

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.

1. The following is a list of the names of the persons who have been appointed as members of the Board of Directors of the Corporation for the year ending December 31, 2010. The names of the persons who have been appointed as members of the Board of Directors for the year ending December 31, 2010 are listed in the table below.

No.	Name	Address	Age	Nationality	Profession	Shareholding		Date of Appointment	Term of Office
						Number of Shares	Percentage		
1	Mr. A. B. C.	123 Street, City, State, Country	45	Indian	Director	1000	10%	1/1/2010	31/12/2011
2	Mr. D. E. F.	456 Street, City, State, Country	52	Indian	Director	2000	20%	1/1/2010	31/12/2011
3	Mr. G. H. I.	789 Street, City, State, Country	38	Indian	Director	500	5%	1/1/2010	31/12/2011
4	Mr. J. K. L.	101 Street, City, State, Country	60	Indian	Director	3000	30%	1/1/2010	31/12/2011
5	Mr. M. N. O.	202 Street, City, State, Country	48	Indian	Director	1500	15%	1/1/2010	31/12/2011
6	Mr. P. Q. R.	303 Street, City, State, Country	55	Indian	Director	2500	25%	1/1/2010	31/12/2011
7	Mr. S. T. U.	404 Street, City, State, Country	42	Indian	Director	1000	10%	1/1/2010	31/12/2011
8	Mr. V. W. X.	505 Street, City, State, Country	58	Indian	Director	2000	20%	1/1/2010	31/12/2011
9	Mr. Y. Z. A.	606 Street, City, State, Country	40	Indian	Director	1000	10%	1/1/2010	31/12/2011
10	Mr. B. C. D.	707 Street, City, State, Country	50	Indian	Director	2000	20%	1/1/2010	31/12/2011

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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.

