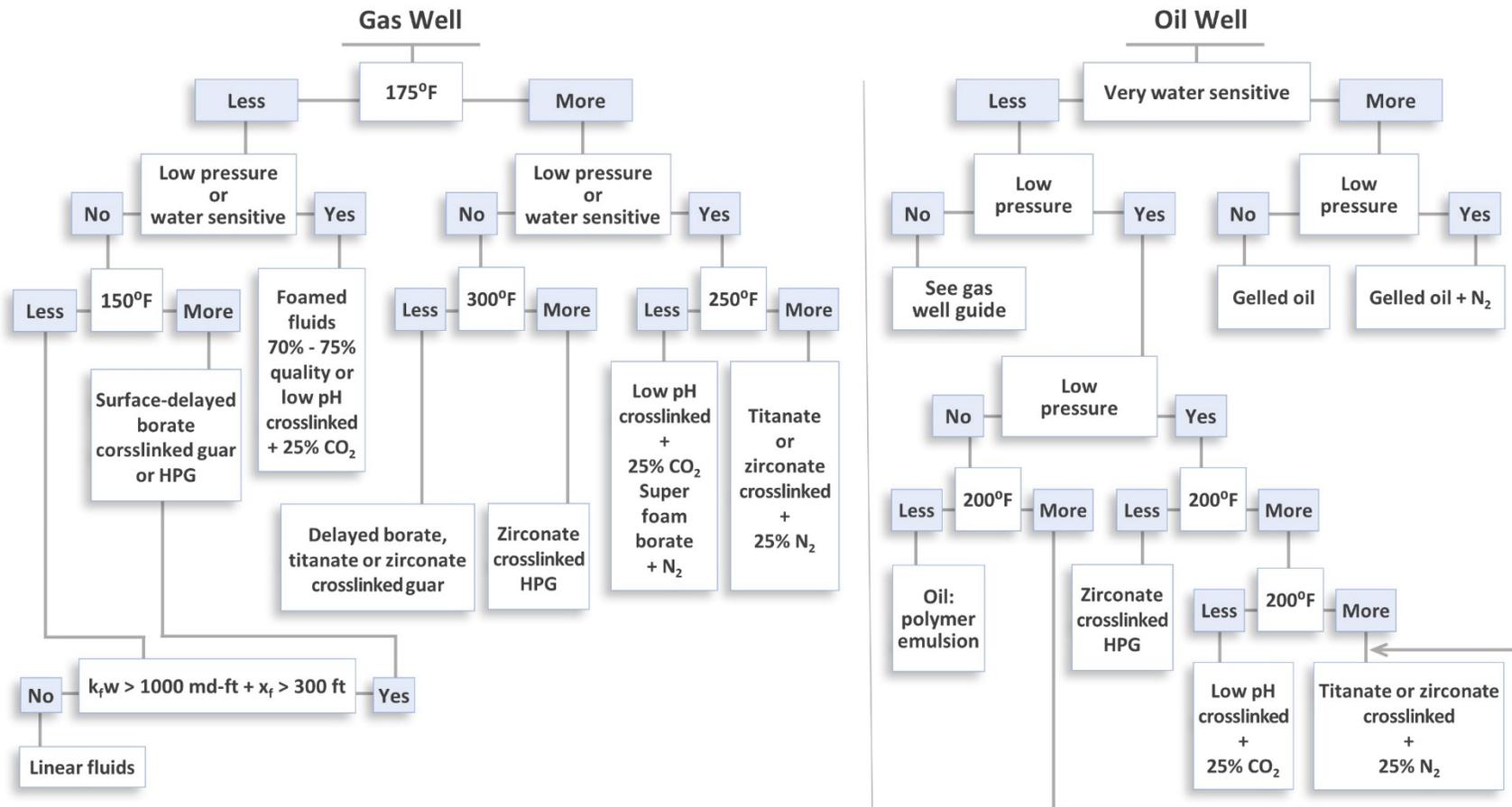


Figure 5-4. Example fracturing fluid decision tree for gas and oil wells.

Adapted from [Elbel and Britt \(2000\)](#).

1 Table 5-1 provides a list of common types of additives, their functions, and the most frequently
 2 used chemicals for each purpose based on the EPA’s analysis of disclosures to FracFocus 1.0
 3 (hereafter EPA FracFocus report; [U.S. EPA \(2015a\)](#)), the EPA’s project database of disclosures to
 4 FracFocus 1.0 [hereafter EPA FracFocus database; [U.S. EPA \(2015b\)](#)], and other literature sources.
 5 Additional information on more additives can be found in [U.S. EPA \(2015a\)](#).

Table 5-1. Examples of common additives, their function, and the most frequently used chemicals reported to FracFocus for these additives.

The list of examples of common additives was developed from information provided in multiple sources ([U.S. EPA, 2015a, b](#); [Stringfellow et al., 2014](#); [Montgomery, 2013](#); [Vidic et al., 2013](#); [Spellman, 2012](#); [GWPC and ALL Consulting, 2009](#); [Arthur et al., 2008](#); [Gupta and Valkó, 2007](#); [Gidley et al., 1989](#)). The additive functions are based on information the EPA received from service companies ([U.S. EPA, 2013a](#)).

Additives	Function	Chemicals reported in ≥20% of FracFocus disclosures for additive^{a,b}
Acid	Dissolves cement, minerals, and clays to reduce clogging of the pore space	Hydrochloric acid
Biocide	Controls or eliminates bacteria, which can be present in the base fluid and may have detrimental effects on the fracturing process	Glutaraldehyde; 2,2-dibromo-3-nitrilopropionamide
Breaker	Reduces the viscosity of specialized treatment fluids such as gels and foams	Peroxydisulfuric acid diammonium salt
Clay control	Prevents the swelling and migration of formation clays in reaction to water-based fluids	Choline chloride
Corrosion inhibitor	Protects the iron and steel components in the wellbore and treating equipment from corrosive fluids	Methanol; propargyl alcohol; isopropanol
Crosslinker	Increases the viscosity of base gel fluids by connecting polymer molecules	Ethylene glycol; potassium hydroxide; sodium hydroxide
Emulsifier	Facilitates the dispersion of one immiscible fluid into another by reducing the interfacial tension between the two liquids to achieve stability	2-Butoxyethanol; polyoxyethylene(10)nonylphenyl ether; methanol; nonyl phenol ethoxylate
Foaming agent	Generates and stabilizes foam fracturing fluids	2-Butoxyethanol; Nitrogen, liquid; isopropanol; methanol; ethanol

Additives	Function	Chemicals reported in $\geq 20\%$ of FracFocus disclosures for additive ^{a,b}
Friction reducer	Reduces the friction pressures experienced when pumping fluids through tools and tubulars in the wellbore	Hydrotreated light petroleum distillates
Gelling agent	Increases fracturing fluid viscosity allowing the fluid to carry more proppant into the fractures and to reduce fluid loss to the reservoir	Guar gum; hydrotreated light petroleum distillates
Iron control agent	Controls the precipitation of iron from solution	Citric acid
Nonemulsifier	Separates problematic emulsions generated within the formation	Methanol; isopropanol; nonyl phenol ethoxylate
pH control	Affects the pH of a solution by either inducing a change (pH adjuster) or stabilizing and resisting change (buffer) to achieve desired qualities and optimize performance	Carbonic acid, dipotassium salt; potassium hydroxide; sodium hydroxide; acetic acid
Resin curing agents	Lowers the curable resin coated proppant activation temperature when bottom hole temperatures are too low to thermally activate bonding	Methanol; nonyl phenol ethoxylate; isopropanol; alcohols, C12-14-secondary, ethoxylated
Scale inhibitor	Controls or prevents scale deposition in the production conduit or completion system	Ethylene glycol; methanol
Solvent	Controls the wettability of contact surfaces or prevents or breaks emulsions	Hydrochloric acid

^a Chemicals (excluding water and quartz) listed as reported to FracFocus in more than 20% of disclosures for a given purpose when that purpose was listed as used on a disclosure. These are not necessarily the active ingredients for the purpose, but rather are listed as being commonly present for the given purpose. Chemicals may be disclosed for more than a single purpose (e.g., 2-butoxyethanol is listed as being used as an emulsifier and a foaming agent).

^b 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.

1 A general description of typical hydraulic fracturing fluid formulations nationwide is difficult
2 because fracturing fluids vary from well to well. Based on the FracFocus report, the median number
3 of chemicals reported for each disclosure was 14, with the 5th to 95th percentile ranging from four to
4 28. The median number of chemicals per disclosure was 16 for oil wells and 12 for gas wells ([U.S.
5 EPA, 2015b](#)). Other sources have stated that between three and 12 additives and chemicals are
6 used ([Schlumberger, 2015](#); [Carter et al., 2013](#); [Spellman, 2012](#); [GWPC and ALL Consulting, 2009](#)).¹

7 Water, the most commonly used base fluid for hydraulic fracturing, is inferred to be used as a base
8 fluid in more than 93% of FracFocus disclosures. Alternatives to water-based fluids, such as
9 hydrocarbons and gases, including carbon dioxide or nitrogen-based foam, may also be used based
10 on formation characteristics, cost, or preferences of the well operator or service company ([ALL
11 Consulting, 2012](#); [GWPC and ALL Consulting, 2009](#)). Non-aqueous base fluid ingredients were
12 identified in 761 (2.2%) of FracFocus 1.0 disclosures ([U.S. EPA, 2015a](#)). Gases and hydrocarbons
13 may be used alone or blended with water; more than 96% of the disclosures identifying non-
14 aqueous base fluids are blended ([U.S. EPA, 2015a](#)). There is no standard method to categorize the
15 different fluid formulations ([Patel et al., 2014](#); [Montgomery, 2013](#); [Spellman, 2012](#); [Gupta and
16 Valkó, 2007](#)). Therefore, we broadly categorize the fluids as water-based or alternative fluids.

5.3.1. Water-Based Fracturing Fluids

17 The advantages of water-based fracturing fluids are low cost, ease of mixing, and ability to recover
18 and recycle the water. The disadvantages are low viscosity, the narrowness of the fractures created,
19 and they may not provide optimal performance in water-sensitive formations (see Section 5.3.2)
20 ([Montgomery, 2013](#); [Gupta and Valkó, 2007](#)). Water-based fluids can be as simple as water with a
21 few additives to reduce friction, such as “slickwater,” or as complex as water with crosslinked
22 polymers, clay control agents, biocides, and scale inhibitors ([Spellman, 2012](#)).

23 Gels may be added to water-based fluids to increase viscosity, which assists with proppant
24 transport and results in wider fractures. Gelling agents include natural polymers, such as guar,
25 starches, and cellulose derivatives, which requires the addition of biocide to minimize bacterial
26 growth ([Spellman, 2012](#); [Gupta and Valkó, 2007](#)). Gels may be linear or crosslinked. Crosslinking
27 increases viscosity without adding more gel. Gelled fluids require the addition of a breaker, which
28 breaks down the gel after it carries in the proppant, to reduce fluid viscosity to facilitate fluid
29 flowing back after treatment. ([Spellman, 2012](#); [Gupta and Valkó, 2007](#)). The presence of residual
30 breakers may make it difficult to reuse recovered water ([Montgomery, 2013](#)).

5.3.2. Alternative Fracturing Fluids

31 Alternative hydraulic fracturing fluids can be used for water-sensitive formations (i.e., formations
32 where permeability is reduced when water is added) or as dictated by production goals
33 ([Halliburton, 1988](#)). Examples of alternative fracturing fluids include acid-based fluids; non-
34 aqueous-based fluids; energized fluids, foams or emulsions; viscoelastic surfactant fluids; gels;

¹ Sources may differ based on whether they are referring to additives or chemicals.

1 methanol; and other unconventional fluids ([Montgomery, 2013](#); [Saba et al., 2012](#); [Gupta and Hlidek,](#)
2 [2009](#); [Gupta and Valkó, 2007](#); [Halliburton, 1988](#)).

3 **Acid fracturing** removes the need for a proppant and is generally used in carbonate formations.
4 Fractures are initiated with a viscous fracturing fluid, and the acid (gelled, foamed, or emulsified) is
5 added to irregularly etch the wall of the fracture and prop open the formation for a higher
6 conductivity fracture ([Spellman, 2012](#); [Gupta and Valkó, 2007](#)).

7 **Non-aqueous fluids** are used in water-sensitive formations. Non-aqueous fluids may also contain
8 additives, such as gelling agents, to improve performance ([Gupta and Valkó, 2007](#)). The use of non-
9 aqueous fluids has decreased due to safety concerns, and because water-based and emulsion fluid
10 technologies have improved ([Montgomery, 2013](#); [Gupta and Valkó, 2007](#)). Methanol, for example,
11 was previously used as a base fluid in water-sensitive reservoirs beginning in the early 1990s, but
12 was discontinued in 2001 for safety concerns and cost ([Saba et al., 2012](#); [Gupta and Hlidek, 2009](#);
13 [Gupta and Valkó, 2007](#)). Methanol is still used as an additive or in additive mixtures in hydraulic
14 fracturing fluid formulations.

15 **Energized fluids, foams, and emulsions** minimize fluid leakoff, have high proppant-carrying
16 capacity, improve fluid recovery, and are sometimes used in water-sensitive formations ([Barati and](#)
17 [Liang, 2014](#); [Gu and Mohanty, 2014](#); [Spellman, 2012](#); [Gupta and Valkó, 2007](#); [Martin and Valko,](#)
18 [2007](#)).¹ However, these treatments tend to be expensive, require high pressure, and pose potential
19 health and safety concerns ([Montgomery, 2013](#); [Spellman, 2012](#); [Gupta and Valkó, 2007](#)).

20 **Energized fluids** are mixtures of liquid and gas ([Patel et al., 2014](#); [Montgomery, 2013](#)). Nitrogen
21 (N₂) or carbon dioxide (CO₂), the gases used, make up less than 53% of the fracturing fluid volume,
22 typically ranging from 25% to 30% by volume ([Montgomery, 2013](#); [Gupta and Valkó, 2007](#);
23 [Mitchell, 1970](#)). **Energized foams** are liquid-gas mixtures, with N₂ or CO₂ gas comprising more than
24 53% of the fracturing fluid volume, with a typical range of 70% to 80% by volume ([Mitchell, 1970](#)).
25 **Emulsions** are liquid-liquid mixtures, typically a hydrocarbon (e.g., condensate or diesel) with
26 water, with the hydrocarbon typically 70% to 80% by volume.² Both water-based fluids, including
27 gels, and non-aqueous fluids can be energized fluids or foams.

28 Foams and emulsions break easily using gravity separation and are stabilized by using additives
29 such as foaming agents ([Gupta and Valkó, 2007](#)). Emulsions may be used to stabilize active chemical
30 ingredients or to delay chemical reactions, such as the use of carbon dioxide-miscible, non-aqueous
31 fracturing fluids to reduce fluid leakoff in water-sensitive formations ([Taylor et al., 2006](#)).

32 **Other types of fluids** not addressed above include viscoelastic surfactant fluids, viscoelastic
33 surfactant foams, crosslinked foams, liquid carbon dioxide-based fluid, and liquid carbon dioxide-
34 based foam fluid, and hybrids of other fluids ([King, 2010](#); [Brannon et al., 2009](#); [Curtice et al., 2009](#);

¹ Leakoff is the fraction of the injected fluid that infiltrates into the formation (e.g., through an existing natural fissure) and is not recovered during production ([Economides et al., 2007](#)). See Chapter 6, Section 6.3 for more discussion on leakoff.

² Diesel is a mixture typically of C8 to C21 hydrocarbons.

1 [Tudor et al., 2009](#); [Gupta and Valkó, 2007](#); [Coulter et al., 2006](#); [Boyer et al., 2005](#); [Fredd et al., 2004](#);
2 [MacDonald et al., 2003](#)).

3 Alternative fluids have been developed to work in tight formations, shales, and coalbeds, where
4 production is based on desorption of the natural gas, or in formations where the fracturing fluid
5 must displace a fluid that is already in place.

5.3.3. Proppants

6 Proppants are small particles carried down the well and into fractures by fracturing fluid. They hold
7 the fractures open after hydraulic fracturing fluid has been removed ([Brannon and Pearson, 2007](#)).
8 The propped fractures provide a path for the hydrocarbon to flow from the reservoir. Sand is most
9 commonly used, but other proppants include man-made or specially engineered particles, such as
10 resin-coated sand, high-strength ceramic materials, or sintered bauxite ([Schlumberger, 2014](#);
11 [Brannon and Pearson, 2007](#)). Proppant types can be used individually or in combinations.

5.4. Frequency and Volume of Hydraulic Fracturing Chemical Use

12 This section highlights the different chemicals used in hydraulic fracturing and discusses the
13 frequency and volume of use. Based on the U.S. EPA analysis of the FracFocus 1.0 database (see Text
14 Box 5-2), we focus our analysis on individual chemicals rather than mixtures of chemicals used as
15 additives. Chemicals are reported to FracFocus by using the chemical name and the Chemical
16 Abstract Services Registration Number (CASRN), which is a unique number identifier for every
17 chemical substance.¹ The information on specific chemicals, particularly those most commonly
18 used, can be used to assess potential impacts to drinking water resources. The volume of chemicals
19 stored on-site provides information on the potential volume of a chemical spill.

¹ A CASRN and chemical name combination identify a chemical substance, which can be a single chemical (e.g., hydrochloric acid, CASRN 7647-01-0) or a mixture of chemicals (e.g., hydrotreated light petroleum distillates (CASRN 64742-47-8), a complex mixtures of C9 to C16 hydrocarbons). For simplicity, we refer to both pure chemicals and chemical substances that are mixtures, which have a single CASRN, as “chemicals.”

Text Box 5-2. The FracFocus Registry and EPA FracFocus Report.

1 The Ground Water Protection Council (GWPC) and the Interstate Oil and Gas Compact Commission (IOGCC)
2 developed a national hydraulic fracturing chemical registry, FracFocus (www.fracfocus.org). Well operators
3 can use the registry to disclose information about chemicals they use during hydraulic fracturing. The EPA
4 accessed data from FracFocus 1.0 from January 1, 2011 to February 28, 2013, which included more than
5 39,000 disclosures from 20 states that had been submitted by operators prior to March 1, 2013.

6 Submission to FracFocus was initially voluntary and varied from state to state. During the timeframe of the
7 EPA's study, six of the 20 states with data in the project database began requiring operators to disclose
8 chemicals used in hydraulic fracturing fluids to FracFocus (Colorado, North Dakota, Oklahoma, Pennsylvania,
9 Texas, and Utah). Three other states started requiring disclosure to either FracFocus or the state (Louisiana,
10 Montana, and Ohio), and five states required or began requiring disclosure to the state (Arkansas, Michigan,
11 New Mexico, West Virginia, and Wyoming). Alabama, Alaska, California, Kansas, Mississippi, and Virginia did
12 not have reporting requirements during the period of the EPA's study.

13 Disclosures from the five states reporting the most disclosures to FracFocus (Texas, Colorado, Pennsylvania,
14 North Dakota, and Oklahoma) comprise over 78% of the disclosures in the database; nearly half (47%) of the
15 disclosures are from Texas. Thus, data from these states are most heavily represented in the EPA's analyses.
16 The EPA's analysis may or may not be nationally representative.

17 The EPA summarized information on the locations of the wells in the disclosures, water volumes used, and
18 the frequency of use and concentrations (% by mass, reported as maximum ingredient concentration) of the
19 chemicals in the additives and the hydraulic fracturing fluid. Additional information can be found in the EPA
20 FracFocus report ([U.S. EPA, 2015a](#)).

21 The EPA compiled a list of 1,076 chemicals known to be have been used in the hydraulic fracturing
22 process (see a full list, methodology, and the source citations in Appendix A). The chemicals used in
23 hydraulic fracturing fall into different chemical classes and include both organic and inorganic
24 chemicals. The chemical classes of commonly used hydraulic fracturing chemicals include but are
25 not limited to:

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

1 **Text Box 5-3. Confidential Business Information (CBI)**

2 This assessment relies in large part upon information provided to the EPA or to other organizations. The
3 submitters of that information (e.g., businesses that operate wells or perform services to hydraulically
4 fracture the well) may view some of the information as confidential business information (CBI), and
5 accordingly asserted CBI claims to protect such information. Information deemed to be CBI may include
6 information such as trade secrets or other proprietary business information, entitled to confidential
7 treatment under Exemption 4 of the Freedom of Information Act (FOIA) and other applicable laws. FOIA and
8 the EPA's CBI regulations may allow for information claimed as CBI provided to the EPA to be withheld from
9 the public, including in this document.

10 The EPA evaluated data from FracFocus 1.0, a national hydraulic fracturing chemical registry used and relied
11 upon by some states, industry groups and non-governmental organizations. A company submitting a
12 disclosure to FracFocus may choose to not report the identity of a chemical it considers CBI. As part of the
13 EPA's analysis, more than 39,000 FracFocus 1.0 disclosures over the period January 1, 2013 to March 1, 2013
14 were analyzed and more than 70% of disclosures contained at least one chemical designated as CBI. Of the
15 disclosures containing CBI chemicals, there was an average of five CBI chemicals per disclosure ([U.S. EPA,
16 2015a](#)). The prevalence of CBI claims in FracFocus 1.0 limits completeness of the data set.

