National Human Health Risk Evaluation for Hydraulic Fracturing Fluid Additives

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Introduction

Improvements in directional drilling and hydraulic fracturing (HF) technologies have allowed for the extraction of large reserves of natural gas and oil from formerly uneconomical low-permeability formations (*e.g.*, shale, tight sand, tight carbonate). The increasing use of HF in the US and globally to develop oil and gas reserves in these "tight formations" has brought with it heightened attention to its alleged impacts. We have previously examined HF procedures used in the Marcellus Shale and the chemical constituents commonly used during the HF process (Gradient, 2012). That earlier analysis addressed whether adverse human health impacts relating to drinking water could be associated with HF fluids in the Marcellus Shale as a result of their intended use (to aid in fracturing deeply buried hydrocarbon deposits) or in the event that there were unintended surface releases (spills) of these constituents. The purpose of this report is to expand the scope of these prior analyses to address the use of HF fluids and their potential impacts on drinking water in a broad range of shale plays and other tight formations across the contiguous United States.

ES.1 Hydraulic Fracturing Process Overview

Recent advances in well drilling techniques, especially the increased use of "horizontal" drilling in conjunction with high volume hydraulic fracturing, have expanded the capacity of oil and gas extraction from a single well. In addition, it is increasingly common to install multiple horizontal wells at a single "well pad" in order to maximize gas/oil production and minimize the amount of land disturbance when developing the targeted formations.

Hydraulic fracturing is a multi-step process aimed at opening up fractures within the natural hydrocarbon-bearing geologic formations and keeping fractures open to maximize the flow of oil and/or natural gas to a production well. The HF process involves pumping fluid (referred to here as "HF fluid") into the target formation to create fractures, and then pumping proppants (*e.g.*, sand) into the induced fractures to prevent them from closing. After the proppant is in place, all readily recoverable HF fluid is pumped from the well or flows under pressure to the surface along with water from the formation that was hydraulically fractured; this process is referred to as "flowback" and we use the term "flowback fluid" to describe the fluid that flows back out of the well during the initial period following hydraulic fracturing.[1]

The fluids used in the HF process generally consist mostly of water with small amounts of chemical additives, typically comprising approximately 0.5% by weight of the fluid, to enhance the efficiency of the fracturing process. Hydraulic fracturing additives serve many functions in HF, such as limiting the growth of bacteria, preventing corrosion of the well casing, and reducing friction to minimize energy losses during the fracturing phase. The HF additives used in a given hydraulic fracture treatment depend on the geologic conditions of the target formation.

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[1] The composition of the fluid that flows out of the well once the HF process has concluded and production begins changes over time. Initially, the fluid is generally a mixture of the fluid used to hydraulically fracture the well and water and other constituents that are naturally present in the formation (sometimes referred to as "formation water"). Over time, the proportion of HF fluid in the fluid flowing out of the well declines, and after a period of time the fluid flowing out is almost entirely formation water. As a matter of convenience, industry generally refer to the fluid that flows out of the well for the first several weeks as "flowback," "flowback water," or "flowback fluid," and the fluid that continues to flow from the well over the longer term production period as "produced water," although there is no bright line separating the two.

Every step in the well development process – well installation, fracturing, fluids management, and well operation – adheres to a carefully designed set of protocols and is managed to minimize the potential for incidents that could result in unintentional releases of fluids and to maximize gas/oil yield. The process is extensively regulated at the federal, state, and even the local level. A detailed description of the HF process can be found in a variety of documents (*e.g.*, CRS, 2009; API, 2009).[2]

ES.2 Scope of This Evaluation

While it is beyond the scope of this report to cover all natural hydrocarbon-bearing formations which use hydraulic fracturing to develop the resource, we have examined a broad range of current oil and gas "plays," focusing on tight formations in the contiguous US, specifically those that occur in deep shales, tight sands, and tight carbonates (Figure ES.1 shows the regional extent of these sedimentary basins across the contiguous US).[3]