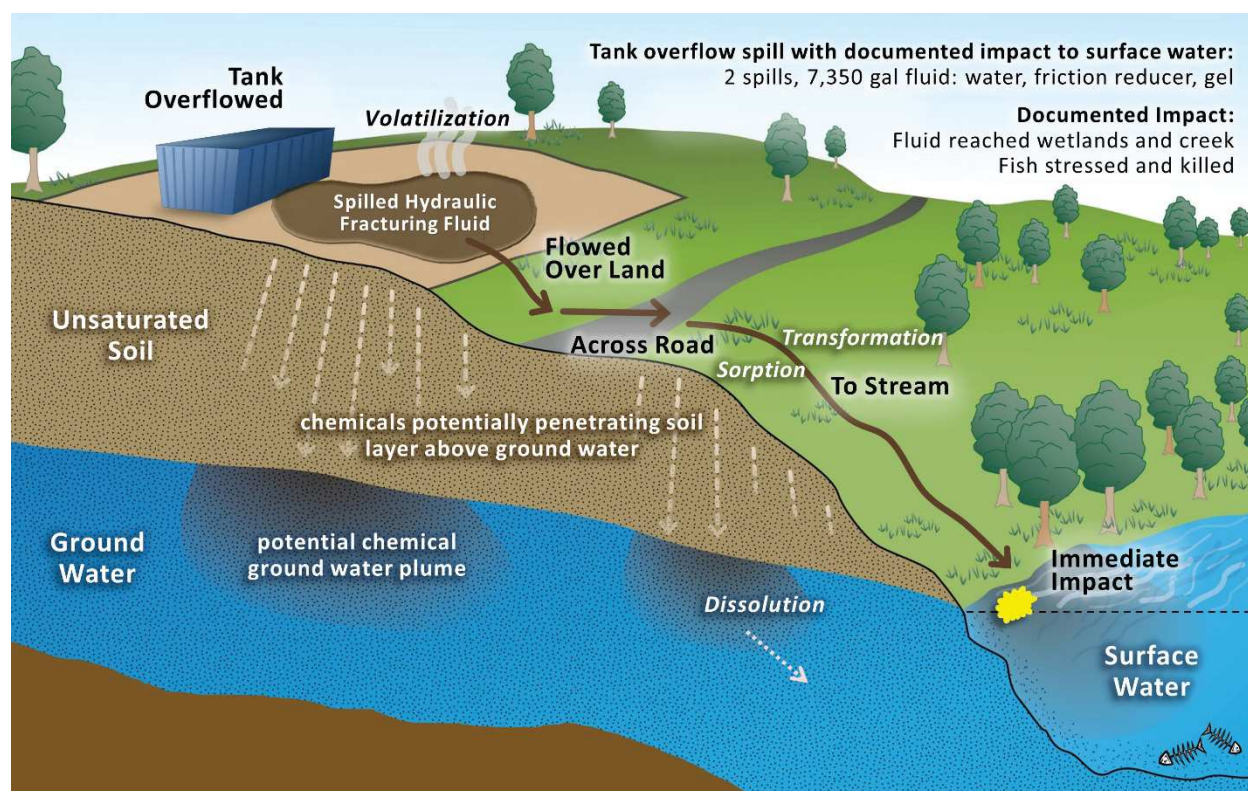


Figure 5-19. Fate and Transport Spill Example: Case 1.

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.

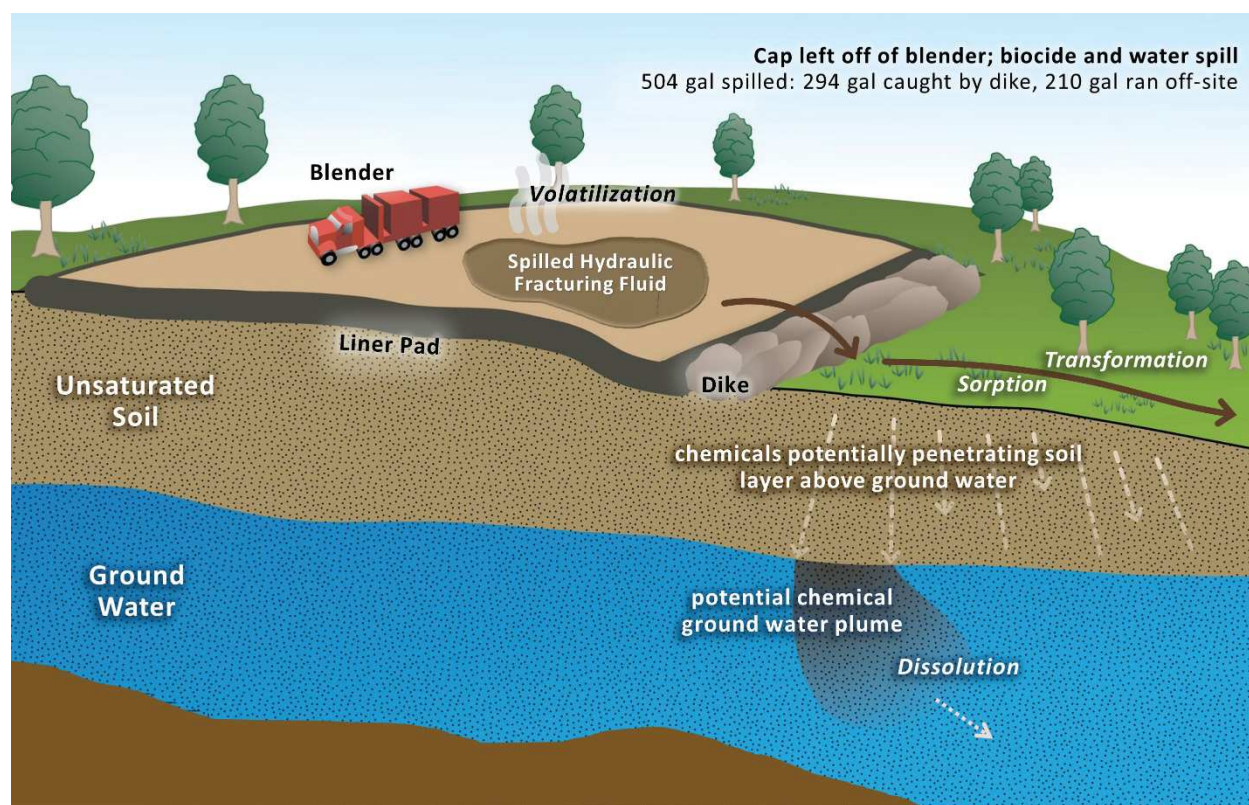


Figure 5-20. Fate and Transport Spill Example: Case 2.