17 Consistent with the hydraulic fracturing study plan, data were submitted by nine service companies to the
18 EPA regarding chemicals used in hydraulic fracturing from 2005 to 2009. Because this submission was to the
19 EPA, the EPA was given the actual names and CASRNs of any chemicals the company considered CBI. This
20 included a total of 381 CBI chemicals, with a mean of 42 CBI chemicals per company and a range of 7 to 213
21 ([U.S. EPA, 2013a](#)).

5.4.1. National Frequency of Use of Hydraulic Fracturing Chemicals

22 The EPA reported that 692 chemicals were reported to FracFocus 1.0 for use in hydraulic fracturing
23 from January 1, 2011, to February 28, 2013, with a total of 35,957 disclosures ([U.S. EPA, 2015a](#)).¹

24 Table 5-2 presents the 35 chemicals (5% of all chemicals identified in the EPA's study) that were
25 reported in at least 10% of the FracFocus 1.0 disclosures for all states reporting to FracFocus
26 during this time. This table also includes the top four additives that were reported to include the
27 given chemical in FracFocus disclosures from January 1, 2011 to February 28, 2013.

¹ The EPA reported that 692 chemicals were reported to FracFocus 1.0 for use in hydraulic fracturing from January 1, 2011, to February 28, 2013, with a total of 35,957 disclosures. 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 5-2. Chemicals reported to FracFocus 1.0 from January 1, 2011 to February 28, 2013 in 10% or more disclosures, with the percent of disclosures for which each chemical is reported and the top four reported additives for the chemical.

For chemicals with fewer than four reported additives, the table presents all additives ([U.S. EPA, 2015b](#)).

No.	Chemical name ^a	CASRN	Percent of disclosures ^b	Chemical used in these additives (four most common, FracFocus 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	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
14	Ethanol	64-17-5	29%	surfactants, biocides, corrosion inhibitors, fluid foaming agents and energizers

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No.	Chemical name ^a	CASRN	Percent of disclosures ^b	Chemical used in these additives (four most common, FracFocus database) ^c
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 ^e	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
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

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No.	Chemical name ^a	CASRN	Percent of disclosures ^b	Chemical used in these additives (four most common, FracFocus database) ^c
32	Tetrakis(hydroxymethyl)p hosphonium 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).

^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, was 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.

1 There is no single chemical used at all wells across the nation. Methanol is the most commonly used
2 chemical, reported at 72.1% of wells in FracFocus 1.0, and is associated with 33 types of additives,
3 including corrosion inhibitors, surfactants, non-emulsifiers, and scale control ([U.S. EPA, 2015b](#)).

4 Table 5-2 also shows the variability in different chemicals reported to FracFocus 1.0. The
5 percentage of disclosures reporting a given chemical suggests the likelihood of that chemical's use
6 at a site. Only three chemicals (methanol, hydrotreated light petroleum distillates, and hydrochloric
7 acid) were used at more than half of the sites nationwide, and only 12 were used at more than one-
8 third.

9 In addition to providing information on frequency of use, FracFocus 1.0 data provides the
10 maximum concentration by mass of a given chemical in an additive. For example, for the most
11 frequently used chemical, methanol, the median maximum additive concentration reported in
12 FracFocus disclosures is 30%, by mass, with a range of 0.44% to 100% (5th to 95th percentile). This
13 suggests that methanol is generally used as part of a mixture of chemicals in the hydraulic
14 fracturing fluid, and may be stored in a mixture of chemicals or as pure methanol. This wide range

1 of possible concentrations of methanol further complicates assessing the potential impact of spills,
2 as the properties of the fluid will depend on the different chemicals present and on their
3 concentrations. For all chemicals, spills of a highly concentrated chemical can have different
4 potential impacts than spills of dilute mixtures.

5.4.2. Nationwide Oil versus Gas

5 FracFocus 1.0 data also can elucidate the differences between the chemicals used for oil production
6 and those used for gas production, providing a better understanding of potential spill impacts from
7 each. Table C-1 and C-2 in Appendix C present the chemicals reported in at least 10% of all gas (34
8 chemicals) and oil (39 chemicals) disclosures nationwide.

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

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

16 We conducted a state-by-state analysis of chemical use based on FracFocus 1.0 disclosures ([U.S.
17 EPA, 2015b](#)). Some states reported more disclosures than other states, because they have relatively
18 more hydraulic fracturing activity and/or greater numbers of disclosures to FracFocus 1.0.
19 Reporting can bias national numbers towards those states with a disproportionate number of
20 disclosures. For example, the EPA ([2015a](#)) reported that Texas had 16,405 of the 34,675
21 disclosures with parsed ingredients and valid CASRNs and concentrations, making up almost half
22 (47%) of all disclosures for the 20 states reporting to FracFocus 1.0. We attempt to account for the
23 possible effect of having a large number of disclosures in Texas by looking at a compilation of the
24 top 20 chemicals reported to FracFocus for all states.

25 Table 5-3 presents and ranks chemicals reported most frequently to FracFocus 1.0 for each state
26 ([U.S. EPA, 2015b](#)). There are 94 unique chemicals comprising the top 20 chemicals for each state,
27 indicating similarity in chemical usage among states.

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

31 Ten chemicals (excluding water) are among the 20 most frequently reported in 14 of the 20 states.
32 These chemicals are: methanol; hydrotreated light petroleum distillates; ethylene glycol;

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.

1 isopropanol; quartz; sodium hydroxide; ethanol; guar gum; hydrochloric acid; and peroxydisulfuric
2 acid, diammonium salt.¹ These 10 chemicals are also the most frequently reported chemicals
3 nationwide.

4 By performing this analysis by state, we observed that methanol is used across the continental U.S.
5 (not Alaska), and there are 9 other chemicals that are frequently used across the U.S. Beyond those,
6 however, there are a number of different chemicals that are used in one state more commonly than
7 others and many may not be used at all in other states. This suggests that there is regional
8 variability in some chemicals and a common set of the same chemicals that are frequently used.

¹ Quartz was the most commonly reported proppant and also reported as an ingredient in other additives ([U.S. EPA, 2015a](#)).

Table 5-3. The percentage of disclosures of the 20 most commonly reported chemical by state, where a chemical is reported in at least three states.

The 20 most frequently reported chemicals were identified for all 20 states that reported to FracFocus 1.0 ([U.S. EPA, 2015b](http://www.epa.gov/fracfocus)). The chemicals were ranked by counting the number of states where that chemical was in the top 20. Chemicals were then ranked so that chemicals used most widely among the most states come first. Methanol is reported in 19 of 20 states, so methanol is ranked first. A chemical was only presented on the list if it were reported in at least three states, resulting in 33 chemicals. The full table of top 20 chemicals (91 chemicals) is presented in Appendix C.

Chemical name	CASRN	Percentage of disclosures per state ^a																			
		AL	AK	AR	CA	CO	KS	LA	MI	MS	MT	NM	ND	OH	OK	PA	TX	UT	VA	WV	WY
Methanol	67-56-1	100%		100%	39%	63%	79%	59%	93%	75%	63%	91%	53%	52%	70%	69%	78%	79%	61%	64%	38%
Distillates, petroleum, hydrotreated light	64742-47-8		45%	56%	55%	74%	90%	84%	100%	100%	60%	63%	47%	84%	70%	60%	66%	75%		82%	51%
Ethylene glycol	107-21-1	100%	100%	22%	60%		63%	34%	71%	75%	49%	45%	36%	57%	47%	34%	59%	85%	28%	59%	
Isopropanol	67-63-0	100%	65%	44%		57%	25%	51%	79%		64%	62%	37%	49%	42%	31%	48%	53%	54%	31%	43%
Quartz	14808-60-7		100%		89%	23%	23%	37%		50%	64%	68%	46%	45%	27%		43%	40%		22%	30%
Sodium hydroxide	1310-73-2		100%	21%	69%	22%	28%	53%		50%	54%	30%	52%		27%	17%	46%	37%			57%
Ethanol	64-17-5			45%		50%	80%	42%		100%		47%	27%	60%	46%	16%	21%		63%	54%	25%
Guar gum	9000-30-0		50%		93%			49%		50%	43%	63%	55%	51%	25%	23%	43%	43%		23%	69%
Hydrochloric acid	7647-01-0	100%		99%		53%	85%	57%			23%	79%		99%	76%	96%	71%	85%	86%	96%	
Peroxydisulfuric acid, diammonium salt	7727-54-0		50%		83%		22%	27%	57%		62%	75%	55%	64%	39%		54%	39%		54%	64%
Propargyl alcohol	107-19-7			61%			71%	30%	36%			68%		49%	41%	58%	39%	36%	28%	58%	
Glutaraldehyde	111-30-8			55%			75%	36%		50%		57%		72%	55%	34%	40%			71%	22%
Naphthalene	91-20-3	100%				30%	42%	29%	86%		49%		43%		25%			38%	9%		
2-Butoxyethanol	111-76-2	100%	100%						79%			37%				21%	24%	53%	89%	26%	

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Chemical name	CASRN	Percentage of disclosures per state ^a																			
		AL	AK	AR	CA	CO	KS	LA	MI	MS	MT	NM	ND	OH	OK	PA	TX	UT	VA	WV	WY
Citric acid	77-92-9						46%					40%		66%	36%	29%	24%	79%	80%	41%	
Sodium chloride	7647-14-5					35%		41%		50%			25%				21%		9%	22%	23%
Solvent naphtha, petroleum, heavy aromatics	64742-94-5					33%	43%				70%		49%		31%		17%		9%		35%
Quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl, chlorides	68424-85-1				28%						50%			37%	33%	16%					22%
2,2-Dibromo-3-nitrilopropionamide	10222-01-2	100%				49%			71%		36%					34%				28%	
Potassium hydroxide	1310-58-3							34%		100%	60%		59%	73%			39%				
Acetic acid	64-19-7					21%		28%							24%		31%				31%
Choline chloride	67-48-1					27%						34%		38%				52%	57%		
Polyethylene glycol	25322-68-3	100%							50%		36%		29%			29%					
1,2,4-Trimethylbenzene	95-63-6					27%	40%						25%						9%		
Ammonium chloride	12125-02-9			21%		28%										31%				21%	
Diatomaceous earth, calcined	91053-39-3		100%		71%							38%						35%			
Didecyl dimethyl ammonium chloride	7173-51-5			24%						50%				32%						21%	
Sodium chlorite	7758-19-2							35%		100%			24%								23%
Sodium erythorbate	6381-77-7			33%			30%												13%	32%	
N,N-Dimethylformamide	68-12-2													47%	20%			33%			

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Chemical name	CASRN	Percentage of disclosures per state ^a																			
		AL	AK	AR	CA	CO	KS	LA	MI	MS	MT	NM	ND	OH	OK	PA	TX	UT	VA	WV	WY
Nonyl phenol ethoxylate	9016-45-9											30%						36%	32%		
Poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy (mixture)	127087-87-0					25%	40%												9%		
Sodium persulfate	7775-27-1									100%						16%					26%
Tetramethylammonium chloride	75-57-0										44%		29%								26%

^a 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.

5.4.4. Volumes of Chemicals Used

1 Understanding the volume of chemicals used at each hydraulic fracturing site is important for
 2 understanding potential impacts of chemicals to drinking water resources, because the chemical
 3 volume governs how much will be stored on-site, the types of containers required, and the total
 4 amount that could spill. While the on-site operator has precise knowledge of the composition and
 5 volume of chemicals stored on-site, this information is generally not publicly available. We
 6 conducted a comprehensive review of publicly available sources and found two sources ([OSHA,](#)
 7 [2014a, b;](#) [Sjolander et al., 2011](#)) that identify specific chemicals used at a hydraulic fracturing site
 8 and provide information on volumes. These are presented in Table 5-4. The volume of chemicals
 9 totaled 7,500 gal (28,000 L) and 14,700 gal (56,000 L) for the two sources, with a mean volume for
 10 an individual chemical of 1,900 gal (7,000 L) and 1,225 gal (4,600 L), respectively. The range of
 11 volumes for each chemical used is 30 to 3,690 gal (114 to 14,000 L).

Table 5-4. Example list of chemicals and volumes used in hydraulic fracturing.

Volumes are for wells with and unknown number of stages and at least one perforation zone. Every well and fluid formation is unique. Volumes may be larger for longer horizontal laterals and with a greater number of stages.

Ingredient	Examples	Sjolander et al. (2011) ^a		Occupational Safety and Health Administration (OSHA, 2014a, b) ^b	
		Volume (gal) or mass (lbs)	Percent overall ^c	Volume (gal)	Percent by volume
Water		4,000,000 gal	94.62	2,700,000	90
Proppant	Sand	~ 1,500,000 lbs ^d	5.17	285,300	9.51
Acid	Hydrochloric acid or muriatic acid	1,338 gal	0.03	3,690	0.123
Friction reducer	Polyacrylamide, mineral oil	2,040 gal	0.05	2,640	0.088
Surfactant	Isopropanol			2,550	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			1,290	0.043

Ingredient	Examples	Sjolander et al. (2011) ^a		Occupational Safety and Health Administration (OSHA, 2014a, b) ^b	
		Volume (gal) or mass (lbs)	Percent overall ^c	Volume (gal)	Percent by volume
pH buffer	Carbonate			330	0.011
Preservative	Ammonium persulfate			300	0.01
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, ethanol, methanol	2,040 gal	0.05	30	0.001
Gel-breaker	Ammonium persulfate	- ^e	- ^e		
All chemicals		7,458 gal	0.21	14,700	0.49
Chemical Volume: Mean (full range)		1,864.5 gal (1,338 – 2,040 gal)		1,225 (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 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 The Penn State publication presented proppant in pounds instead of gallons.

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

1 Because of the limited information on chemical volumes publicly available, we estimated chemical
2 volumes used across the nation based on the information provided in the FracFocus database.
3 Figure 5-5 plots median estimated chemical volumes, ranked from high to low, with the range of 5th
4 to 95th percentiles.¹ Volumes used are presented for the 74 chemicals that were reported to
5 FracFocus in at least 100 disclosures and for which density data were available.² The estimated
6 median volumes vary widely among the different chemicals, covering a range of near zero to 27,000
7 gal (98,000 L). The mean of the estimated median volumes was 650 gal (2,500 L).³

8 With the median chemical volume, we can estimate total chemical volume for all chemicals used.
9 Based on the above mean of median chemical volumes of 650 gal (2,500 L) per chemical, and given
10 that the median number of chemicals used at a site is 14 ([U.S. EPA, 2015a](#)), an estimated 9,100 gal

¹ Volumes were estimated using FracFocus disclosures. The total hydraulic fracturing fluid volume reported was used to calculate the total fluid mass by assuming the fluid has a density of 1 g/mL. This is a simplifying assumption based on the fact that more than 93% of disclosures are inferred to use water as a base fluid. Water had a median concentration of 88% by mass in the fracturing fluid. Some disclosures reported using brine, which has a density between 1.0 and 1.1 g/mL. This would introduce at most an error of 10% for the fluid calculation (the difference of a chemical being present at 10 versus 9 gal, 1,000 versus 900 gal). We also assume that the mass of chemicals present in calculating the total fluid mass is negligible. Given that $\leq 2\%$ of the fluid volume is non-water chemicals, and assuming the density of which is 3 mg/L, the error introduced is approximately 6%. For reference, for the chemicals we are calculating volumes, chlorine dioxide is the densest at 2.757 mg/L. Chemical with densities less than 1 mg/L introduce approximately $<1\%$ error.

Next, the mass of each chemical per disclosure was calculated. Each chemical is reported to FracFocus 1.0 as a maximum concentration by mass in the hydraulic fracturing fluid. This introduces error, as we only know that it is equal to or less than this mass fraction. In the [U.S. EPA \(2015a\)](#) EPA's analysis of the FracFocus 1.0 database, an additive is comprised of three chemicals with maximum ingredient concentration of 60% in the additive and a maximum concentration of 0.22% in the hydraulic fracturing fluid. Each of the three chemicals cannot be present at 60%. We have no way to know the actual proportions of each chemical in the additive and thus must calculate chemical mass based on the given information. Therefore, our calculations likely overestimate actual volumes. However, in some cases, the concentration in the additive that is given is less than 100% and only one chemical is listed in the additive. In these cases, it appears that the disclosure is reporting the concentration of that chemical in water. Hydrogen chloride is listed as the sole ingredient in the acid additive, and the maximum concentration is 40% by mass. In this case, the HCl is diluted down to 40%, so the total volume would be underestimated.

After all the chemical masses are calculated, the volume is calculated by dividing chemical mass by density. Given the limited information available, due to the limits of the FracFocus database and general lack of publicly available data, and despite the errors associated with these calculations, these calculations provide context for the general magnitude of volumes for each of the chemicals used on-site. These calculations are used to calculate median volumes for each chemical. These volume calculations are for the chemicals themselves, not the additives.

Analysis considered 34,495 disclosures and 672,358 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; criteria for water volumes; valid CASRN; and valid concentrations. Disclosures that did not meet quality assurance criteria (4,035) or other, query-specific criteria were excluded from analysis.

² Density data were gathered from Reaxys® and other sources as noted. Reaxys® (<http://www.elsevier.com/online-tools/reaxys>) is an online database of chemistry literature and data. Direct density source, as provided by Reaxys®, is provided in Table C-7 in Appendix C.

³ Reporting records to FracFocus 1.0 was required in six of the 20 states between January 1, 2011 and February 28, 2013. An additional three states required disclosure to either FracFocus or the state, and five states required reporting to the state. Reporting to FracFocus 1.0 was optional in other states. Some states changed their reporting requirements during the course of the study. The FracFocus 1.0 database therefore does not encompass all data on chemicals used in hydraulic fracturing. As stated in Text Box 4-2, this mix of voluntary versus mandatory disclosure requirements limits the completeness of data extracted from FracFocus 1.0 for estimating hydraulic fracturing fluid. According to a comparison between FracFocus reported fluid volumes and literature values, water use per well was reported to be about 86% of the actual used (median of estimated values. See Chapter 4, Text Box 4-1). If the fluid volume is underreported, then estimated chemical volumes based on fluid volume would be similarly underestimated. Using the underreporting of 86%, then the estimated median chemical volume would be 760 gal.

1 (34,000 L) of chemicals may be used per well. Given that the number of chemicals per well ranges
2 from 4 to 28 (U.S. EPA, 2015a), the total volume of chemicals per well may range from 2,600 to
3 18,000 gal (9,800 to 69,000 L).

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

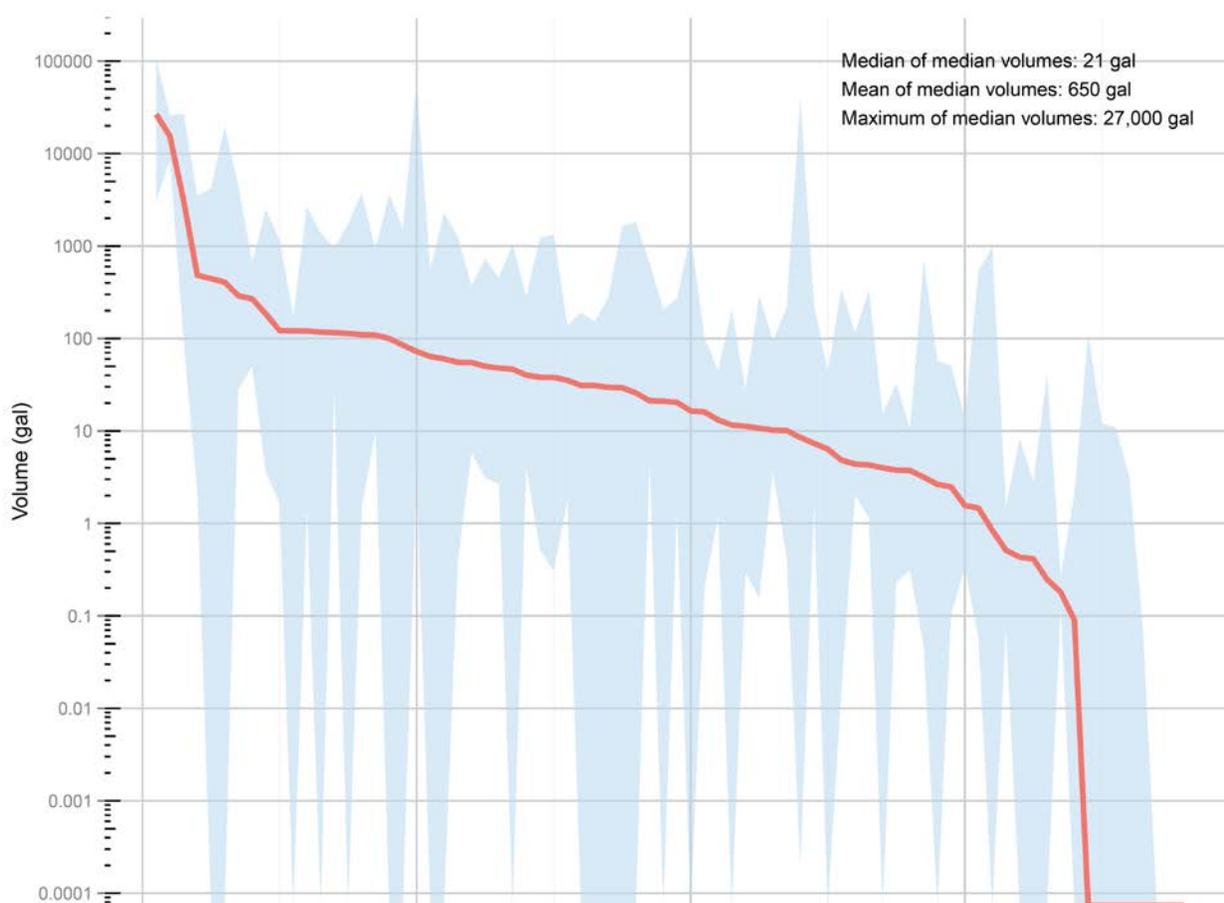


Figure 5-5. Estimated median volumes for chemicals reported in at least 100 FracFocus disclosures by February 28, 2013 for use in hydraulic fracturing from January 1, 2011 to February 28, 2013.