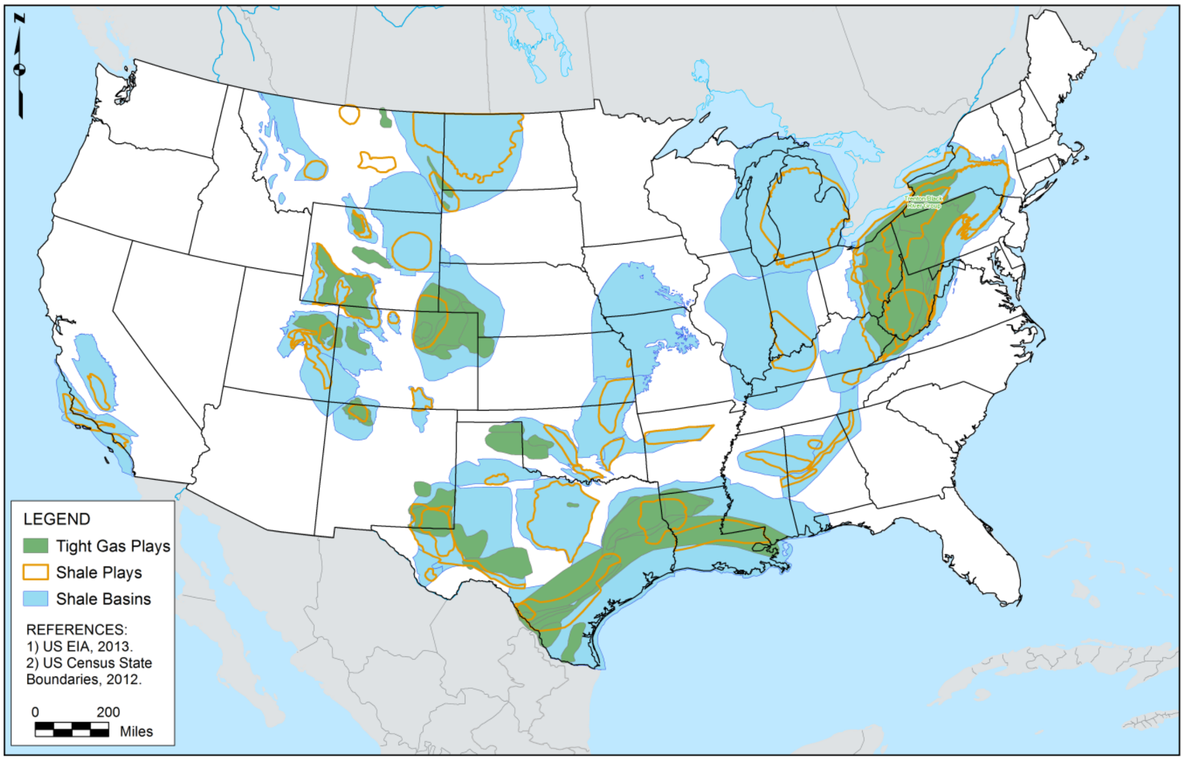

Figure ES.1 Major Hydrocarbon Reservoirs in Tight Formations

Tight formations around the country are estimated to contain significant oil and gas reservoirs (Biewick, 2013). Oil and gas exploration activities are expanding in these formations, thereby attracting interest from multiple stakeholders, including the public, regulators, scientific community, and industry. Concerns have been expressed over the potential for the additives used in the HF process to impact drinking water resources. The United States Environmental Protection Agency (US EPA) is conducting a Congress-mandated study evaluating the potential impacts of HF on drinking water resources which focuses "primarily on hydraulic fracturing of shale for gas extraction" (US EPA, 2012b, p. 6). State

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[2] See also web resources: http://fracfocus.org/hydraulic-fracturing-process; http://www.energyindepth.org/; and http://www.halliburton.com/public/projects/pubsdata/hydraulic_fracturing/fracturing_101.html.

[3] The contiguous US has a wide range of sedimentary basins with different characteristics and our analysis applies more broadly to sedimentary basins around the world with characteristics similar to those considered in our report.

environmental agencies are also assessing the potential environmental impacts of HF, including the likelihood of impacts on drinking water supplies.[4]