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.

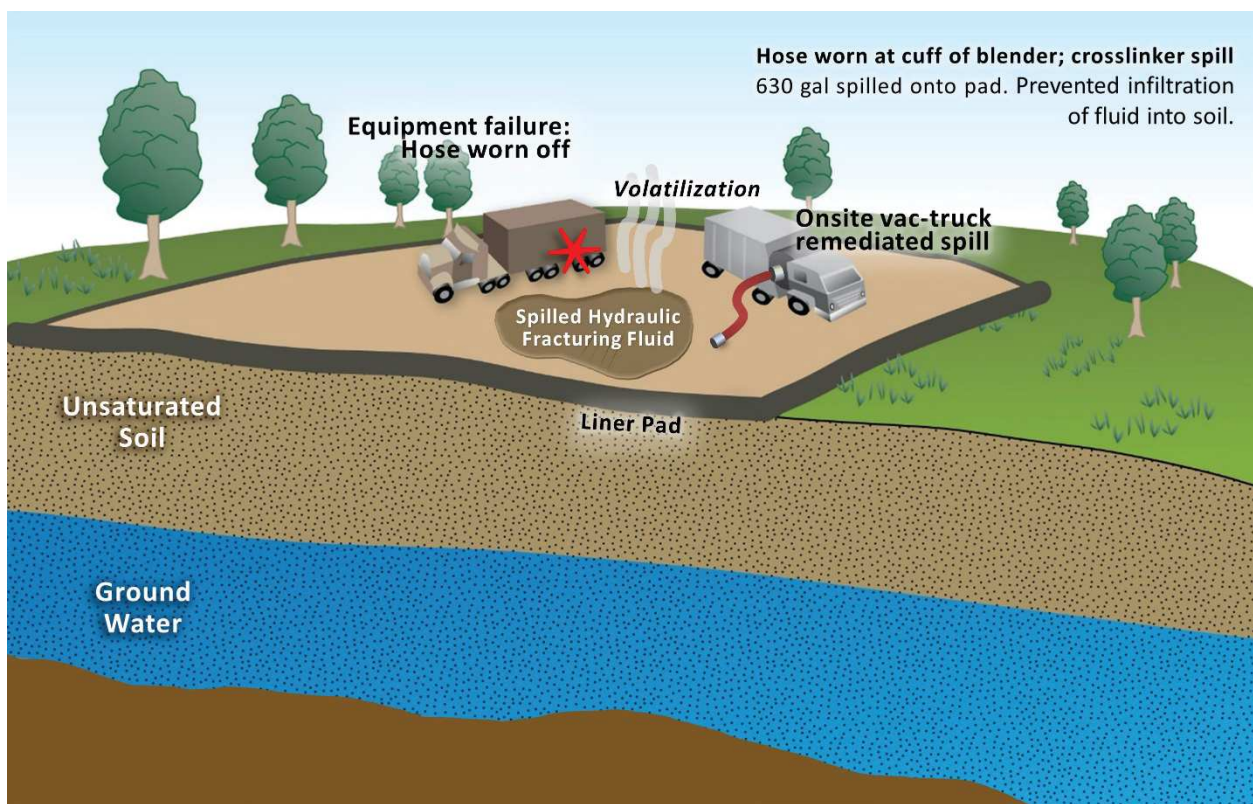


Figure 5-21. Fate and Transport Spill Example: Case 3.

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.

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