Shaded area represents the zone of 5% and 95% confidence limits. Derived from (U.S. EPA, 2015b).

8 Using the mean of the median chemical volumes from disclosures in FracFocus 1.0, we can also
9 estimate volume per additive and extrapolate to estimate on-site chemical storage. If we assume
10 three to five chemicals per additive, then total volume per additive stored on-site would
11 approximate 1,900 to 3,200 gal (7,400 to 12,000 L). On-site containers generally store 20% to

1 100% more additive volume than needed ([Houston et al., 2009](#); [Malone and Ely, 2007](#)). This would
2 suggest that 2,300 to 6,500 gal (8,800 to 25,000 L) per additive are stored on-site.

3 The volume that may be released during a spill depends on where in the chemical mixing process
4 the spill occurs. Spills from chemical or additive containers may result in higher volume spills than
5 the estimated volumes in Figure 5-5 suggest. However, if the spill is of the hydraulic fracturing fluid
6 downstream of the blender, then the total volume of chemical spilled may be less than the
7 estimated total volumes held on site.

5.5. Chemical Management and Spill Potential

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

17 Hydraulic fracturing operations are mobile and must be assembled at each well site, and each
18 assembly and disassembly presents a potential for spills. Equipment used in the chemical mixing
19 and well injection processes typically consists of chemical storage trucks, oil storage tanks/tanker
20 trucks; a slurry blender; one or more high-pressure, high-volume fracturing pumps; the main
21 manifold; surface lines and hoses; and a central control unit. There are many potential sources for
22 leaks and spills in this interconnected system.

23 Equipment varies in age and technological advancement depending upon service company
24 standards and costs associated with purchase and maintenance. Older equipment may have
25 experienced wear and tear, which may be a factor in spills caused by equipment failure. New
26 equipment may be more automated, reducing opportunities for human error. Information detailing
27 the extent of technological and age differences in fracturing equipment across sites and operators is
28 limited. Table 5-5 provides a description of typical hydraulic fracturing equipment.

Table 5-5. Examples of typical hydraulic fracturing equipment and their functions.

Equipment	Function
Acid transport truck	Transports acids to job sites, the truck has separate compartments for multiple acids or additives.
Chemical storage truck	Transport 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	Store the required volume of base fluid to be used in the hydraulic fracturing process.
Proppant storage units	Hold proppant and feed 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	Pressurize mixed fluids received from the blender and injected into the well.
Manifold trailer with hoses and pipes	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	A wellhead connection that allows fracture equipment to be attached to the well.

- 1 While the primary equipment and layout is generally the same across well sites, the type, size, and
 2 number of pieces of equipment may vary depending on a number of factors ([Malone and Ely, 2007](#)):
- 3 • The size and type of the fracture treatment;
 - 4 • The number of wells drilled per well pad;
 - 5 • The location, depth, and length of the fractures;
 - 6 • The volumes and types of additives, proppants, and fluids used; and
 - 7 • The operating procedures of the well operator and service company (e.g., some companies
 8 require backup systems in case of mechanical failure, while others do not).
- 9 Figure 5-6 provides a schematic diagram of a typical layout of hydraulic fracturing equipment.

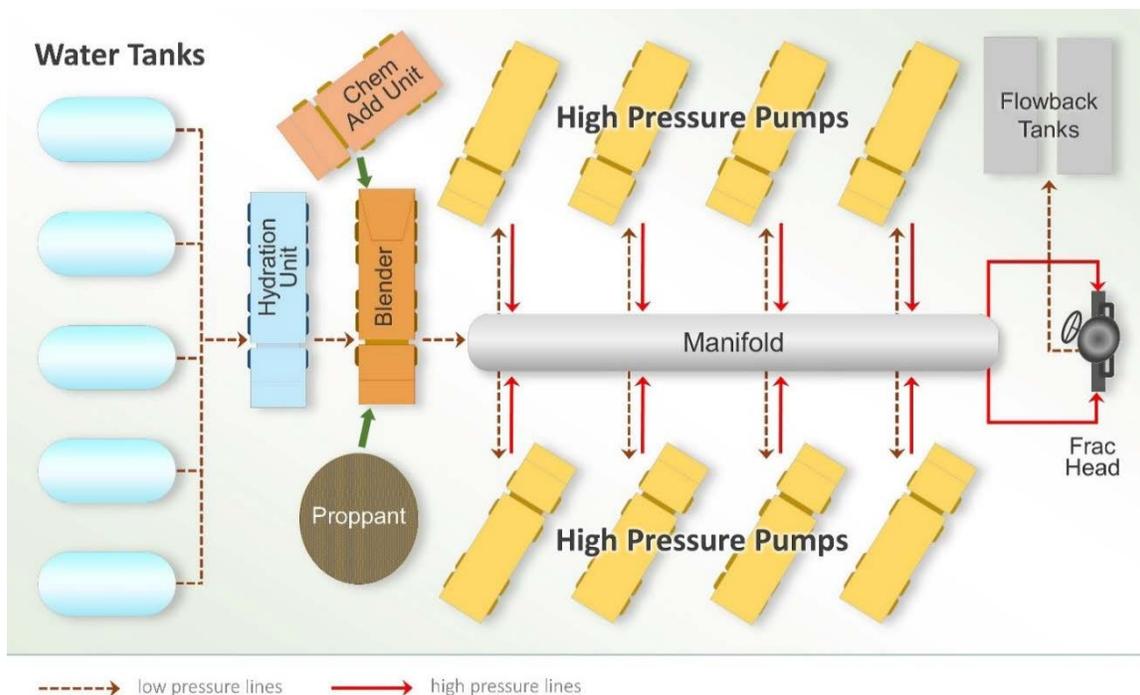


Figure 5-6. Typical hydraulic fracturing equipment layout.

This illustration shows how the various components of a typical hydraulic fracturing site fit together. 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

- 1 This section provides an overview of publicly available information on storage and containment of
- 2 chemicals used in the hydraulic fracturing process. Most public sources provide general
- 3 information on the types and sizes of containment units. While operators maintain a precise
- 4 inventory of volumes of chemicals stored and used for each site, this information is typically not
- 5 made public.
- 6 The volumes of each chemical used are based on the size and site-specific characteristics of each
- 7 fracture treatment. Sites often store an excess of the design volume of chemicals for contingency
- 8 purposes. Malone and Ely (2007) indicate that companies typically store an excess of 20% of the
- 9 required chemical inventories on location. Houston et al. (2009) recommends maintaining an on-
- 10 site chemical reserve of 100% extra beyond what is necessary for the fracturing treatment
- 11 (Houston et al., 2009). See Text Box 5-4 for documented spills from storage units.

Text Box 5-4. Spills from Storage Units.

1 Of the 151 spills of chemicals, additives, or fracturing fluid discussed and evaluated in ([U.S. EPA, 2015n](#)) (see
2 Text Box 5-13 for more information), 54 spills were from storage units. Storage units include smaller totes or
3 tanks used for storing individual chemicals or additives, and larger tanks containing fracturing fluid. These
4 spills resulted from equipment failure, failure of storage integrity, or human error. Sixteen of these spills were
5 due to failure of container integrity, which includes holes and cracks in containers, demonstrating the need
6 for properly constructed and maintained storage units. The remaining spills from storage containers resulted
7 from human error or equipment malfunctions, or had an unknown cause.

5.5.1.1. Hydraulic Fracturing Base Fluid Storage

8 Base fluids used in hydraulic fracturing are typically stored on-site in large volume tanks. Non-
9 water-based fluids may be stored in specialized containment units designed to prevent or minimize
10 releases. For example, nitrogen and carbon dioxide must be stored in compressed gas or cryogenic
11 liquid cylinders, as required by U.S. Department of Transportation (DOT) and OSHA regulations.
12 Due to the large volume of base fluid storage tanks (about 21,000 gal (80,000 L) ([Halliburton,
13 1988](#)), uncontrolled spills could damage other storage units and equipment, which could result in
14 additional spills. Fresh water used as a base fluid is generally not a source of concern for spills.
15 Reused wastewater, brine, and non-aqueous base fluids have the potential to adversely impact
16 drinking water resources in the event of a spill. An example of a documented spill of hydraulic
17 fracturing fluid is presented in Text Box 5-5.

Text Box 5-5. Spills of Fracturing Fluid Documented to Impact Surface Water.

18 In September 2009, two spills of hydraulic fracturing fluid occurred at the same site in Pennsylvania. A total
19 of approximately 7,350 gal (28,000 L) of fluid comprised of a mixture of water, gel, and friction reducer
20 leaked and migrated to Stevens Creek. While the causes of the spills are not clear, it appears that a
21 pressurized line may have broken and a seal may have failed ([U.S. EPA, 2015n, Appendix B Line 307;
22 Lustgarten, 2009](#)).

5.5.1.2. Chemical Additive Storage

23 Additives are typically stored on-site in the containers in which they were transported and
24 delivered. The chemical additive trailer typically consists of a flatbed truck or van enclosure that
25 holds a number of chemical totes, described below, and is equipped with metering pumps that feed
26 chemicals to the blender. Depending on the size and type of the fracturing operation, there may be
27 one or more chemical additive trailers per site ([ALL Consulting, 2012; NYSDEC, 2011](#)). Additives
28 constitute a relatively small portion of fluids used in a hydraulic fracturing fluid, although they can
29 still be used in volumes ranging from the tens to tens of thousands of gallons.

30 The storage totes generally remain on the transportation trailers, but they also may be unloaded
31 from the trailers and transferred to alternative storage areas before use. Our investigation did not
32 find much information on how often, when, or why these transfers occur. Additional transfers and

1 movement can increase the likelihood of a spill. See Text Box 5-6 for documented spills from an
2 additive storage unit.

Text Box 5-6. Spill from Additive (Crosslinker) Storage Tote.

3 During a tote transfer in Pennsylvania, a tote of crosslinker fell off a forklift, spilling approximately 15–20 gal
4 (60–80 L) onto the well pad. The area was scraped clean with a backhoe and placed in a lined containment
5 area ([U.S. EPA, 2015n, Line 309](#)).

6 The most commonly used chemical totes are 200–400 gal (760–1,500 L) capacity polyethylene
7 containers that may be reinforced with steel or aluminum mesh ([NYSDEC, 2011](#)). Metal containers
8 of the same capacity may also be used ([ALL Consulting, 2012](#); [UWS, 2008](#)). The totes are typically
9 equipped with bottom release ports, which enable the direct feed of the additives to the blending
10 equipment ([NYSDEC, 2011](#)). Spills may occur if lines are improperly connected to these ports or if
11 the connection equipment is faulty.



Figure 5-7. Metal and high-density polyethylene (HDPE) chemical additive units.

The image on the left depicts metal totes (industry source). The image on the right depicts plastic totes ([NYSDEC, 2011](#)).

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

15 Dry additives are typically transported and stored on flatbed trucks in 50 or 55 lb (23 or 25 kg)
16 bags, which are set on pallets containing 40 bags each ([NYSDEC, 2011](#); [UWS, 2008](#); [Halliburton,
17 1988](#)). Proppants are stored on-site in large tanks or bins with typical capacities of 220 to 440 lb
18 (100 to 200 kg) ([ALL Consulting, 2012](#); [BJ Services Company, 2009](#); [Halliburton, 1988](#)).

5.5.1.3. Acid Storage

1 Acids are generally stored on-site in the containment units in which they are transported and
2 delivered. A typical acid transport truck holds 3,000 to 5,000 gal (11,400 to 19,000 L) of acid and
3 can have multiple compartments to hold different kinds of acid ([Arthur et al., 2009b](#)). Acids such as
4 hydrochloric acid and formic acid are corrosive and can be extremely hazardous in concentrated
5 form. Therefore, acid transport trailers and fracture tanks must be lined with chemical-resistant
6 coating designed to prevent leakage and must meet applicable DOT regulatory standards (pursuant
7 to 40 CFR 173) designed to prevent or minimize spills.

8 Acid fracture treatments may use thousands of gallons (thousands of liters) of acid per treatment
9 ([Spellman, 2012](#)). Given the large volumes used, failure of containment vessels during storage or
10 failure of connections and hoses during pumping could result in high-volume acid spills. Eight spills
11 (out of 105 spills from state data sources) of acid or fracturing fluid containing acid were reported
12 to state data sources examined by the EPA ([2015n](#)). The median volume of these acid spills was
13 approximately 1,600 gal (6,000 L) (Lines 240, 241, 248, 258, 264, 272, 278, and 281 in Appendix B
14 of [U.S. EPA \(2015n\)](#)).

15 Details of a documented acid spill are presented in Text Box 5-7.

Text Box 5-7. Spill of Acid from Storage Container.

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

5.5.1.4. Gel Storage

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

5.5.1.5. Batch Mixing

24 In a typical batch mixing process, powdered gelling agents and related additives (e.g., buffers,
25 surfactants, biocides) are mixed on-site with base fluid water in large tanks (typically 20,000 gal or
26 76,000 L) ([BJ Services Company, 2009](#); [Halliburton, 1988](#)).

27 The number of gel slurry tanks used varies based on site-specific conditions and the size of the
28 fracture job. These tanks may be subject to leaks or overflow during the batch mixing process and
29 during storage prior to injection. One of the disadvantages of batch mixing is the need for multiple
30 suction hoses to draw pre-gelled fluids from storage tanks into the blender, which may increase the
31 potential for spills. [Yeager and Bailey \(2013\)](#) state that a drawback of batch mixing is the “fluid
32 spillage and location mess encountered when pre-mixing tanks,” suggesting that small spills are not

1 uncommon during batch mixing. Details of a documented gel slurry spill are presented in Text Box
2 5-8.

Text Box 5-8. Spill of Gel during Mixing.

3 On April 9, 2010, a company was mixing a gel slurry for an upcoming fracture job. The tank had developed a
4 crack, which allowed approximately 10,000 gal (38,000 L) of water mixed with 60 gal (230 L) of gel to leak
5 out. The mixture did not reach a water receptor, and absorbents were used to clean up the gel ([U.S. EPA,](#)
6 [2015n, Appendix B Line 220](#)).

5.5.1.6. Continuous Mixing (On-the-Fly)

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

5.5.2. Hoses and Lines

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



Figure 5-8. A worker adjusts hoses at a hydraulic fracturing site near Mead, Colorado.

Source: AP Photo/Brennan Linsley.

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

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

15 High-pressure flow lines convey pressurized fluids from the high-pressure pumps into the high-
16 pressure manifold, and from the manifold into the wellbore. High-pressure flow lines are subject to
17 erosion caused by the high-velocity movement of abrasive, proppant-laden fluid. Curved sections of
18 flow lines (e.g., swivel joints) where abrasive fluids are forced to turn corners are particularly
19 subject to erosion and are more likely to develop stress cracks or other defects that may result in a
20 leak or spill. Safety restraints are typically used to prevent movement of flow lines in the event of

1 failure and to help control spills. High-pressure flow lines are pressure-tested to detect fatigue or
2 stress cracks prior to the fracturing treatment ([OSHA, 2015](#); [BJ Services Company, 2009](#); [Arthur et](#)
3 [al., 2008](#); [Malone and Ely, 2007](#); [Halliburton, 1988](#)).

4 Nineteen spills of chemicals or fracturing fluids associated with leaks from hoses or lines had a total
5 spill volume of 12,756 gal (48,300 L), with a median volume of 420 gal (1,600 L) ([U.S. EPA, 2015n](#)).

5.5.3. Blender

6 The blender is the central piece of equipment used to create the fracturing fluid for injection. It
7 moves, meters, and mixes precise amounts of the base fluid, additives, and proppant and pumps the
8 mixed slurry to high-pressure pumping equipment ([BJ Services Company, 2009](#); [Malone and Ely,](#)
9 [2007](#); [Halliburton, 1988](#)). A typical blender consists of a centrifugal suction pump for pulling base
10 fluid, one or more chemical metering pumps to apportion the additives, one or more proportioners
11 to measure and feed proppant, and a central agitator tank where fluid components are mixed
12 together.

13 The blending process is monitored to ensure that a uniform mixture is maintained regardless of
14 injection rates and volumes. Excessive or reduced rates of flow during treatment can cause the
15 blender to malfunction or to shut down, which may result in spills. ([Malone and Ely, 2007](#);
16 [Halliburton, 1988](#)). For aqueous hydraulic fracturing fluid blends, spills that occur downstream of
17 the blender will be a dilute mixture comprised primarily of water with a low concentration (less
18 than or equal to 2%) of chemicals. Details of a spill from a blender are presented in Text Box 5-9.

Text Box 5-9. Spill of Hydraulic Fracturing Fluid from Blender.

19 In May 2006, a blender malfunctioned during a fracture job in Oklahoma. Approximately 294 gal (1,100 L) of
20 fluid spilled into a nearby wheat field. The fluid consisted of hydrochloric acid, clay stabilizer, diesel, and
21 friction reducer. Contaminated soil was removed by the operator ([U.S. EPA, 2015n, Appendix B Line 249](#)).

5.5.4. Manifold

22 A trailer-mounted manifold and pump system functions as a central transfer station for all fluids
23 used to fracture the well. The manifold is a collection of low- and high-pressure pipes equipped
24 with multiple fittings for connector hoses. Fluids are pumped from the blender through the low-
25 pressure manifold hoses, which distribute it to high-pressure pump trucks. Pressurized slurry is
26 sent from the pump trucks through high-pressure manifold lines and into additional high pressure
27 lines that lead to the wellhead ([Malone and Ely, 2007](#)).



Figure 5-9. Manifold (pointed to by the white arrow).

Source: Halliburton.

1 Manifold and pump system components require varying amounts of manual assembly and undergo
2 varying amounts of pre-testing ([Malone and Ely, 2007](#)). Improperly tested parts may be more likely
3 to break or lose functionality, leading to a spill. In manifolds requiring more manual assembly, there
4 may be more opportunities for human error. The EPA ([U.S. EPA, 2015n](#)) identified seven spills
5 sourced from manifolds. Three of these spills, out of the 105 chemical or hydraulic fracturing fluid
6 spills reported to state data sources, were fracturing fluid that resulted from either human error of
7 equipment failure. These three spills were responsible for approximately 5,000 gal (19,000 L) of
8 spilled fluids ([U.S. EPA, 2015n, Appendix B Lines 35, 141, 160](#)).

5.5.5. High-Pressure Fracturing Pumps

9 High-pressure fracturing pumps take the fracturing fluid mixture from the blender, pressurize it,
10 and propel it down the well. Typically, multiple high-pressure, high-volume fracturing pumps are
11 needed for hydraulic fracturing ([Upstream Pumping, 2015](#)). Such pumps come in a variety of sizes.
12 Bigger pumps move greater volumes of fluid at higher pressures; therefore, spills from these pumps
13 may be larger. Smaller pumps may require more operators and more maintenance ([BJ Services
14 Company, 2009](#)), and therefore may result in more frequent spills.



Figure 5-10. High-pressure pumps on either side of the manifold.

Source: http://drillingahead.com/roger-payne/gallery/14826/20000-psi-frac-near-caldwelltexas-2005#gallery_img.

- 1 The “fluid ends” of hydraulic fracturing pumps are the pump components through which fluids are
- 2 moved and pressurized. Pump fluid ends must withstand enormous pressure and move a large
- 3 volume of abrasive fluid high in solids content. They have multiple parts (e.g., seals, valves, seats
- 4 and springs, plungers, stay rods, studs) that can wear out under the stress of high-pressure
- 5 pumping ([Upstream Pumping, 2015](#)). Given the sustained pressures involved, careful maintenance
- 6 of fluid ends is necessary to prevent equipment failure ([Upstream Pumping, 2015](#); [API, 2011](#)).
- 7 Details of a documented spill from a fracture pump are presented in Text Box 5-10.

Text Box 5-10. Spill of Fluid from Fracture Pump.

- 8 In December 2011, a fluid end on a fracture pump developed a leak, spilling approximately 840 gal (3,200 L)
- 9 of fracturing fluid. A vacuum truck was used to recover the spilled fluid, and all affected soils were scheduled
- 10 to be neutralized and taken to a landfill at the end of the job, after removal of the equipment ([U.S. EPA, 2015n](#),
- 11 [Appendix B Line 14](#)).

5.5.6. Surface Wellhead for Fracture Stimulation

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



Figure 5-11. Multiple fracture heads.

Source: DOE/NETL.

6 As with all components of hydraulic fracturing operations, repeated and prolonged stress from
7 highly pressurized, abrasive fluids may lead to equipment damage. The presence of minute holes or
8 cracks in the frac head may result in leaks when pressurized fluids are pumped. In addition, surface
9 blowouts or uncontrolled fluid releases may occur at the frac head because of valve failure or
10 failure of other components of the assembly. Details of a documented frac head failure are
11 presented in Text Box 5-11. Details on the Killdeer, ND, blowout and associated spill are presented
12 in Text Box 5-12.

Text Box 5-11. Spill from Frac Head Failure.

1 On March 2, 2011, a frac head failed during fracturing operations in Colorado. Approximately 8,400 gal
2 (32,000 L) of slickwater fracturing fluid leaked. The majority of the spill was contained on-site, though a small
3 amount ran off into a nearby cornrow. Some of the fluid was recovered, and saturated soils were scraped and
4 stockpiled on the well pad ([U.S. EPA, 2015n, Appendix B Line 75](#)).

Text Box 5-12. The Killdeer Case Study.

5 In September 2010, a blowout occurred in the Franchuk 44-20 SWH well, in Dunn County near Killdeer, ND.
6 Hydraulic fracturing fluids, oil, and flowback water spilled onto the land and possibly entered the Killdeer
7 aquifer, which is a source of drinking water. The EPA investigated a reported blowout event at the Killdeer
8 site as part of a retrospective case study. The study area is comprised of historical oil and gas production and
9 current hydraulic fracturing. The discussion below was taken from the EPA Killdeer case study ([U.S. EPA,
10 2015j](#)).

11 **Methods**

12 Water quality samples were collected from three domestic wells, nine monitoring wells (installed by
13 Terracon), two supply wells, one municipal well, and one state well during three rounds in July 2011, October
14 2011, and October 2012. The geochemistry of water samples was investigated by analyzing major ions, trace
15 metals, methane/ethane gas concentrations, volatile organic compounds, semivolatile organic compounds,
16 glycol ethers, diesel- and gasoline-range organics, low-molecular-weight acids, and selected stable isotopes.
17 Data collected from this study were statistically compared with historical water quality data retrieved from
18 the literature and national water quality databases. To help determine whether hydraulic fracturing
19 processes were a cause of alleged impacts on water quality, detailed environmental record searches were
20 conducted to help identify other potential contaminant sources.

21 **Results**

22 Three study wells, NDGW09, NDGW08, and NDGW07, were excluded from the comparisons with historical
23 data. NDGW09 was excluded since it was screened in the Sentinel Butte aquifer so a comparison with
24 historical Killdeer aquifer water quality data was not appropriate. NDGW08 and NDGW07 had significant
25 differences in water quality compared to the remaining study wells. These two wells showed differences in
26 ion concentrations (e.g., chloride, calcium, magnesium, sodium, strontium) as well as tert-butyl alcohol (TBA).
27 The remaining study wells were then compared with historical data to determine if these wells represented
28 background water quality of the Killdeer aquifer. This comparison between the remaining study wells and
29 Killdeer aquifer historical water quality data indicated that these remaining study wells were in general
30 consistent with the historical background data and then used for the data analysis as background wells. There
31 were limited detections of other organic compounds in the study wells. In most cases, with the exception
32 of TBA, the detected organic compounds could not be directly linked to the blowout or hydraulic fracturing,
33 as these chemicals could have originated from other sources including vehicular traffic, generators used to
34 power well pumps, flaring of methane from the pad production wells, and cement used to repair a well the
35 day prior to sampling.

1 Comparisons of TBA between the study data and historical data could not be made since no historical data for
2 TBA were found for the Killdeer aquifer. TBA data were compared with the background study wells and were
3 found to be different. Based on the analysis of other potential sources of contamination, the EPA determined
4 that the only other potential sources of TBA were gasoline spills, leaky underground storage tanks, and
5 hydraulic fracturing fluids. The data from this study suggest the TBA resulted from the degradation of tert-
6 butyl hydroperoxide used during the hydraulic fracturing of the Franchuk well since MTBE and other
7 signature compounds associated with gasoline or fuels were not present in NDGW08 and NDGW07.

8 **Conclusion**

9 The analysis of data from NDGW008 and NDGW07 indicated that the main impact on water quality was from
10 briny water and TBA mixing with Killdeer aquifer water in these wells. In all cases, the fingerprinting
11 techniques used indicated that the impacts on NDGW07 and NDGW08 were consistent with deep formation
12 brines underlying the Killdeer study location. Based on the data analysis performed for the Killdeer case
13 study, the observed impacts on NDGW07 and NDGW08 were likely caused by the blowout that occurred at
14 the Franchuk 44-20. This evidence, along with the absence of another plausible candidate cause, strongly
15 suggests impact on a drinking water resource from the blowout during the hydraulic fracturing of the
16 Franchuk 44-20 SWH well.

5.6. Spill Prevention, Containment, and Mitigation

17 Several factors influence spill prevention, containment, and mitigation, including Federal, State, and
18 local regulations and company practices. State regulations governing spill prevention, containment,
19 and mitigation at hydraulic fracturing facilities vary in scope and stringency ([Powell, 2013](#); [GWPC,
20 2009](#)). Employee training and equipment maintenance are also factors in effective spill prevention,
21 containment, and mitigation. Analysis of these factors was outside the scope of this assessment.

22 Hydraulic fracturing operating companies themselves may develop and implement spill prevention
23 and containment procedures. The American Petroleum Institute has a guidance document *Practices
24 for Mitigating Surface Impacts Associated with Hydraulic Fracturing* ([API, 2011](#)). The document
25 describes practices currently used in the oil and natural gas industry to minimize potential surface
26 environmental impacts. As another example, the province of New Brunswick, Canada, released
27 rules for industry on responsible environmental management of oil and natural gas activities ([GNB,
28 2013](#)). It was beyond the scope of this assessment to evaluate the efficacy of the practices in these
29 documents or the extent to which they are implemented.

30 Spill containment systems include primary, secondary, and emergency containment systems.
31 Primary containment systems are the storage units, such as tanks or totes, in which fluids are
32 intentionally kept. Secondary containment systems, such as liners and berms installed during site
33 set-up, are intended to contain spilled fluids until they can be cleaned up. Emergency containment
34 systems, such as berms, dikes, and booms, can be implemented temporarily in response to a spill.

35 The EPA investigated spill containment and mitigation measures in an analysis of spills related to
36 hydraulic fracturing activities ([U.S. EPA, 2015n](#)). Of the approximately 25% of reports that included
37 information on containment, the most common types of containment systems referenced in the
38 hydraulic fracturing-related spill records included berms, booms, dikes, liners, and pits, though

1 many of the spill reports did not indicate specific containment measures. Some spills were reported
2 to breach the secondary containment systems. Breaches of berms and dikes were most commonly
3 reported.

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

10 Remediation is the action taken to clean up a spill and its affected environmental media. The most
11 commonly reported remediation activity, mentioned in approximately half of the hydraulic
12 fracturing-related spill records evaluated by the EPA, was removal of spilled fluid and/or affected
13 media, typically soil ([U.S. EPA, 2015n](#)). Other remediation methods reported by the EPA ([U.S. EPA,
14 2015n](#)) included the use of absorbent material, vacuum trucks, flushing the affected area with
15 water, and neutralizing the spilled material.

5.7. Overview of Chemical Spills Data

16 Spills of hydraulic fracturing fluids have occurred across the country and have affected the quality
17 of drinking water resources ([U.S. EPA, 2015n](#); [Brantley et al., 2014](#); [COGCC, 2014](#); [Gradient, 2013](#)).
18 Spills may infiltrate drinking water resources by reaching surface water, or by leaching into the
19 ground water. Potential impacts depend upon a variety of factors including the chemical spilled,
20 environmental conditions, and actions taken in response to the spill. However, due to a lack of
21 available data, little is known about the prevalence and severity of actual drinking water impacts.

5.7.1. EPA Analysis of Spills Associated with Hydraulic Fracturing

22 The EPA ([2015n](#)) (see Text Box 5-13 for additional information) evaluated 457 spills related to
23 hydraulic fracturing activities on or near the well pad. Of these spills, 151 spills were of chemicals,
24 additives, or fracturing fluids. Information in the spill reports included: spill causes (e.g., human
25 error, equipment failure), sources (e.g., storage tank, hose or line), volumes, and environmental
26 receptors.

Text Box 5-13. EPA Review of State and Industry Spill Data: Characterization of Hydraulic Fracturing-Related Spills.

27 The EPA ([2015n](#)) used data gathered from select state and industry sources to characterize hydraulic
28 fracturing-related spills with respect to volumes spilled, materials spilled, sources, causes, environmental
29 receptors, containment, and responses. For the purposes of the study, hydraulic fracturing-related spills were
30 defined as those occurring on or near the well pad before or during the injection of hydraulic fracturing fluids
31 or during the post-injection recovery of fluids. Because the main focus of this study is to identify hydraulic
32 fracturing-related spills on the well pad that may reach surface or ground water resources, the following
33 topics were not included in the scope of this project: transportation-related spills, drilling mud spills, and
34 spills associated with disposal through underground injection control wells.

1 Data on spills that occurred between January 2006 and April 2012 were obtained from nine states with
2 online spill databases or other data sources, nine hydraulic fracturing service companies, and nine oil and gas
3 production well operators. The data sources used in this study contained over 36,000 spills. The EPA
4 searched each spill report for keywords related to hydraulic fracturing (e.g., frac, glycol, flowback). Spill
5 records from approximately 12,000 spills (33 percent of the total number of spills reviewed) contained
6 insufficient information to determine whether the event was related to hydraulic fracturing. Of the spills with
7 sufficient information, the EPA identified approximately 24,000 spills (66%) as not related to hydraulic
8 fracturing on or near the well pad. The remaining 457 spills (approximately 1%) occurred on or near the well
9 pad and were definitively related to hydraulic fracturing. These 457 spills occurred in 11 different states over
10 six years (January 2006 and April 2012).

11 The EPA categorized spills according to the following causes: equipment failure, human error,
12 failure of container integrity, other (e.g., well communication, weather, vandalism), and unknown.
13 Figure 5-12 presents the percent distribution of chemical or fracturing fluid spills associated with
14 each cause. Over half of the spills were collectively caused by equipment failure (34%) and human
15 error (25%). Approximately one-quarter of the spill causes were unknown or not reported. A
16 report analyzing spills in Colorado is generally consistent with the EPA's findings ([COGCC, 2014](#)).¹
17 Colorado found that equipment failure was the dominant spill cause, accounting for over 60% of
18 spills between 2010 and 2013, followed by human error accounting for 20%–25% of spills.

¹ The COGCC report included all materials related to oil and gas production and were therefore not specific to chemical and fracturing fluid spills.

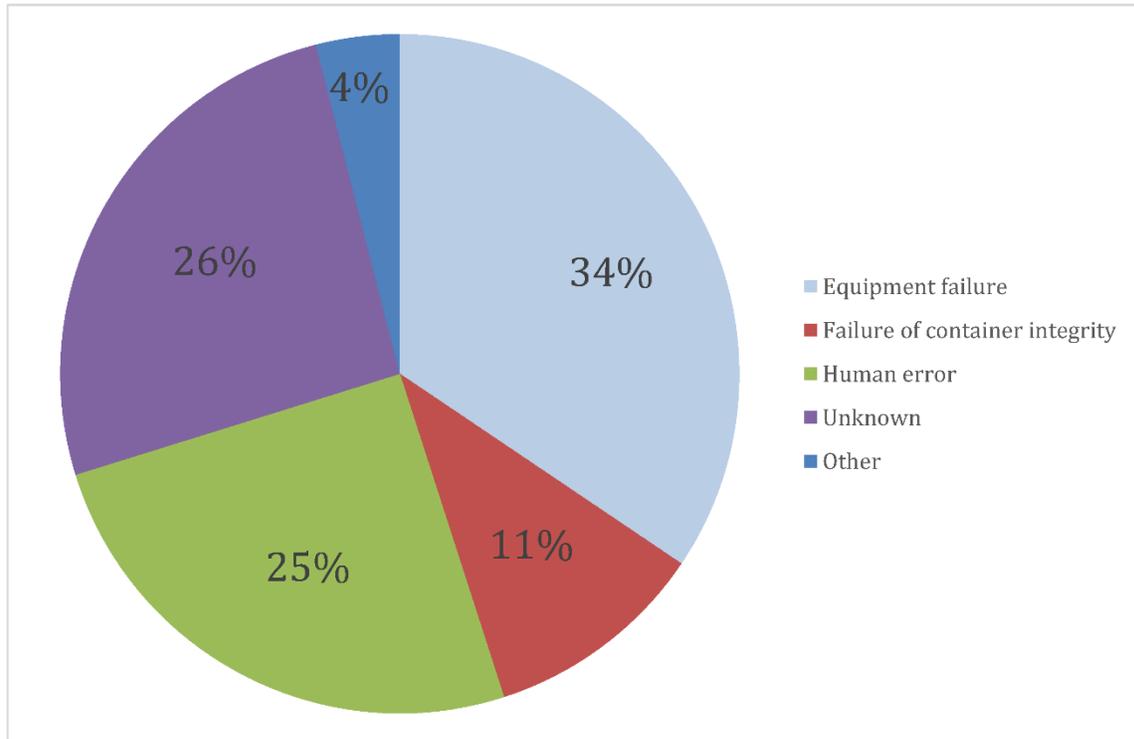


Figure 5-12. Distribution of the causes of 151 hydraulic fracturing-related spills of chemicals and fracturing fluid.

Data from [U.S. EPA \(2015n\)](#).

- 1 Spills in the EPA Spills Report were also categorized by the following sources: storage, equipment,
- 2 well or wellhead, hose or line, and unknown. Figure 5-13 presents the percent distribution for the
- 3 chemical or fracturing fluid spills associated with each source. Storage units (e.g., chemical totes,
- 4 fracturing fluid tanks) were the predominant source of spills, accounting for 36% (54 spills) of spill
- 5 sources. Spills from storage units were predominantly caused by human error (39%), followed by
- 6 failure of container integrity (30%). Spills from equipment were the next most common known
- 7 source (18%), followed by spills from hoses or lines (13%). Twenty-eight percent of spills had an
- 8 unknown source.

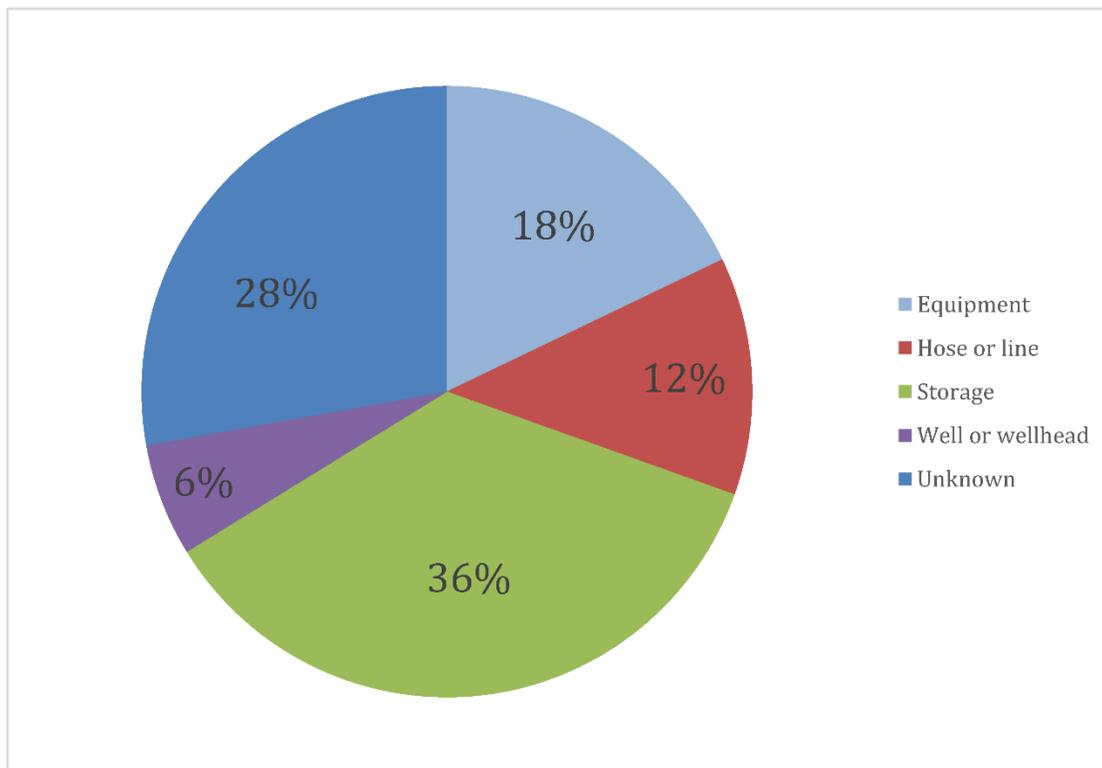


Figure 5-13. Percent distribution of sources of 151 hydraulic fracturing-related spills of chemicals or fracturing fluid.

Data from [U.S. EPA \(2015n\)](#).

1 The reported total volume of 125 of 151 chemical or hydraulic fracturing fluid spills was
2 approximately 184,000 gal (697,000 L). The volume was unknown for 26 of these spills. The spills
3 ranged in volume from 5 to more than 19,000 gal (19 to 72,000 L), with a median volume of 420 gal
4 (1,600 L). The largest source of spills was storage containers, which released approximately 83,000
5 gal (314,000 L) of spilled fluid. Spills from wells or wellheads are often associated with high spill
6 volumes. Nine instances of spills at the well or wellhead were associated with approximately
7 46,000 gal (174,000 L) of spilled fluid (see Figure 5-14). The high pressure associated with frac
8 head blowouts has led to large, high-volume spills (see Text Box 5-11).

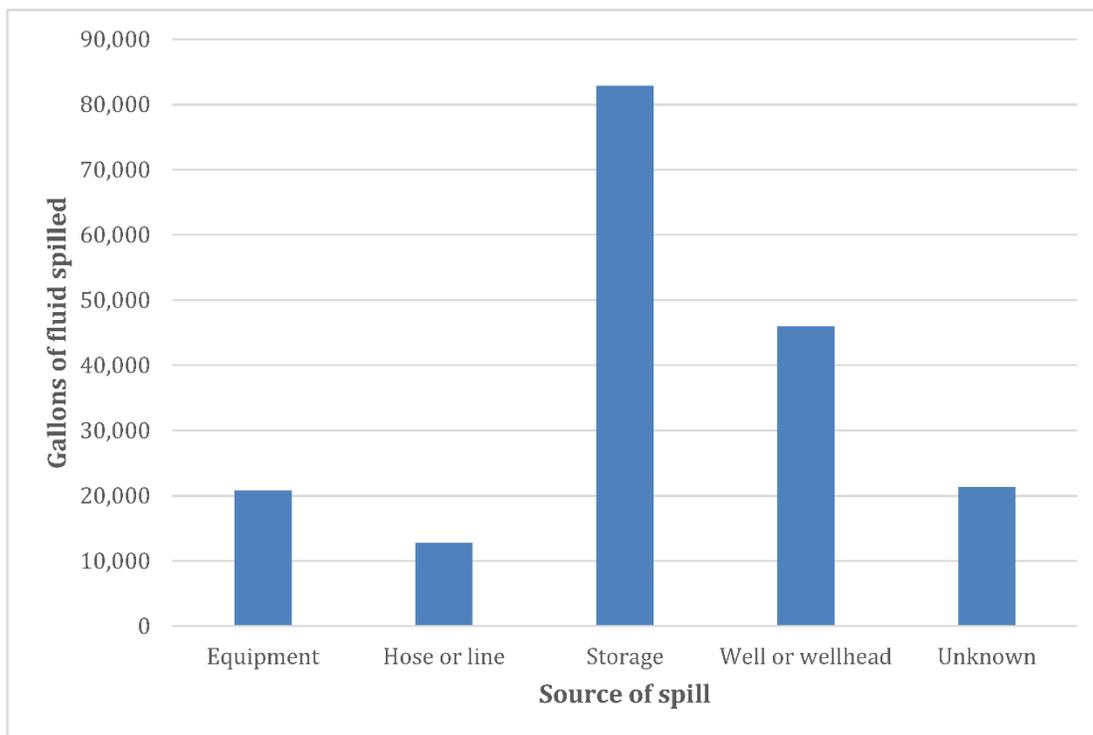


Figure 5-14. Total volume of fluids spilled for 151 hydraulic fracturing-related spills of chemicals and fracturing fluid, by spill source.

Data from [U.S. EPA \(2015n\)](#).

1 Figure 5-15 presents the number of chemical or fracturing fluid spills that reached environmental
 2 receptors, by receptor type. Environmental receptors (i.e., surface water, ground water, soil) were
 3 identified for 101 of the 151 spills, or 67% of the spills in the EPA’s analysis ([U.S. EPA, 2015n](#)). Soil
 4 was by far the dominant environmental receptor, with 97 spills reaching soil. Thirteen spill reports
 5 indicated that the spilled fluid had reached surface water. Nine spill reports identified both soil and
 6 surface water as a receptor. No spill report identified ground water as a receptor. The data contain
 7 few post-spill analyses, so ground water contamination may have occurred but have not been
 8 identified. Additionally, several years may be required for a spilled fluid to leach into the ground
 9 water and therefore impact on a ground water receptor may not be immediately apparent. Storage
 10 units were the predominant sources of spills reaching an environmental receptor.

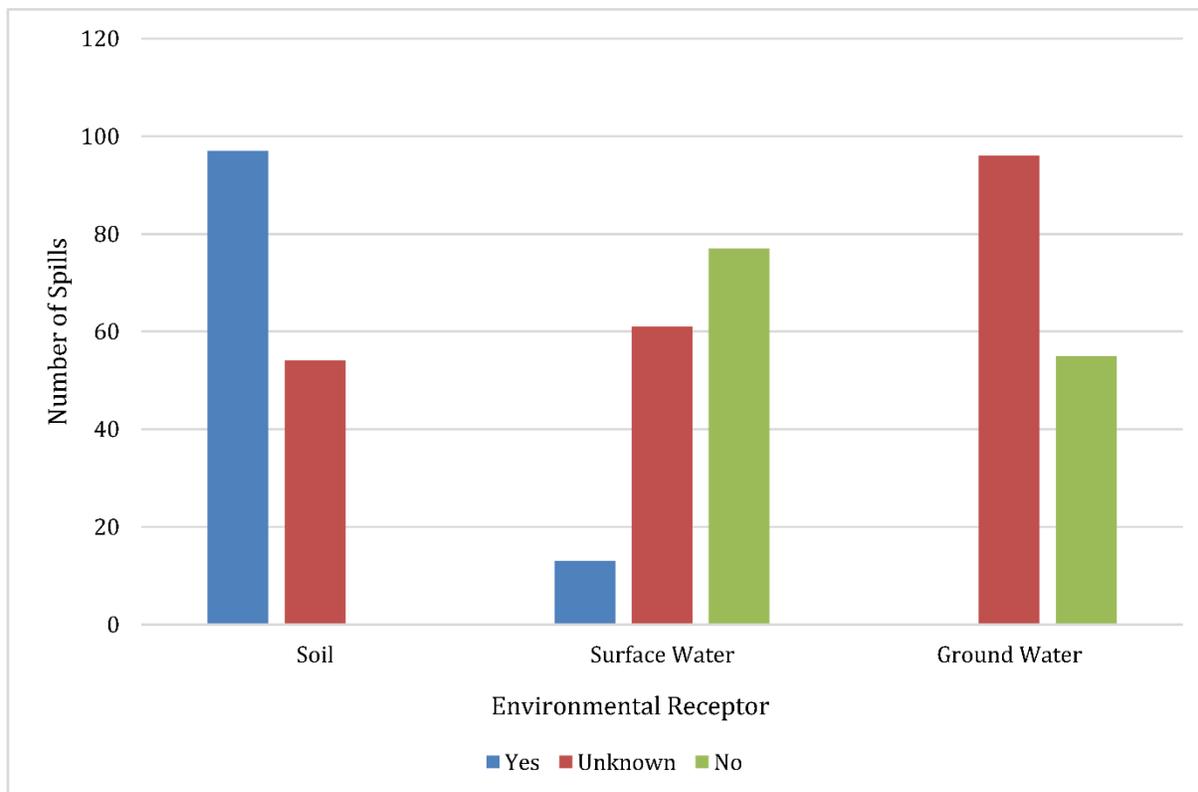


Figure 5-15. Number of hydraulic fracturing-related spills of chemicals or fracturing fluid that reported whether an environmental receptor was reached.

“Unknown” refers to hydraulic fracturing related spill events for which environmental receptors were specified as unknown or not identified (positively or negatively).

Data from [U.S. EPA \(2015n\)](#).

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

7 The EPA analysis demonstrates that spills of chemicals, additives, and fracturing fluids do occur at
 8 well sites and reach both soil and surface water receptors.

5.7.2. Other Spill Reports

9 Surface spills related to hydraulic fracturing activities are not well documented in the scientific
 10 literature, though some evidence of spills and impacts to environmental media exists (e.g., [U.S. EPA](#),

1 [2015j](#); [Brantley et al., 2014](#); [Gross et al., 2013](#); [Papoulias and Velasco, 2013](#)). For example,
2 [Papoulias and Velasco \(2013\)](#) demonstrated that fracturing fluid spilled into surface water likely
3 contributed to the distress and deaths of the threatened blackside dace fish in Kentucky. A variety
4 of chemicals entered the creek and significantly reduced the stream's pH and increased stream
5 conductivity. Using data from post-spill sampling reports in Colorado, [Gross et al. \(2013\)](#) identified
6 concentrations of benzene, toluene, ethylbenzene, and xylene in ground water samples, which the
7 authors attributed to numerous hydraulic fracturing-related spills. The [COGCC \(2014\)](#) published a
8 report analyzing all spills reported to the state of Colorado between 2010 and 2013, and found that
9 approximately 8% of them were related to hydraulic fracturing. Based on the EPA's analyses ([U.S.
10 EPA, 2015n](#)) and available scientific data, we estimate spill rates of chemicals and hydraulic
11 fracturing fluid range from 0.4 and 12.2 spills for every 100 wells. (See Text Box 5-14 for additional
12 information.)

Text Box 5-14. Spill Rates.

13 Several studies have estimated the frequency of hydraulic fracturing-related spills. Three studies ([Rahm et al.,
14 2015](#); [Brantley et al., 2014](#); [Gradient, 2013](#)) calculated a spill rate for the Marcellus Shale in Pennsylvania
15 using reports from the Pennsylvania Department of Environmental Protection (PA DEP) Oil and Gas
16 Compliance Report Database, and here we estimate an on-site spill rate for Colorado. The PA DEP database
17 provides a searchable format based on Notices of Violations from routine inspections or investigations of spill
18 reports or complaints. Each study had different criteria for inclusion, presented in Table 5-6, resulting in a
19 range of rates even when using the same data source. Spills of hydraulic fracturing fluids, flowback/produced
20 water are estimated to occur at a rate of 0.4 per 100 wells fractured. Spills related to hydraulic fracturing
21 activity are estimated to occur at a rate between 3.3 to 12.2 spills per 100 wells installed (PA DEP data) (see
22 Table 5-6).

23 In its study of spills related to hydraulic fracturing, the EPA determined that spill reports from the Colorado
24 Oil and Gas Conservation Commission (COGCC) Information System were the most detailed spill reports from
25 among the nine state data sources investigated and generally provided more of the information needed to
26 determine whether a spill was related to hydraulic fracturing ([U.S. EPA, 2015n](#)). Here, we estimate the spill
27 rate in Colorado by dividing the number of hydraulic fracturing-related spills identified by the EPA ([U.S. EPA,
28 2015n, Appendix B](#)) (Appendix B in U.S. EPA, 2015b) by the number of wells hydraulically fractured in
29 Colorado for specific time periods between January 2006 and April 2012. We used three data sources to
30 estimate the number of wells: (1) there were 172 reported spills in Colorado for the 15,000 wells fractured
31 from January 2006 to April 2012 ([DrillingInfo, 2012](#)), (2) there were 50 reported spills in Colorado for the
32 3,559 wells fractured from January 2011 to April 2012 ([U.S. EPA, 2015b](#)), and (3) there were 41 reported
33 spills in Colorado for the 3,000 wells fractured from September 2009 to October 2010 ([U.S. EPA, 2013a](#)).
34 From these data we estimate an average of 1.3 reported spills on or near the well pad for every 100
35 hydraulically fractured wells.

36

Table 5-6. Estimations of spill rates.

Spill rates from four different sources. Each source used different criteria to identify and include spills in their analysis.

Spill rate ^a	Data source	Time period	Inclusion criteria	Information source
0.4	PA DEP ^b Media	2008–2013	Volume spilled > 400 gal; Spill reported to reach water body.	Brantley et al. (2014) ^d
3.3	PA DEP ^b	2009-2012	“Unconventional” well; Spills with unknown volumes not included, Includes any spill during HF activities	Gradient (2013) ^e
12.2	PA DEP ^b	2007-July 2013	“Unconventional” well based on environmental violation rates.	Rahm et al. (2015) ^e
1.3	COGCC ^c	Jan 2006 – May 2012	Specifically related to hydraulic fracturing on or near well pad	U.S. EPA (2013a) ^d

^aSpill rate is the number of reported spills per 100 wells.

^bPA DEP (http://www.depreportingservices.state.pa.us/ReportServer/Pages/ReportViewer.aspx?/Oil_Gas/OG_Compliance)

^cCOGCC (<https://cogcc.state.co.us/cogis/IncidentSearch.asp>)

^dSpill rate is calculated as the number of spills per 100 wells fractured.

^eSpill rate is calculated as the number of spills per 100 wells installed.

Text Box 5-14 (Spill Rates), continued:

1 The spill rates presented in Table 5-6 are based on spill reports found in two state data sources and are
2 limited by both the spills reported in the state data sources and the inclusion criteria defined by each of the
3 studies. Spills identified from state data sources are likely a subset of the total number of spills that occurred
4 within a state for a specified time period. Some spills may not be recorded in state data sources because they
5 do not meet the spill reporting requirements in place at the time of the spill. Additionally, the PA DEP Notices
6 of Violation may include spills not specifically related to hydraulic fracturing, such as spills of drilling fluids.

7 The inclusion criteria used by each of the studies affects which spills are used to calculate a spill rate. More
8 restrictive criteria, such as only counting spills that were greater than 400 gallons, results in a lower number
9 of spills being used for estimating spill rates, while less restrictive criteria, such as all spills from wells
10 marked unconventional in the PA DEP database, results in a greater number of spills being used for
11 estimating spill rates. Rahm et al. applied the least restrictive criteria of the four studies (i.e., spills from
12 unconventional wells) when identifying spills, while Brantley et al. applied more restrictive criteria (i.e., spills
13 of >400 gallons in which spilled fluids reached a surface water body). This may account for the different spill
14 rates calculated by these two studies.

15 Based on previous studies and the analysis here, hydraulic fracturing-related spills rates in Pennsylvania and
16 Colorado range from 0.4 and 12.2 per 100 wells. These numbers may not be representative of national spill
17 rates or rates in other regions. If this range is applied nationally however, assuming between 25,000 and
18 30,000 wells are fractured each year, we would expect between approximately 100 and 3,700 spills annually
19 from hydraulic fracturing.

5.8. Fate and Transport of Chemicals

20 This section provides an overview of fate and transport of the range of chemicals used in hydraulic
21 fracturing fluid, including the physicochemical properties of these chemicals, and an overview of
22 the potential for a spilled chemical to affect drinking water resources. A general overview of the
23 processes governing the fate and transport of a chemical spill is shown in Figure 5-16. A chemical
24 spill has the potential to migrate to and have an impact on drinking water resources. Once spilled,
25 there are different paths that chemicals can travel and different processes they may undergo.

26 Chemicals may react and transform into other chemicals, volatilize, travel to surface water, leach
27 into and partition to soils, and/or reach ground water. The potential path and the severity of the
28 impact of a spill depend on different factors, including the site conditions; environmental
29 conditions; climate; weather; and chemical properties, concentration, and volume of the release.

30 The point in the chemical mixing process where the spill occurs affects potential impact. If the spill
31 occurs before chemicals are mixed into the base fluid, the chemicals will spill in their most
32 concentrated form. If the hydraulic fracturing fluid spills, then the chemicals will be more diluted,
33 and there may be effects on persistence and mobility due to interactions among chemicals present.

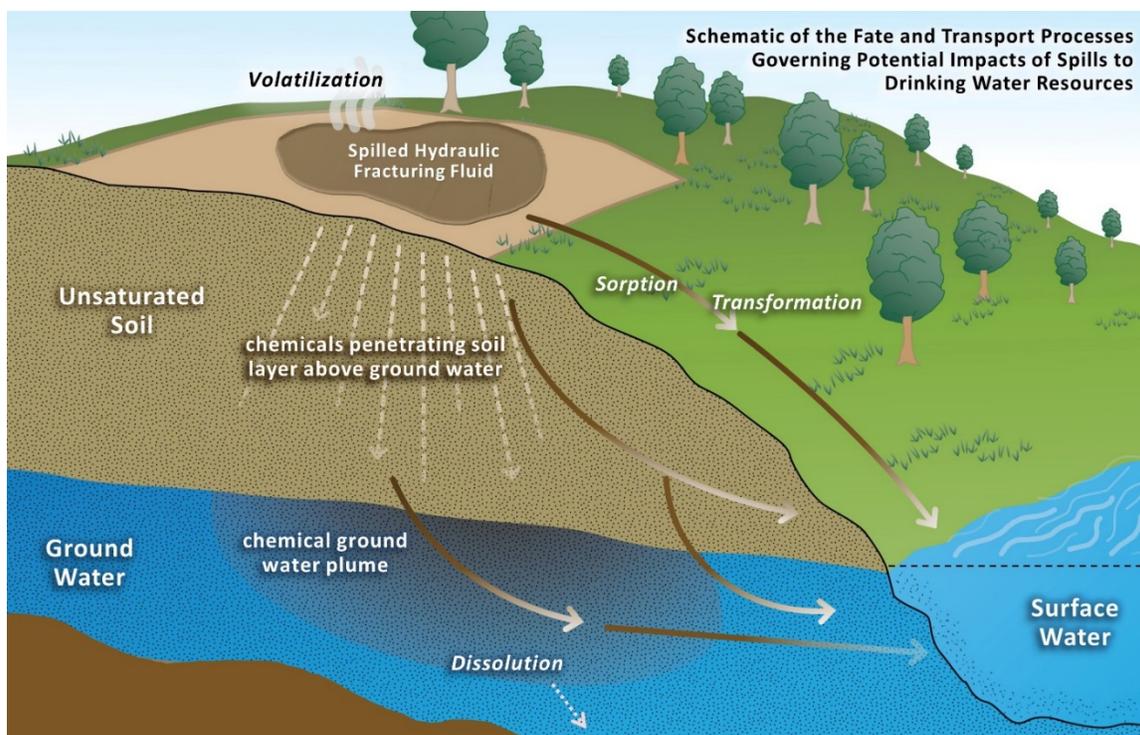


Figure 5-16. Fate and transport schematic for a spilled hydraulic fracturing fluid.

Schematic shows the potential paths and governing processes that spilled chemicals, which may lead to potential impacts to drinking water resources.

- 1 For inorganic chemicals, the properties and processes governing fate and transport depend on pH,
 2 oxidation state, presence of iron oxides, soil organic matter, cation exchange capacity, and major ion
 3 chemistry ([U.S. EPA, 1996](#)).¹ Transport of these chemicals into ground water depends on the nature
 4 of ground water flow and flow through the unsaturated zone above the water table. Potential
 5 transformations of inorganic chemicals differ from those of organic chemicals.² Some inorganic
 6 anions (i.e., nitrate, chloride, and bromide) move with their carrier liquid and are affected mostly by
 7 physical transport mechanisms. For many inorganic chemicals, transport is driven by the physical
 8 flow processes (advection and dispersion), sorption, and precipitation. The relative role of each of
 9 these depends on both chemical and environmental characteristics.^{3,4}
- 10 Determining the fate and transport of organic chemicals and mixtures is a complex problem,
 11 because of the many processes and different environmental media (air, soil, water) that can have an

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, hence “unsaturated zone.”

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.

1 impact. Unlike inorganic chemicals, organic chemicals degrade, which may affect their movement
2 and potential impact. [Schwarzenbach et al. \(2002\)](#) formalized a general framework for organic
3 chemical transport, where transport and transformation depend on both the nature of the chemical
4 and the properties of the environment. The fate and transport of organic compounds in soils has
5 been presented in the literature (e.g., [Bouchard et al., 2011](#); [Rivett et al., 2011](#); [Abriola and Pinder,](#)
6 [1985a, b](#)) and in textbooks (e.g., [Domenico and Schwartz, 1997](#); [Schnoor, 1996](#); [Freeze and Cherry,](#)
7 [1979](#)).

5.8.1. Potential Paths

8 Chemicals, additives, and hydraulic fracturing fluids that are released into the environment travel
9 along different potential paths, as detailed in Figure 5-16. Liquids may flow overland to nearby
10 surface water or infiltrate the subsurface, where they may eventually reach the underlying ground
11 water or travel laterally to reach surface water. Movement can occur quickly or be delayed and
12 have a later or longer-term impact. Surface water and ground water gain or lose flow to each other,
13 and may transport chemicals in the process.

14 A dry chemical (e.g., gelling agents, biocides, friction reducers) released to the environment will
15 generally remain where it is spilled. Any spill that is not removed could act as a long-term source of
16 contamination. Wind could cause the chemical to disperse, or rain could dissolve a soluble chemical.
17 Dissolved chemicals may infiltrate into soil or flow overland. Insoluble chemicals and those sorbed
18 to soil particles could be mobilized by rain events via runoff and erosion.

5.8.1.1. Movement across the Land Surface

19 In low permeability soils, there may be little infiltration and greater overland flow. Higher
20 permeability soils will allow fluid to penetrate into the soil layer. In either case, some of the
21 chemicals in the fluid may sorb to the soil particles and the vegetation, and then these chemicals
22 may be mobilized during rainfall, runoff, or erosion. As rainwater percolates through the soil, it may
23 dissolve stored chemicals, which can then migrate toward ground water.

24 The type of release is also important. If the spill is a slow leak, then the liquid may pond and the
25 affected area will expand slowly. If a more rapid release occurs, like a blowout or tank failure, then
26 momentum may result in greater overland movement and less soil infiltration during the event.

5.8.1.2. Movement through the Subsurface

27 The unsaturated and saturated zones are the two zones of soils below the ground surface.
28 Movement through the unsaturated zone is driven by the depth of ponding of the spilled fluid,
29 gravity, and capillary properties of the subsurface.¹ In fractured rock or highly permeable soils,
30 fluids may move quickly through the subsurface. In low permeability soil, the movement of the fluid
31 is slower. As chemicals pass through the subsurface, some may sorb to soil or remain in the open
32 spaces between soil particles, effectively slowing their movement. Chemicals may again be

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

1 mobilized during future precipitation events, resulting in infiltration towards ground water or
2 movement through the unsaturated zone towards surface water.

3 Fluids that move through the subsurface into the saturated zone will move in the direction of the
4 flowing ground water. Generally, fluids travel further in systems with high ground water flow rates
5 and high recharge (e.g., sandy aquifers in humid climates) than in systems with low flow and low
6 recharge. Chemicals may sorb to suspended soil particles or complex with naturally occurring
7 chemicals (e.g., dissolved organic carbon) and be transported with the flowing water.¹ These
8 mechanisms can mobilize sparingly soluble chemicals that would otherwise be immobile.

5.8.2. Physicochemical Properties

9 Three physicochemical properties are useful to describe the movement of chemicals in the
10 environment: (1) K_{ow} , the octanol-water partition coefficient, (2) the aqueous solubility, and (3) the
11 Henry's law constant.² These properties describe whether a chemical will sorb to soil and organic
12 matter or stay in water (K_{ow}), how much of a chemical may dissolve in water (aqueous solubility),
13 and whether a chemical will tend to remain in the water or volatilize (Henry's law constant).³

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

20 Estimates and measured values for physicochemical properties were obtained by using the
21 Estimation Program Interface Suite 4.1 (see Appendix C).⁴ Of the 1,076 chemicals the EPA listed as
22 used in hydraulic fracturing (see Appendix A), EPI Suite™ has estimated properties for 453 (42%).
23 EPI Suite™ does not have data available for the remaining 58% of the chemicals. The 453 chemicals
24 with physicochemical property data were chemicals with structures that are considered suitably
25 representative of the substance to compute properties within the constraints of EPI Suite™
26 software. Only unique defined organic desalted structures were submitted for property calculation.
27 Figure 5-17 presents histograms of all 453 of the chemicals, sorted by four physicochemical
28 parameters: measured $\log K_{ow}$ ($n = 247$, 23%), estimated $\log K_{ow}$ ($n=453$, 42%) estimated log of the

¹ 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.

² 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.

³ We present the physicochemical parameter values using \log_{10} because of the wide range of values that these parameters cover.

⁴ EPI Suite™, version 4.1, <http://www.epa.gov/opptintr/exposure/pubs/episuite.htm> (U.S. EPA, 2012b). 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.

- 1 aqueous solubility ($n = 453$, 42%), and estimated log of Henry’s law constant (at 25°C, $n = 453$,
 2 42%).

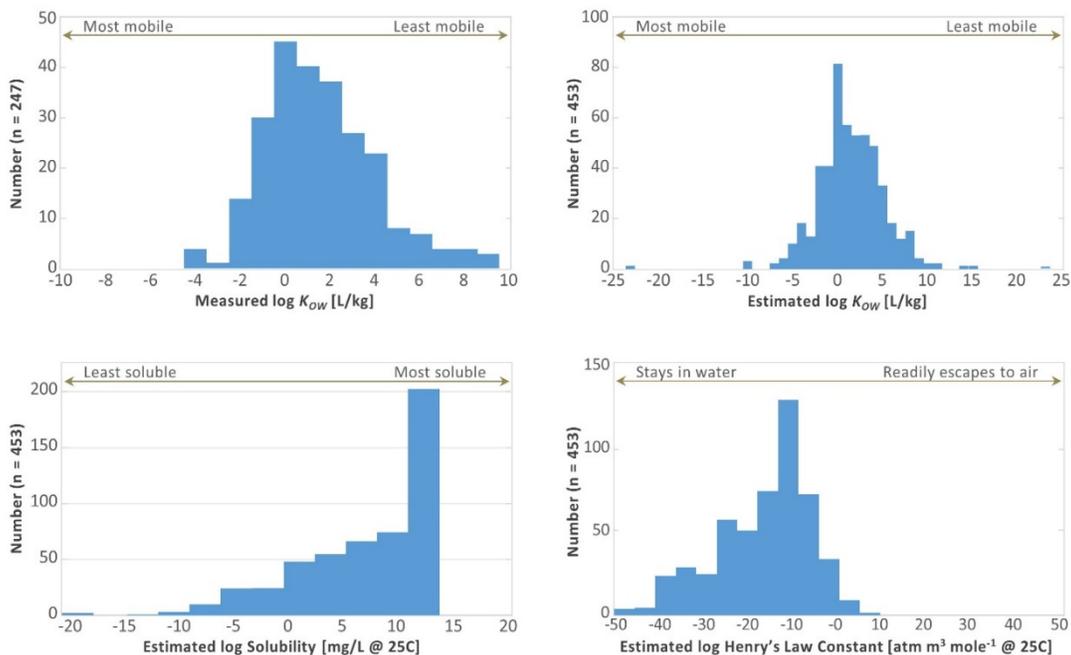


Figure 5-17. Histograms of physicochemical properties of chemicals used in the hydraulic fracturing process.

Measured values of $\log K_{ow}$ (upper left). Estimated physicochemical properties for $\log K_{ow}$ (upper right), \log Solubility (lower left), and \log Henry’s law constant (lower right) for all chemicals. Physicochemical properties ($\log K_{ow}$, solubility, and Henry’s Law constant) estimated by EPI Suite™.

- 3 The EPA also used EPI Suite™ to determine the physicochemical properties for 19 chemicals
 4 provided to the EPA as confidential business information (CBI) (See Text Box 5-3 for discussion on
 5 CBI).¹ The CBI chemical physicochemical properties are plotted as histograms in Figure 5-18. The
 6 values of the physicochemical properties of known and CBI chemicals are similar, covering similar
 7 ranges centered on similar values, suggesting that even though these chemicals are not publicly
 8 known, their physicochemical properties are not appreciably different from the known chemicals.
 9 This means that their fate and transport would not be appreciably different than the chemicals that
 10 are publicly known.

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 USEPA by 9 service companies.

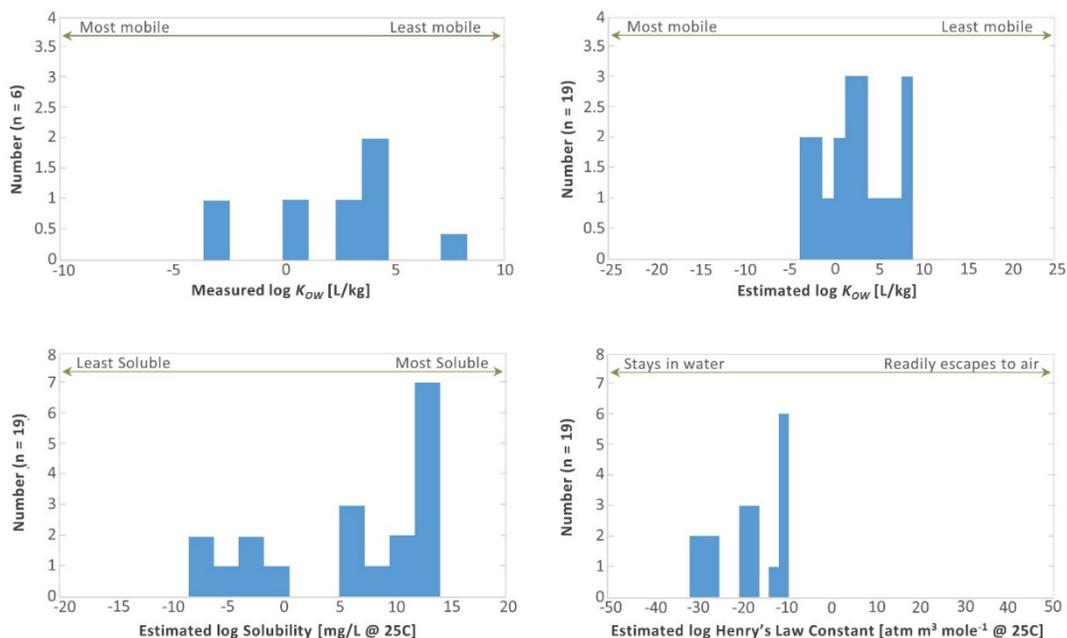


Figure 5-18. Histograms of physicochemical properties of confidential chemicals used in the hydraulic fracturing process.

Source: ([U.S. EPA, 2013a](#))

Measured values of $\log K_{ow}$ (upper left). Estimated physicochemical properties for $\log K_{ow}$ (upper right), \log solubility (lower left), and \log Henry's law constant (lower right) for all chemicals.

Physicochemical properties ($\log K_{ow}$, solubility, and Henry's Law constant) estimated by EPI Suite™.

5.8.3. Mobility of Chemicals

1 Figure 5-17 shows the distribution of the three properties. The $\log K_{ow}$ distribution demonstrates
 2 that the chemicals cover a wide range from the more mobile to the less mobile. The more
 3 hydrophilic chemicals are more mobile (i.e., they move with water). The more hydrophobic
 4 chemicals tend to associate with organic matter and soil particles and to be less mobile in the
 5 environment, and they may serve as long-term sources of contamination. A large number of the
 6 chemicals fall near $\log K_{ow} = 0$, which indicates that these chemicals are likely to associate roughly
 7 equally with organic or aqueous phases. However, overall the $\log K_{ow}$ values are skewed positively,
 8 indicating less mobile chemicals, which may result in their being later-term or long-term sources of
 9 impact to drinking water. The $\log S$ values span a wide range from fully miscible to sparingly
 10 soluble. Many of the chemicals have high aqueous solubilities, with a large number being fully
 11 miscible. Most of the chemicals have \log Henry's law constants less than 0, indicating that most are
 12 not volatile. Once these chemicals dissolve into water they will tend to stay there rather than
 13 volatilize. Therefore, volatilization does not generally serve as a loss process for most hydraulic
 14 fracturing chemicals.

15 Table 5-7 and Table 5-8 present the 20 most mobile and least mobile chemicals, known to be used
 16 in hydraulic fracturing fluids, respectively, as ranked by $\log K_{ow}$. These were taken from the list of

1 515 chemicals with estimated values for physicochemical properties. These tables also include
 2 values for aqueous solubility and Henry's law constant, as well as frequency of use, based on
 3 FracFocus disclosures ([U.S. EPA, 2015a](#)).

4 Table 5-7 shows the chemicals that have the *lowest* log K_{ow} and are, thus, the *most* mobile. These
 5 chemicals are fully miscible (i.e., they will mix completely with water), which means they may move
 6 through the environment at high concentrations, leading to greater severity of impact. These
 7 chemicals generally have low volatility, based on their negative log Henry's law constants (i.e., will
 8 remain in water and will not be lost to the air). These chemicals will dissolve in water and move
 9 rapidly through the environment (e.g., via infiltration into the subsurface or via overland flow to
 10 surface waters). Chemicals exhibiting this combination of properties have greater potential to cause
 11 immediate impacts to drinking water resources. Most of the chemicals in the table were
 12 infrequently reported ($\leq 2\%$ of wells) in FracFocus ([U.S. EPA, 2015a](#)). However, choline chloride
 13 (14% of wells), used for clay control, and tetrakis(hydroxymethyl)phosphonium sulfate (11% of
 14 wells), a biocide, were more commonly reported.

Table 5-7. Ranking of the 20 most mobile organic chemicals, as determined by the largest log K_{ow} , with CASRN, percent of wells where the chemical is reported from January 1, 2011 to February 28, 2013 (U.S. EPA, 2015b), and physicochemical properties (log K_{ow} , solubility, and Henry's Law constant) as estimated by EPI Suite™.

([U.S. EPA, 2015b](#))

For organic salts, parameters are estimated using the desalted form.

Rank	Chemical Name	CASRN	Percent of wells (U.S. EPA, 2015b) ^a	Estimated Log K_{ow} (unitless) ^b	Estimated Water Solubility (mg/L @ 25°C) ^c	Estimated Henry's Law Constant (atm m ³ /mole @ 25°C) ^d
1	1,2-Ethanediaminium, N,N'-bis[2-bis(2-hydroxyethyl)methylammonio]ethyl)-N,N'-bis(2-hydroxyethyl)-N,N'-dimethyl-, tetrachloride	138879-94-4	2%	-23.19	1.00×10^6	2.33×10^{-35}
2	Phosphonic acid, [[[phosphonomethyl]imino]bis[2,1-ethanediylnitrilobis(methylene)]]tetrakis-	15827-60-8	0.2%	-9.72	1.00×10^6	NA
3	Phosphonic acid, [[[phosphonomethyl]imino]bis[2,1-ethanediylnitrilobis(methylene)]]tetrakis-, sodium salt	22042-96-2	0.07%	-9.72	1.00×10^6	NA

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Rank	Chemical Name	CASRN	Percent of wells (U.S. EPA, 2015b) ^a	Estimated Log K_{ow} (unitless) ^b	Estimated Water Solubility (mg/L @ 25°C) ^c	Estimated Henry's Law Constant (atm m ³ /mole @ 25°C) ^d
4	Phosphonic acid, [[[phosphonomethyl]imino]bis[2,1-ethanediylnitrilobis(methylene)]]tetrakis-, ammonium salt (1:x)	70714-66-8	NA	-9.72	1.00×10^6	NA
5	Phosphonic acid, (((2-[(2-hydroxyethyl)(phosphonomethyl)amino]ethyl)imino]bis(methylene))bis-, compd. with 2-aminoethanol	129828-36-0	NA	-6.73	1.00×10^6	5.29×10^{-42}
6	2-Hydroxy-N,N-bis(2-hydroxyethyl)-N-methylethanaminium chloride	7006-59-9	NA	-6.7	1.00×10^6	4.78×10^{-19}
7	N-(3-Chloroallyl)hexaminium chloride	4080-31-3	0.02%	-5.92	1.00×10^6	1.76×10^{-8}
8	3,5,7-Triazatricyclo(3.3.1.1 (superscript 3,7))decane, 1-(3-chloro-2-propenyl)-, chloride, (Z)-	51229-78-8	NA	-5.92	1.00×10^6	1.76×10^{-8}
9	(2,3-dihydroxypropyl) trimethylammonium chloride	34004-36-9	NA	-5.8	1.00×10^6	9.84×10^{-18}
10	Phosphonic acid, [[[phosphonomethyl]imino]bis[6,1-hexanediylnitrilobis(methylene)]]tetrakis-	34690-00-1	0.006%	-5.79	1.00×10^6	NA
11	[Nitrilotris(methylene)]tris-phosphonic acid pentasodium salt	2235-43-0	0.5%	-5.45	1.00×10^6	1.65×10^{-34}
12	Aminotrimethylene phosphonic acid	6419-19-8	2%	-5.45	1.00×10^6	1.65×10^{-34}
13	Choline chloride	67-48-1	14%	-5.16	1.00×10^6	2.03×10^{-16}
14	Choline bicarbonate	78-73-9	0.2%	-5.16	1.00×10^6	2.03×10^{-16}
15	alpha-Lactose monohydrate	5989-81-1	NA	-5.12	1.00×10^6	4.47×10^{-22}
16	Lactose	63-42-3	NA	-5.12	1.00×10^6	4.47×10^{-22}

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Rank	Chemical Name	CASRN	Percent of wells (U.S. EPA, 2015b) ^a	Estimated Log K_{ow} (unitless) ^b	Estimated Water Solubility (mg/L @ 25°C) ^c	Estimated Henry's Law Constant (atm m ³ /mole @ 25°C) ^d
17	Tetrakis(hydroxymethyl)phosphonium sulfate	55566-30-8	11%	-5.03	1.00×10^6	9.17×10^{-13}
18	Disodium ethylenediaminediacetate	38011-25-5	0.6%	-4.79	1.00×10^6	1.10×10^{-16}
19	Nitrilotriacetamide	4862-18-4	NA	-4.75	1.00×10^6	1.61×10^{-18}
20	1,3,5-Triazine-1,3,5(2H,4H,6H)-triethanol	4719-04-4	0.2%	-4.67	1.00×10^6	1.08×10^{-11}

^a Some of the chemicals in these tables have NA (not available) listed as the number of wells, which means that these chemicals have been used in hydraulic fracturing, but they were not reported to FracFocus program for the time period of the study (January 1, 2011, to February 28, 2013) (U.S. EPA, 2015b). 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.

^b Log K_{ow} is estimated using the KOWWIN™ model, which uses an atom/fragment contribution method.

^c Water solubility is estimated using the WSKOWWIN™ model, which estimates a chemical's solubility from K_{ow} and any applicable correction factors.

^d Henry's Law constant is estimated using the HENRYWIN™ model using the bond contribution method.

1 Table 5-8 shows the chemicals that have the *highest* log K_{ow} and are, thus, the *least* mobile. The
2 estimated aqueous solubilities for some of these chemicals are extremely low, with highest
3 solubilities of <10 µg/L. Therefore, the concentration of these chemicals dissolved in water will be
4 low. The estimated Henry's law constants are more variable for these low-mobility chemicals.
5 Chemicals with high log K_{ow} values (>0) and high Henry's law constants will sorb strongly to organic
6 phases and solids and may volatilize. However, their strong preference for the organic or solid
7 phase may slow or reduce volatilization. The chemicals with low Henry's law constants will readily
8 sorb to organic phases and solids. Less mobile chemicals will move slowly through the soil and have
9 potentially delayed and longer-term impacts to drinking water resources. Seven of the chemicals in
10 Table 5-8 were reported to FracFocus (U.S. EPA, 2015b). Five were reported infrequently (<1% of
11 wells). Tri-n-butyltetradecylphosphonium chloride (6% of wells), used as a biocide, and
12 C>10-alpha-alkenes (8% of wells), a mixture of alpha-olefins with carbon numbers greater than 10
13 used as a corrosion inhibitor, were more commonly reported. The least mobile organic chemical is

- 1 sorbitan, tri-(9Z)-9-octadecenoate, a mineral oil co-emulsifier (0.05% of wells), with an estimated
 2 log K_{ow} of 22.56.¹

Table 5-8. Ranking of the 20 least mobile organic chemicals, as determined by the largest log K_{ow} , with CASRN, percent of wells where the chemical is reported from January 1, 2011 to February 28, 2013 (U.S. EPA, 2015b), and physicochemical properties (log K_{ow} , solubility, and Henry's Law constant) as estimated by EPI Suite™.

Source: (U.S. EPA, 2015b)

For organic salts, parameters are estimated using the desalted form.

Rank	Chemical Name	CASRN	Percent of wells (U.S. EPA, 2015b) ^a	Estimated Log K_{ow} (unitless) ^b	Estimated Water Solubility (mg/L @ 25°C) ^c	Estimated Henry's Law Constant (atm m ³ /mole @ 25°C) ^d
1	Sorbitan, tri-(9Z)-9 octadecenoate	26266-58-0	0.05%	22.56	1.12×10^{-19}	4.02×10^{-11}
2	Fatty acids, C18-unsatd., dimers	61788-89-4	NA	14.6	2.31×10^{-10}	4.12×10^{-08}
3	Sorbitan sesquioleate	8007-43-0	0.02%	14.32	2.31×10^{-11}	7.55×10^{-12}
4	Tri-n-butyltetradecyl-phosphonium chloride	81741-28-8	6%	11.22	7.90×10^{-7}	2.61×10^{-1}
5	Sodium bis(tridecyl) sulfobutanedioate	2673-22-5	NA	11.15	7.46×10^{-9}	8.51×10^{-11}
6	1-Eicosene	3452-07-1	NA	10.03	1.26×10^{-5}	1.89×10^1
7	D&C Red 28	18472-87-2	NA	9.62	1.64×10^{-8}	6.37×10^{-21}
8	C.I. Solvent Red 26	4477-79-6	NA	9.27	5.68×10^{-5}	5.48×10^{-13}
9	1-Octadecene	112-88-9	NA	9.04	1.256×10^{-4}	1.07×10^1
10	Alkenes, C>10 alpha-	64743-02-8	8%	8.55	3.941×10^{-4}	8.09×10^0
11	Diocetyl phthalate	117-84-0	NA	8.54	4.236×10^{-4}	1.18×10^{-5}
12	Benzene, C10-16-alkyl derivs.	68648-87-3	0.5%	8.43	2.099×10^{-4}	1.78×10^{-1}

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).

Rank	Chemical Name	CASRN	Percent of wells (U.S. EPA, 2015b) ^a	Estimated Log K_{ow} (unitless) ^b	Estimated Water Solubility (mg/L @ 25°C) ^c	Estimated Henry's Law Constant (atm m ³ /mole @ 25°C) ^d
13	Di(2-ethylhexyl) phthalate	117-81-7	NA	8.39	1.132×10^{-3}	1.18×10^{-5}
14	1-Octadecanamine, N,N-dimethyl-	124-28-7	NA	8.39	8.882×10^{-3}	4.51×10^{-3}
15	N,N-dimethyloctadecylamine hydrochloride	1613-17-8	NA	8.39	8.882×10^{-3}	4.51×10^{-3}
16	Butyryl trihexyl citrate	82469-79-2	0.03%	8.21	5.56×10^{-5}	3.65×10^{-9}
17	1-Hexadecene	629-73-2	NA	8.06	1.232×10^{-3}	6.10×10^0
18	Benzo(g,h,i)perylene	191-24-2	NA	7.98	7.321×10^{-4}	1.26×10^{-2}
19	Dodecylbenzene	123-01-3	NA	7.94	1.015×10^{-3}	1.34×10^{-1}
20	Isopropanolamine dodecylbenzene	42504-46-1	0.02%	7.94	1.015×10^{-3}	1.34×10^{-1}

^a Some of the chemicals in these tables have NA (not available) listed as the number of wells, which means that these chemicals have been used in hydraulic fracturing, but they were not reported to FracFocus program for the time period of the study (January 1, 2011, to February 28, 2013) (U.S. EPA, 2015b). 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.

^b Log K_{ow} is estimated using the KOWWIN™ model, which uses an atom/fragment contribution method.

^c Water solubility is estimated using the WSKOWWIN™ model, which estimates a chemical's solubility from K_{ow} and any applicable correction factors.

^d Henry's Law constant is estimated using the HENRYWIN™ model using the bond contribution method.

1 Table 5-9 shows the EPI Suite™ estimated physicochemical property values of the 20 chemicals
2 most frequently reported to FracFocus nationwide, with estimated mean and median volumes
3 based on FracFocus data. Most have log $K_{ow} < 1$, meaning that they are generally hydrophilic and
4 will associate with water. These chemicals also have very high solubilities, so they will be mobile in
5 the environment and go where the water goes. These chemicals have the potential for immediate
6 impacts to drinking water resources. Naphthalene has a measured log $K_{ow} = 3.3$ with an estimated
7 solubility of 142.1 mg/L, which means it will be less mobile in the environment. Naphthalene will
8 sorb to particles and move slowly through the environment, and have the potential to act as long-

- 1 term sources of contamination.¹ All of these chemicals have low Henry's law constants, so they tend
- 2 not to volatilize.

¹ Chemicals may have the potential to be long-term sources of contamination because 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 the right conditions, for example, naphthalene is biodegradable, which may reduce or remove it from the environment, and thus may not be a long-term source of contamination.

Table 5-9. The 20 chemicals reported most frequently nationwide for hydraulic fracturing based on reported FracFocus 1.0 disclosures (U.S. EPA, 2015b), with EPI Suite™ physicochemical parameters where available, and estimated mean and median volumes of those chemicals, where density was available.

Source: (U.S. EPA, 2015b)

Excludes water, sodium chloride, and quartz. NA means that the physicochemical parameter is not provided by EPI Suite™. For organic salts, parameters are estimated using the desalted form.

Rank	Chemical Name	CASRN	Number Of Wells Using Chemical (% of wells)	Log K_{ow} (unitless)		Water Solubility Estimate From Log K_{ow} (mg/L @ 25°C)	Henry's Law Constant (atm m ³ /mole @ 25°C)			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	1.00×10^6	4.27×10^{-6}	3.62×10^{-6}	4.55×10^{-6}	1,218	110
2	Distillates, petroleum, hydrotreated light	64742-47-8	22,463 (65%)	NA	NA	NA	NA	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	4.024×10^5	7.52×10^{-6}	1.14×10^{-5}	8.10×10^{-6}	2,095	55
5	Ethylene glycol	107-21-1	15,800 (46%)	-1.2	-1.36	1.00×10^6	1.31×10^{-7}	5.60×10^{-11}	6.00×10^{-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	1.672×10^5	1.10×10^{-7}	2.39×10^{-8}	NA	1,313	122
10	Propargyl alcohol	107-19-7	11,410 (33%)	-0.42	-0.38	9.355×10^5	5.88×10^{-7}	NA	1.15×10^{-6}	183	2
11	Potassium hydroxide	1310-58-3	10,049 (29%)	NA	NA	NA	NA	NA	NA	NA	NA

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Rank	Chemical Name	CASRN	Number Of Wells Using Chemical (% of wells)	Log K_{ow} (unitless)		Water Solubility Estimate From Log K_{ow} (mg/L @ 25°C)	Henry's Law Constant (atm m ³ /mole @ 25°C)			Estimated Volume, per disclosure (gal)	
				Estimated	Measured		Estimated, Bond Method	Estimated, Group Method 25	Measured	Mean	Median
12	Ethanol	64-17-5	9,861 (29%)	-0.14	-0.31	7.921×10^5	5.67×10^{-6}	4.88×10^{-6}	5.00E-06	831	121
13	Acetic acid	64-19-7	8,186 (24%)	0.09	-0.17	4.759×10^5	5.48×10^{-7}	2.94×10^{-7}	1.00×10^{-7}	646	47
14	Citric acid	77-92-9	8,142 (24%)	-1.67	-1.64	1.00×10^6	8.33×10^{-18}	NA	4.33×10^{-14}	163	20
15	2-Butoxyethanol	111-76-2	7,347 (21%)	0.57	0.83	6.447×10^4	9.79×10^{-8}	2.08×10^{-8}	1.60×10^{-6}	385	26
16	Solvent naphtha, petroleum, heavy arom.	64742-94-5	7,108 (21%)	NA	NA	NA	NA	NA	NA	NA	NA
17	Naphthalene	91-20-3	6,354 (19%)	3.17	3.3	1.421×10^2	5.26×10^{-4}	3.7×10^{-4}	4.4×10^{-4}	72	12
18	2,2-Dibromo-3-nitrilopropionamide	10222-01-2	5,656 (16%)	1.01	0.82	2.841×10^3	6.16×10^{-14}	NA	1.91×10^{-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	1.00×10^6	2.03×10^{-16}	NA	NA	2,131	290

Note: 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.

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5.8.4. Transformation Processes

1 It is important to understand the processes governing transformation of chemicals in the
2 environment. The transformation of a chemical reduces its concentration over time. Chemicals may
3 completely degrade before reaching a drinking water resource. Transformation processes may be
4 biotic or abiotic. The transformation process may transform a chemical into a less or more harmful
5 chemical.

6 Biodegradation is a biotic process where microorganisms transform a chemical from its original
7 form into another chemical. For example, the biodegradation pathway of methanol is
8 $\text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{O} \rightarrow \text{CHOOH} \rightarrow \text{CO}_2$, or methanol \rightarrow formaldehyde \rightarrow formic acid \rightarrow carbon dioxide.
9 This pathway shows how the original chemical transforms through a series of steps until it becomes
10 the final product, carbon dioxide. Some chemicals are readily biodegraded, while others break
11 down slowly over time. Biodegradation is a highly site-specific process, requiring nutrients, a
12 carbon source, water, and an energy source. A highly biodegradable chemical could be persistent if
13 the conditions for biodegradability are not met. Conversely, a highly biodegradable chemical could
14 biodegrade quickly under the right conditions, before it can impact a water resource. The
15 relationship between mobility and biodegradability is complex, and therefore a variety of factors
16 can influence a particular compound's movement through the environment.

17 Abiotic processes, such as oxidation, reduction, photochemical reaction, and hydrolysis, can
18 transform or break apart chemicals. In hydrolysis, for example, a water molecule substitutes for a
19 group of atoms. The typical results are products that are more polar than the original, and thus
20 have different physicochemical properties than the original compounds ([Schwarzenbach et al.,
21 2002](#)).¹

5.8.5. Fate and Transport of Chemical Mixtures

22 Chemicals at hydraulic fracturing sites are often present as mixtures, which may act differently in
23 the environment than individual chemicals do. Individual chemicals can affect the fate and
24 transport of other chemicals in a mixture primarily by changing their solubility and biodegradation
25 rates.

26 Mixtures of chemicals may be more mobile than individual chemicals due to cosolvency, which
27 increases solubility in the aqueous phase. Methanol and ethanol are examples of cosolvent alcohols
28 used frequently in hydraulic fracturing fluids ([U.S. EPA, 2015a](#)). The presence of either greatly
29 increases BTEX solubility ([Rasa et al., 2013](#); [Corseuil et al., 2011](#); [Heermann and Powers, 1998](#)).² By
30 increasing solubility, ethanol can affect the fate and transport of other compounds. For example,

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.

1 BTEX has been observed to travel farther in the subsurface in the presence of ethanol ([Rasa et al.](#),
2 [2013](#); [Corseuil et al., 2011](#); [Corseuil et al., 2004](#); [Powers et al., 2001](#); [Heermann and Powers, 1998](#)).

3 The presence of surfactants lowers fluid surface tension and increases solubility of organic
4 compounds, and can mobilize less soluble/less mobile organic compounds. Two common
5 surfactants reported to FracFocus 1.0 from January 1, 2011 to February 2013 were 2-
6 butoxyethanol (CASRN 111-76-2, 21% of disclosures) and poly(oxy-1,2-ethanediyl)-nonylphenyl-
7 hydroxy (mixture) (CASRN 127087-87-0, 20% of disclosures). Additionally, surfactants can
8 mobilize bacteria in the subsurface, which can increase the impact of pathogens on drinking water
9 resources ([Brown and Jaffé, 2001](#)).

10 When chemicals are present as mixtures, one chemical may decrease or enhance the
11 biodegradability of another through inhibition or co-metabolism. The process of inhibition can
12 occur when multiple chemicals compete for the same enzyme, so only one chemical is degraded at a
13 time, which can ultimately slow biodegradation of each of the chemicals present. For example, the
14 biodegradation of ethanol and methanol may inhibit the biodegradation of BTEX or other organic
15 compounds present ([Rasa et al., 2013](#); [Powers et al., 2001](#)). Co-metabolism may increase the
16 biodegradation rate of other compounds. For example, when methane or propane is present with
17 tetrachloroethylene, the enzyme produced by bacteria to degrade methane also degrades
18 tetrachloroethylene (e.g., [Alvarez-Cohen and Speitel, 2001 and references therein](#)). For the
19 purposes of chemicals used in hydraulic fracturing, the presence of other chemicals in additives and
20 hydraulic fracturing fluids could result in increased or decreased biodegradation if the chemicals
21 are spilled. A chemical that may have otherwise been biodegradable may be inhibited and act as a
22 long-term source.

5.8.6. Site and Environmental Conditions

23 Environmental conditions at and around the spill site affect the movement and transformation of
24 the chemical. We discuss the following: site conditions (e.g., proximity, land cover, and slope), soil
25 conditions (e.g., permeability and porosity), and weather and climate.

26 The proximity of a spill to a drinking water resource, either laterally in the case of a surface water
27 body or downward for an aquifer, affects the potential for impact. Land cover will affect how
28 readily a fluid moves over land. For example, more rugged land cover such as forest will impede
29 flow, and an asphalt road will facilitate flow. A spill that occurs on or near a sloped site may move
30 overland faster, making it more likely to reach a nearby surface water body. Flatter surfaces would
31 result in a greater chance for infiltration to the subsurface, which could increase the potential for a
32 ground water impact.

33 Soil characteristics that affect the transport and transformation of spill chemicals include soil
34 texture (e.g., clay, silt, sand), permeability, porosity, and organic content.^{1,1} Fluids will move more

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.

1 quickly through permeable soil (e.g., sand) than through less permeable soil (e.g., clay). A soil with a
2 high porosity provides more volume to hold water and spilled chemicals. Another important factor
3 for a site is the organic content, of which there are two competing types: soil organic carbon and
4 dissolved organic carbon. Each type of carbon acts as a strong substance for chemicals to adhere to.
5 Soil organic carbon present in a solid phase, such as dead and decaying leaves and roots, is not
6 mobile and slows the movement of chemicals through the soil. Dissolved organic carbon (DOC)
7 moves with the water and can act as a shuttling mechanism to move insoluble chemicals across the
8 surface and through the subsurface. Chemicals may also associate with particulates and colloids,
9 which may act as an important transport mechanism.

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

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

15 There has been limited peer-reviewed research investigating the fate and transport of chemicals
16 spilled at hydraulic fracturing sites. [Aminto and Olson \(2012\)](#) modeled a hypothetical spill of
17 1,000 gal (3,800 L) of hydraulic fracturing fluid using equilibrium partitioning. The authors
18 evaluated how 12 chemicals typically used for hydraulic fracturing in the Marcellus Shale would
19 partition amongst different phases: air, water, soil, and biota.² They presented a ranking of
20 concentrations for each phase. In water, they showed that sodium hydroxide (a pH buffer), 4,4-
21 dimethyl oxazolidine (a biocide), hydrochloric acid (a perforation clean-up additive), and 3,4,4-
22 trimethyl oxazolidine (a biocide) had the highest simulated water concentrations; however, these
23 concentrations depended on the chemicals included in the simulated mixture and the
24 concentrations of each. Their analysis also suggested that after a spill, a large fraction would enter
25 the air and leave the soil; however, some constituents would be left behind in the water, soil, and
26 biota compartments, which could effectively act as long-term contamination sources. [Aminto and
27 Olson \(2012\)](#) only studied this one scenario. Other scenarios could be constructed with different
28 chemicals in different concentrations. These scenarios may result in different outcomes with
29 greater impacts.

5.8.8. Potential and Documented Fate and Transport of Documented Spills

30 There is limited information on the fate and transport of hydraulic fracturing fluids and chemicals.
31 In this section, we highlight the potential and documented impacts for three documented spills ([U.S.
32 EPA, 2015n](#)). In each case, we provide the documented and potential paths (surface, subsurface, or
33 combination) and the associated fate and transport governing processes by which a spill has been

¹ 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.

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

1 documented to or has the potential to have an impact on drinking water resources. The three cases
 2 involve a tank overflow with a surface water impact, a human error blender spill with a soil impact,
 3 and an equipment failure that had no impact. These three spills were chosen to highlight cases
 4 where there was a documented impact, a potential impact, and no impact.

5 In the first documented spill, shown in Figure 5-19, a tank overflowed twice, releasing a total of
 6 7,350 gal (980 ft³ or 28 m³).¹ The spilled fluid was documented as containing a friction reducer and
 7 gel. The spill traveled across the land surface, crossed a road, and then continued to a nearby
 8 stream. The spill affected wetlands and a stream, where fish were killed. The fish kill indicates that
 9 the chemicals present were in high enough concentrations to have an adverse impact.

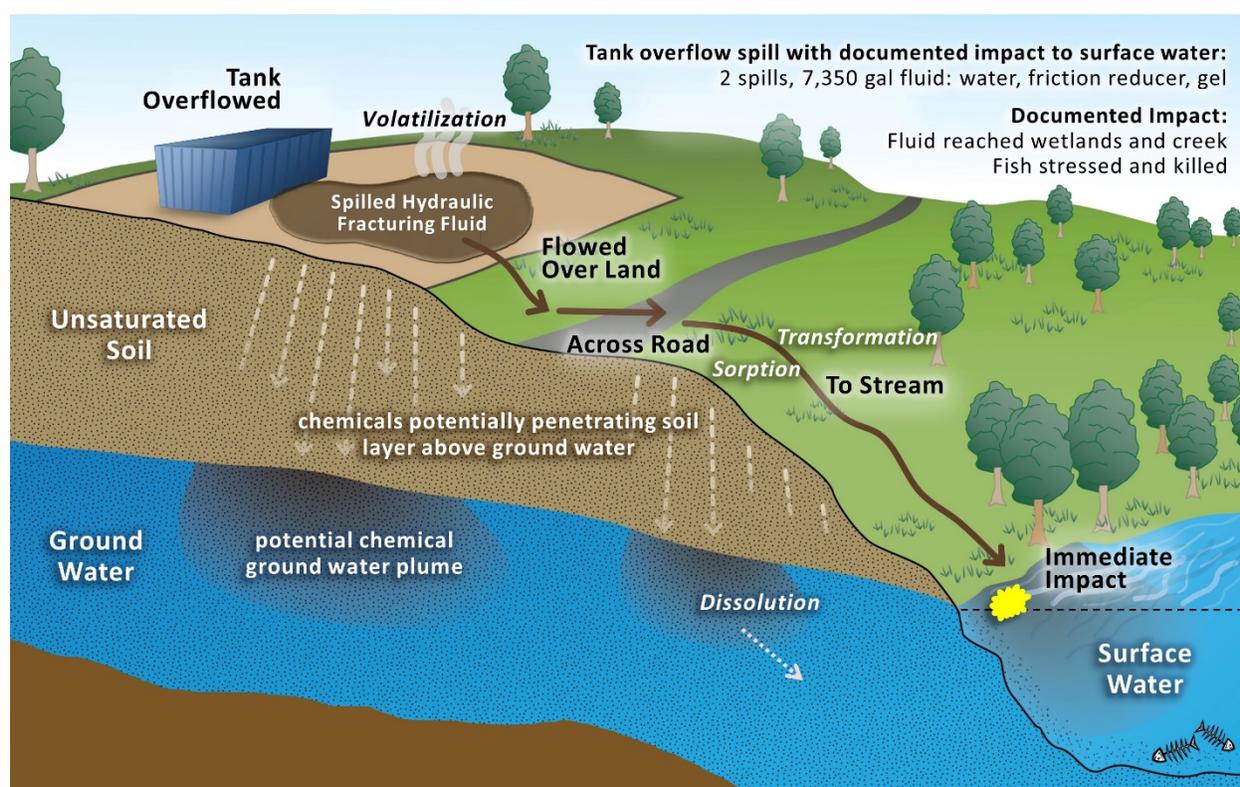


Figure 5-19. Fate and Transport Spill Example: Case 1.

Spills information from [U.S. EPA \(2015n\)](#).

10 For this first spill, the documented path was overland flow from the tank to the stream with a
 11 documented, immediate impact. In addition to this documented path, there are potential paths for
 12 potential impacts to drinking water resources. The spilled chemicals may have penetrated into the
 13 soils or sorbed to soils and vegetation as the fluid moved across the ground towards the stream.

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 might travel.

1 Chemicals could be mobilized during later rainfall, runoff, or erosion events. Chemicals that
2 infiltrated the subsurface could serve as long-term sources, as well as travel laterally across the
3 unsaturated zone, or continue downwards to the ground water. Additionally, some chemicals could
4 be lost to transformation processes. The lack of reported soil or ground water sampling data
5 prevents the ability to know if these potential paths occurred or not.

6 The second documented spill ([U.S. EPA, 2015n, line 144](#)), shown in Figure 5-20, occurred when a
7 cap was left off the blender, and 504 gal (70 ft³ or 2 m³) of biocide and hydraulic fracturing fluid
8 were released; 294 gal (39 ft³ or 1.1 m³) were retained by a dike with a lined secondary
9 containment measure, demonstrating the partial effectiveness of this containment mechanism.
10 However, 210 gal (28 ft³ or 0.8 m³) did run off-site and were vacuumed up. There was no
11 documented impact to surface or ground water.

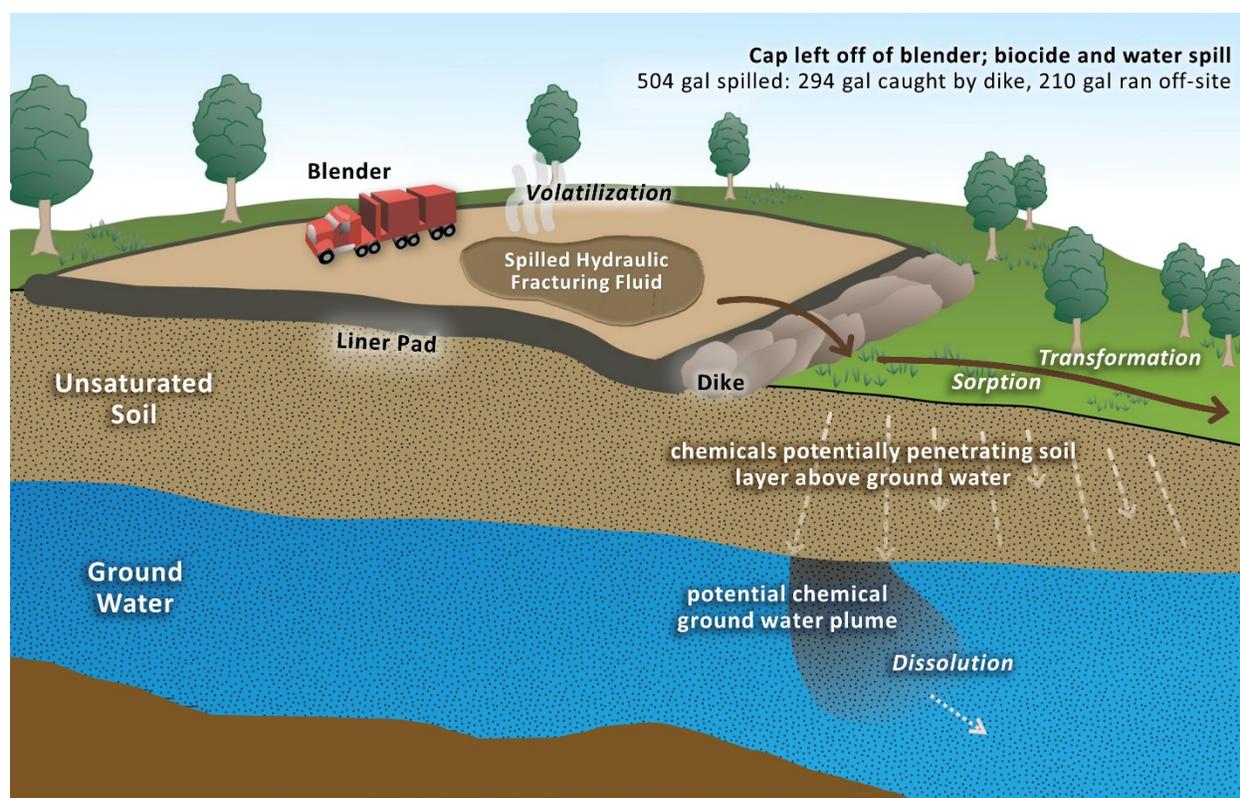


Figure 5-20. Fate and Transport Spill Example: Case 2.

Spills information from [U.S. EPA \(2015n\)](#).

12 In this second case, the uncontained 210 gal could have infiltrated the subsurface, creating a
13 potential path to ground water. There is no documented information on the composition of the
14 spilled fluid. Highly mobile chemicals would have penetrated the soil more quickly than less mobile
15 chemicals, which would have sorbed to soil particles. As the chemicals penetrated into the soil,
16 some could have moved laterally in the unsaturated zone, or traveled downward to the water table

1 and moved with the ground water. These chemicals could have served as a long-term source. These
2 chemicals could have transformed into other chemicals with different physicochemical properties,
3 and any volatile chemicals could have moved to the air as a loss process. As in the first case, there
4 was no reported sampling of soil or groundwater, so there is no way to demonstrate whether
5 chemicals did or did not follow this path.

6 In the third documented spill ([U.S. EPA, 2015n, line 188](#)), shown in Figure 5-21, 630 gal (84 ft³ or
7 2.4 m³) of crosslinker spilled onto the well pad when a hose wore off at the cuff. The spill was
8 contained in the berm and an on-site vacuum truck was used to clean up the spill. No impact to soil
9 or water was reported.

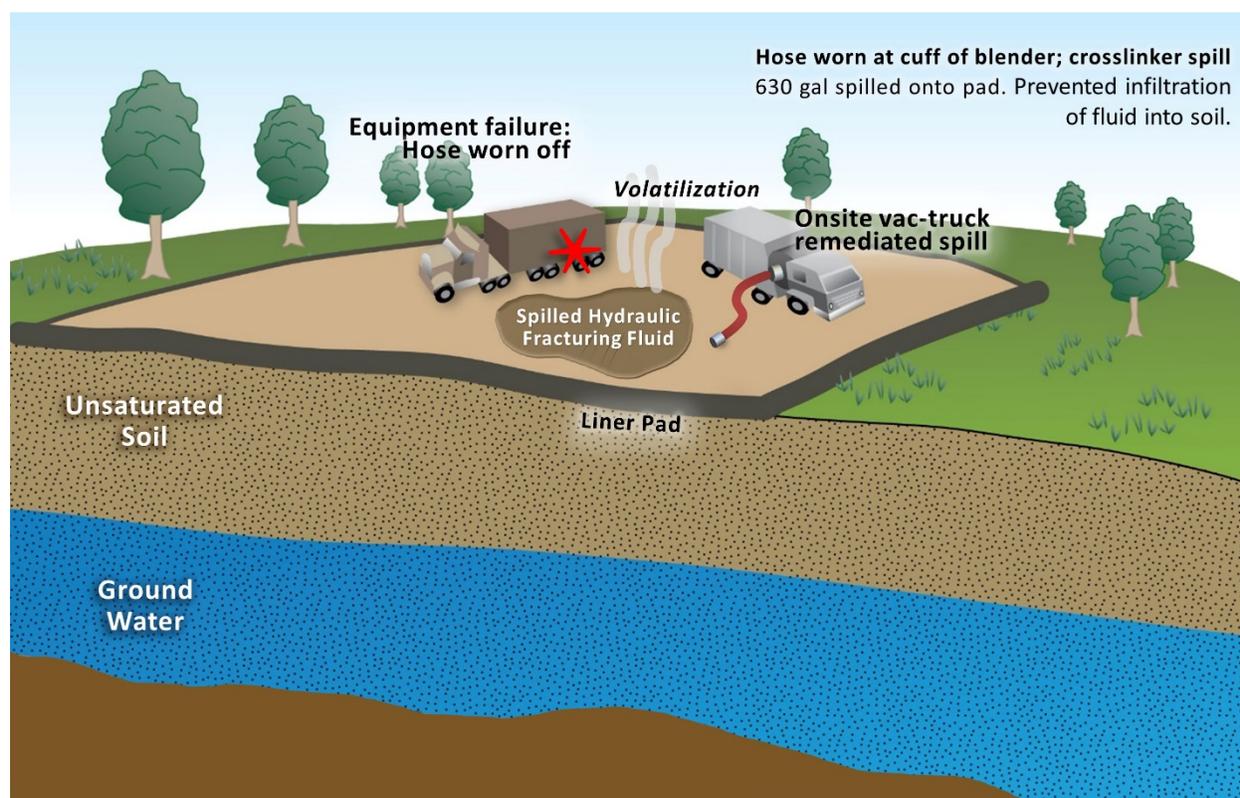


Figure 5-21. Fate and Transport Spill Example: Case 3.

Spills information from [U.S. EPA \(2015n\)](#).

10 For this third case, we do not have any information on whether the well pad was lined or not. If the
11 site had a liner, the spill could have been fully contained, not infiltrated the subsurface, and been
12 fully cleaned up. Without a liner or if the liner was not completely successful (e.g., had a tear), the
13 potential paths would have been similar to those above in the second case, where the chemicals
14 may sorb to the soils and penetrate into the subsurface. There was no reported sampling of soil or
15 ground water to determine whether or not chemicals migrated into the soil.

5.9. Trends in Chemicals Use in Hydraulic Fracturing

1 This section provides an overview of ongoing changes in chemical use in hydraulic fracturing, with
2 an emphasis on efforts to reduce potential impacts from surface spills by using fewer and safer
3 chemicals.

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

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

- 17 • A renewable citrus-based replacement for conventional surfactants ([Fisher, 2012](#));
- 18 • A crosslinked gel system comprised of chemicals designated as safe food additives by the
19 U.S. Food and Drug Administration ([Holtsclaw et al., 2011](#));
- 20 • A polymer-free gel additive ([Al-Ghazal et al., 2013](#));
- 21 • A dry, hydrocarbon-free powder to replace liquid gel concentrate ([Weinstein et al., 2009](#));
- 22 • Biodegradable polymers ([Irwin, 2013](#));
- 23 • The use of ultraviolet light to control bacteria ([Rodvelt et al., 2013](#));
- 24 • New chelating agents that reduce the use of strong acids ([LePage et al., 2013](#)), and
- 25 • The recovery and reuse of flowback and produced water as hydraulic fracturing fluids,
26 which may reduce need to add additional chemicals ([Horn et al., 2013](#)).

27 In addition to efforts to address environmental concerns, the oil and gas industry continues to
28 research and develop less expensive and more effective fracturing fluid additives. A review of the
29 EPA's new chemicals program found that from 2009 to April 2015, the Agency received pre-
30 manufacturing notices (PMN) for about 110 chemicals that have the potential for use as hydraulic
31 fracturing fluid additives. Examples include chemicals intended for use as clay control agents,
32 corrosion inhibitors, gel crosslinkers, emulsifiers, foaming agents, hydrate inhibitors, scale
33 inhibitors, and surfactants. At the time of PMN submission, these chemicals were not in commercial
34 use in the United States. As of April 2015, the EPA had received 30 notices of commencement,
35 indicating that some of those chemicals are now used commercially.

1 The FracFocus 1.0 data extracted by the EPA cannot be used to identify temporal trends in additive
2 usage. A data set with a much longer duration of data collection would be needed to distinguish
3 actual temporal trends from the normal diversity of chemicals in use as a result of geologic and
4 geographic variability. However, the current FracFocus 1.0 database provides a point of comparison
5 for use in the future.

5.10.Synthesis

6 Chemical mixing is the process by which a base fluid, chemicals, and proppant are mixed prior to
7 injection into the well. This chapter addressed the potential for on-site spills of chemicals used in
8 the hydraulic fracturing process to affect the quality of drinking water resources, which is governed
9 by three overarching factors: (1) fluid characteristics, (2) chemical management and spill
10 characteristics, and (3) chemical fate and transport.

5.10.1. Summary of Findings

11 Documented on-site chemical spills have occurred during the chemical mixing process and reached
12 soil and surface water receptors, with potential impacts to drinking water resources. The EPA
13 analysis of 497 spills reports found no documented impacts to ground water from those particular
14 chemical spills, though there was little information on post-spill testing and sampling ([U.S. EPA,
15 2015n](#)). The EPA's case study in Killdeer, ND strongly suggests that there was impact to ground
16 water, but it is unclear if the path was via the surface spill caused by the blowout ([U.S. EPA, 2015j](#)).
17 The EPA found 151 spills of chemicals or fracturing fluid on or near the well pad in a six-year time
18 period. The chemical spills were primarily caused by equipment failure (34%), closely followed by
19 human error (25%). The remaining spills were caused by a failure of container integrity, weather,
20 vandalism, well communication, or unknown causes. Reported spills cover a large range of volumes,
21 from five to 19,000 gal (19 to 72,000 L), with a median of 420 gal (1,700 L).

22 If a spilled fluid reaches a drinking water resource, the potential to affect the water quality is largely
23 governed by the fluid characteristics. A typical water-based fracturing fluid is composed of 90%–
24 94% water, 5%–9% proppant, and less than 2% chemical additives ([Carter et al., 2013](#); [Knappe and
25 Fireline, 2012](#)). According to the EPA's analysis of disclosures to FracFocus 1.0, approximately 93%
26 of hydraulic fracturing fluids are inferred to use water as a base fluid ([U.S. EPA, 2015a](#)). Non-
27 aqueous constituents, such as nitrogen, carbon dioxide, and hydrocarbons, are also used as base
28 fluids or used in combination with water as base fluids.

29 The EPA has identified 1,076 unique chemicals used in hydraulic fracturing fluids. The chemicals
30 include acids, aromatic hydrocarbons, bases, hydrocarbon mixtures, polysaccharides, and
31 surfactants. Of the 1,076 chemicals, 453 have physicochemical properties in the EPI Suite™
32 database. These chemicals range from fully miscible to insoluble, and from highly hydrophobic to
33 highly hydrophilic. The majority of the chemicals are not volatile.

34 According to the EPA's analysis of FracFocus, a median of 14 chemicals are used per well, with a
35 range of four to 28 (5th and 95th percentiles). The volumes used range from tens to tens of
36 thousands of gallons (tens to tens of thousands of liters) per well; therefore, operators typically

1 store chemicals on-site in large volumes (typically 200 to 400 gal (760–1,500 L) totes), often in
2 multiple containers. The ten most common chemicals (excluding quartz) are methanol,
3 hydrotreated light petroleum distillates, hydrochloric acid, isopropanol, ethylene glycol,
4 peroxydisulfuric acid diammonium salt, sodium hydroxide, guar gum, glutaraldehyde, and
5 propargyl alcohol. These chemicals are present in multiple additives. Methanol was reported in
6 72% of the FracFocus disclosures, and hydrotreated light petroleum distillates and hydrochloric
7 acid were both reported in over half the disclosures ([U.S. EPA, 2015b](#)).

5.10.2. Factors Affecting the Frequency or Severity of Impacts

8 The potential for spills from the chemical mixing process to affect drinking water resources
9 depends on three factors: fluid characteristics, chemical management and spill characteristics, and
10 chemical fate and transport. Specific factors affecting the frequency and severity of impacts include
11 size and type of spill, volume of chemicals spilled, type of chemicals and their properties,
12 combinations of chemicals spilled, environmental conditions, proximity to drinking water
13 resources, employee training and experience, quality and maintenance of equipment, and spill
14 containment and mitigation.

15 The size and type of a fracturing operation, including the number of wellheads, the depth of the
16 well, the length of the horizontal leg, and the number of stages and phases, affect the likelihood and
17 potential impacts of spills. Larger operations may require larger volumes of chemicals, more
18 storage containers, more equipment, and additional transfers between different pieces of
19 equipment. Larger storage containers increase the maximum volume of a spill or leak from a
20 storage container, and additional transfers between equipment increase the possibility of human
21 error.

22 The type of chemical spilled governs how it will move and transform in the environment. More
23 mobile chemicals move faster through the environment, causing a quicker impact. More mobile
24 chemicals are also generally more soluble and may reach the drinking water resource at higher
25 concentrations. Less mobile chemicals will move more slowly, and may have delayed and longer-
26 term impacts, at lower concentrations. The severity of impact is also governed by how the chemical
27 adversely impacts water quality. Water quality impacts may range from aesthetic effects (e.g., taste,
28 smell) to adverse health effects.

29 The environmental conditions at and around the spill site affect the fate and transport of a given
30 chemical. These conditions include soil properties, climate, weather, and terrain. Permeable soils
31 may allow for rapid transport of the spilled fluid through the soil and into a nearby drinking water
32 resource. Precipitation can re-mobilize trapped chemicals and move them over land or through the
33 subsurface.

34 The proximity of a spill to drinking water resources affects the frequency and severity of impact.
35 The closer a spill is to a drinking water resource, the higher potential to reach it. Also, as a fluid
36 moves toward a drinking water resource, it may decrease in concentration, which will affect the
37 severity of an impact. More concentrated chemicals have the potential to have a bigger impact on

1 water quality. The characteristics of the drinking water resource will also influence the magnitude
2 of the impact of a spill.

3 The most successful way to prevent impacts to drinking water resources is to prevent spills from
4 occurring in the first place and to quickly and effectively contain spills. Effective spill containment
5 and mitigation measures can prevent or reduce the frequency and severity of impacts. Spill
6 containment measures include well pad containment liners, diversion ditches, berms, dikes,
7 overflow prevention devices, drip pans, and secondary containers. These may prevent a spill from
8 reaching soil and water receptors. Spill mitigation, including removing contaminated soils,
9 vacuuming up spilled fluids, and using sorbent materials may limit the severity of a spill.
10 Implementation of these measures varies from site-to-site and may not always be effective.

5.10.3. Uncertainties

11 The lack of information regarding the composition of chemical additives and fracturing fluids,
12 containment and mitigation measures in use, and the fate and transport of spilled fluids greatly
13 limits our ability to assess potential impacts to drinking water resources.

14 There is no standard design for hydraulic fracturing fluids. Detailed information on the chemicals
15 used is limited, and volumes of chemicals stored on-site are generally not publicly available. These
16 limitations in data preclude the ability to know what volumes of chemicals may be spilled.
17 FracFocus, which currently holds the most comprehensive information on water and chemicals
18 used in hydraulic fracturing fluids, identifies well-specific chemicals and the concentration of those
19 chemicals as a maximum percentage of the mass of fracturing fluid. Accuracy and completeness of
20 original FracFocus disclosure information was not verified. In applying the EPA-standardized
21 chemical list to the ingredient records in the FracFocus database, standardized chemical names
22 were assigned to only 65% of the ingredient records from the more than 36,000 unique, fully
23 parsed disclosures. The remaining ingredient records could not be assigned a standardized
24 chemical name and were excluded from analyses ([U.S. EPA, 2015a](#)).

25 Operators may specify certain ingredients as confidential business information (CBI) and not
26 disclose the chemical used. More than 70% of disclosures to FracFocus contained at least one CBI
27 chemical. Of disclosures with at least one CBI chemical, the average number of CBI chemicals was
28 five. Approximately 11% of all ingredients were reported to FracFocus as CBI ([U.S. EPA, 2015a](#)). No
29 data are available in FracFocus for any chemical listed as CBI. Therefore, FracFocus CBI chemicals
30 are not included in analyses of volume, physical properties, or any other analysis in this
31 assessment, although we were able to do limited physicochemical analysis of 19 CBI chemicals.

32 Of the 1,076 hydraulic fracturing fluid chemicals identified by the EPA, 623 did not have estimated
33 physicochemical properties reported in the EPI Suite™ database. Knowing the chemical properties
34 of a spilled fluid is essential to predicting how and where it will travel in the environment. Although
35 we can make some generalizations about the physicochemical properties of these chemicals and
36 how spilled chemicals may move in the environment, the distribution of properties could change if
37 we obtained data for all known fracturing fluid chemicals (as well as for those listed as CBI).

1 In order to determine the potential impact of a spill, the physicochemical properties, the site-
2 specific environmental conditions, and proximity to drinking water resources must be known. This
3 information is generally lacking.

4 There is a lack of baseline surface water and ground water quality data. This lack of data limits our
5 ability to assess the relative change to water quality from a spill or attribute the presence of a
6 contaminant to a specific source.

7 In addition to limited information on chemical usage, we cannot complete a thorough assessment of
8 the potential impact of chemical spills due to limited information on actual spills. Data sources used
9 in the EPA's spills analysis do not cover all states with hydraulic fracturing activity. The available
10 data provide limited information on the types and volumes of chemicals spilled, spill causes,
11 containment and mitigation measures, and sources of spills. In addition, there is little available data
12 on impacts of spills, due to a lack of baseline data and incomplete documentation of follow-up
13 actions and testing.

14 In general, then, we are limited in our ability to fully assess potential impacts to drinking water
15 resources from chemical spills, based on available current information. To improve our
16 understanding we need: more information on the chemical composition of additives and fracturing
17 fluid; the physicochemical properties of chemicals used; baseline monitoring and field studies of
18 spilled chemicals; drinking water resources quality conditions before and after hydraulic fracturing
19 is performed; detailed site-specific environmental conditions; more information on the
20 containment and mitigation measures and their effectiveness; and the types and volumes of spills.

5.10.4. Conclusions

21 The chemical mixing stage of the hydraulic fracturing process has the potential to cause impacts to
22 drinking water resources by way of surface spills of chemicals and fracturing fluids. There are
23 documented chemical spills at fracturing sites, but a lack of available data limits our ability to
24 determine impacts. Potential impacts to drinking water resources are governed by the fluid
25 characteristics, chemical management and spill characteristics, and the fate and transport of spilled
26 chemicals through the environment.

Text Box 5-16. Research Questions Revisited.

1 ***What is currently known about the frequency, severity, and causes of spills of hydraulic fracturing fluids***
2 ***and additives?***

- 3 • The frequency of on-site spills from hydraulic fracturing operations could be obtained for two states.
4 Frequency estimates from data and literature ranged from 0.4 to 1.3 spills for every 100 wells
5 hydraulically fractured in Pennsylvania and Colorado, respectively, and between 3.3 and 12.2 spills for
6 every 100 wells installed in Pennsylvania ([Rahm et al., 2015](#); [U.S. EPA, 2015n](#); [Brantley et al., 2014](#);
7 [Gradient, 2013](#)).¹ These estimates include spills of hydraulic fracturing chemicals and fluids, and
8 flowback and produced water reported in state databases. It is unknown whether these spill estimates
9 are representative of national occurrences. Estimates of the frequency of on-site spills from hydraulic
10 fracturing operations were unavailable for other areas. If the estimates are representative, the number of
11 spills nationally could range from 100 to 3,700 spills annually, assuming 25,000 to 30,000 new wells are
12 fractured per year.
- 13 • In an analysis of spills, EPA characterized volumes and causes of hydraulic fracturing-related spills
14 identified from selected state and industry data sources. The spills occurred between January 2006 and
15 April 2012 in 11 states and included 151 cases in which fracturing fluid or additives spilled on or near a
16 well pad ([U.S. EPA, 2015n](#)). These cases were likely a subset of all chemical and fracturing fluid spills
17 during the study's time period. The reported volume of chemicals or fracturing fluid spilled ranged from
18 5 gal to more than 19,000 gal (19 to 72,000 L), with a median volume of 420 gal (1,600 L) per spill. Spill
19 causes included equipment failure, human error, failure of container integrity, and other causes (e.g.,
20 weather and vandalism). The most common cause was equipment failure. Specific causes of equipment
21 failure included blowout preventer failure, corrosion, and failed valves. More than 30% of the chemical or
22 fracturing fluid spills characterized by the EPA came from fluid storage units (e.g., tanks, totes, and
23 trailers) ([U.S. EPA, 2015n](#)).

¹ Spill frequency estimates are for a given number of wells over a given period of time. These are not annual estimates nor are they for over a lifetime of the wells.

1 **What are the identities and volumes of chemicals used in hydraulic fracturing fluids, and how might this**
2 **composition vary at a given site and across the country?**

- 3 • In this assessment, we compiled a list of 1,076 chemicals used to formulate hydraulic fracturing fluids.
4 These chemicals include acids, alcohols, aromatic hydrocarbons, bases, hydrocarbon mixtures,
5 polysaccharides, and surfactants. This is a cumulative list over multiple wells and years. Operators used
6 an median of 14 unique chemicals per well according to the EPA's analysis of disclosures to FracFocus
7 ([U.S. EPA, 2015a](#)).
- 8 • Our analysis showed that chemical use varies and that no single chemical is used at all well sites across
9 the country, although several chemicals are widely used. Methanol, hydrotreated light petroleum
10 distillates, and hydrochloric acid were reported in 65% or more of FracFocus disclosures analyzed by the
11 EPA ([U.S. EPA, 2015a](#)). The composition of hydraulic fracturing fluids varies by state, by well, and within
12 the same service company and geologic formation. This variability likely results from several factors,
13 including the geology of the formation, the availability and cost of different chemicals, and operator
14 preference ([U.S. EPA, 2015a](#)).
- 15 • Estimates from the EPA's database developed from disclosures made to FracFocus suggest median
16 volumes of individual chemicals injected per well ranged from a few gallons to thousands of gallons, with
17 a median of 650 gal (2,500 L) per chemical per well ([U.S. EPA, 2015b](#)). If 14 unique chemicals are used
18 per well, then an estimated 9,100 gal (34,000 L) of chemicals may be injected per well ([U.S. EPA, 2015a](#)).

19 **What are the chemical and physical properties of hydraulic fracturing chemical additives?**

- 20 • Measured or estimated physicochemical properties were obtained for 453 of the 1,076 chemicals
21 reported in hydraulic fracturing fluids. The wide variety of chemicals results in a wide range of
22 physicochemical properties.
- 23 • Many hydraulic fracturing chemicals fully dissolve in water, but the aqueous solubilities range from fully
24 miscible to sparingly soluble.
- 25 • The octanol-water partition coefficient ranges from the highly hydrophilic to the highly hydrophobic.
26 Many chemicals used in hydraulic fracturing fluid fall in the middle of this range, suggesting that they will
27 divide equally between water and solid phase, so that they may move slower through the environment
28 than those that associate more with water. More chemicals will associate strongly with soils and organic
29 materials, suggesting the potential of these chemicals to be long-term contaminants if they are spilled.
- 30 • There are few hydraulic fracturing chemicals that are volatile. Most hydraulic fracturing chemicals will
31 tend to remain in water as opposed to volatilizing to the air.

- 1 • The chemicals for which we know physicochemical properties are not necessarily the chemicals most
2 frequently reported as used in hydraulic fracturing activities. Of the 453 chemicals for which
3 physicochemical properties were available, 18 of the top 20 most mobile chemicals were included in 2%
4 or less of disclosures ([U.S. EPA, 2015b](#)). However, two more common, but highly mobile chemicals,
5 choline chloride and tetrakis (hydroxymethyl) phosphonium sulfate were reported in 14% and 11% of
6 disclosures, respectively. These two chemicals are thus relatively more common, and, if spilled, their
7 properties of high mobility means they would move quickly through the environment with the flow of
8 water.

9 ***If spills occur, how might hydraulic fracturing chemical additives contaminate drinking water***
10 ***resources?***

- 11 • When chemicals are spilled, there are several paths by which a chemical could contaminate drinking
12 water resources. The chemical could flow overland to nearby surface water, penetrate into the soil that
13 could travel laterally and impact surface waters, or infiltrate and contaminate the underlying ground
14 water.
- 15 • Of the 151 spills characterized by the EPA, fluids reached surface water in 13 (9%) and soil in 97 (64%)
16 of those cases. None of the spills reportedly reached ground water ([U.S. EPA, 2015n](#)), but it could take
17 several years for spilled fluids to infiltrate soil and leach into ground water. Thus, it may not be
18 immediately known whether a spill reaches ground water or not
- 19 • The timing of a potential impact varies, but it could occur quickly, be delayed, have a continual impact
20 over time, or occur much later. Which path the spill takes depends on different conditions, such as
21 distance to a water receptor, spill volume, soil characteristics, and the physicochemical properties of the
22 chemical.

5.11. References for Chapter 5

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