This report, which Gradient has prepared on behalf of Halliburton Energy Services, Inc. (HESI), presents our evaluation of the potential human health impacts relating to drinking water that are associated with the use of typical HF fluids. We examine the human health risks posed by the "intended" use of these fluids, *i.e.*, the pumping of the fluids into a target formation to create fractures in the formation. Specifically, we note the steps that are taken in well construction to prevent the HF fluids being pumped down the well from escaping the wellbore and coming into contact with drinking water aquifers and to ensure that the HF fluids reach their intended destination, *i.e.*, the formation to be hydraulically fractured ("zonal isolation"). We then examine whether it is possible for HF fluids pumped into tight formations to migrate upward from those formations. We address this concern in this report, although we note at the outset that the New York State Department of Environmental Conservation (NYSDEC) (2011) and other stakeholders have evaluated this issue and concluded that it would not be plausible for the fluids to migrate upward and contaminate shallow drinking water aquifers. We also examine the human health risks associated with "unintended" (accidental) releases of fluids containing HF fluid and flowback fluid constituents, focusing on surface spills. We evaluate the potential for such spills to impact groundwater or surface water and the human health implications of exposure to HF constituents if such water is then used for drinking water purposes.

The possible exposure scenarios evaluated in our risk analysis are illustrated in the figure below, and addressed in turn in the summary that follows.

Exposure Pathways Evaluated:

1. Upward from deep, hydraulically fractured formation to shallow groundwater
2. Migration of a surface spill to groundwater
3. Migration of a surface spill to a stream or river

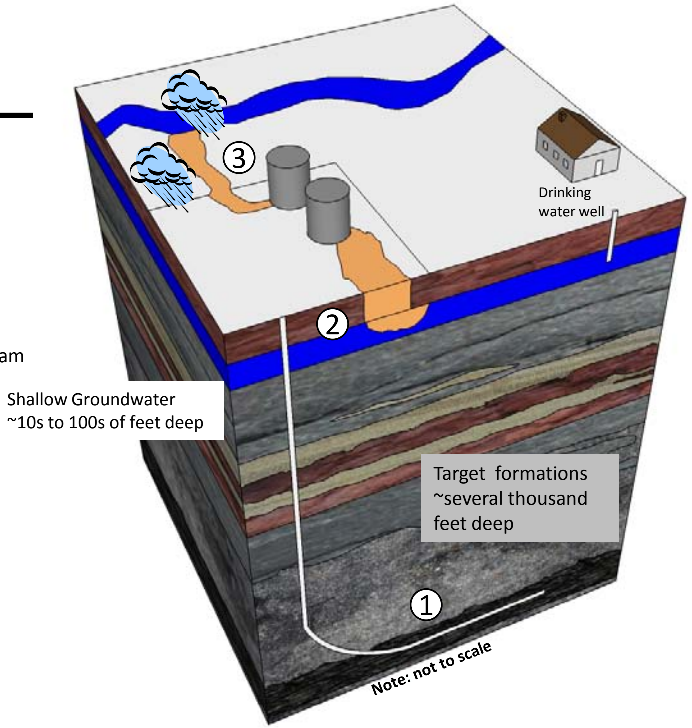

Figure ES.2 Illustration of Exposure Pathways Examined in Risk Analysis

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[4] For example, the NYSDEC has prepared several versions of its Supplemental Generic Environmental Impact Statement (NYSDEC, 2009, 2011), which contains generic permit requirements for the development of natural gas production wells utilizing HF in the Marcellus Shale, which underlies significant areas of New York, extending also under large portions of Pennsylvania, West Virginia, and Ohio.

ES.3 Implausibility of Migration of HF Constituents from Target Formations

As part of the HF process, HF fluids are pumped down the well and into the target formation to create fractures that will facilitate the production of oil/gas from the well. Production wells are carefully constructed with multiple layers of casing and cement in accordance with state requirements and industry standards in order to ensure that the fluids in the well do not come into contact with drinking water aquifers or subsurface layers other than the formation being targeted for production; this is often referred to as "zonal isolation" (API, 2009; GWPC and ALL Consulting, 2009).

When installed in accordance with these standards and requirements, casing and cementing are effective in protecting Underground Sources of Drinking Water ("USDWs") from the fluids used in HF operations. As we discuss, NYSDEC concluded, using the analogy of underground injection wells, that the likelihood of a properly constructed well contaminating a potable aquifer was less than 1 in 50 million wells.[5]

Accordingly, the only pathway by which HF fluids pumped into a properly constructed well during the HF process could reach a USDW would be for the fluids to migrate upward from the target formation. We therefore considered whether fluid could migrate upward through intact bedrock, through the fractures created as a result of the HF process ("induced fractures"), or along natural faults.[6]

Our analysis indicates that contamination of USDWs *via* any of these theoretical migration pathways is not plausible. Tight oil and gas formations are set in very restrictive environments that greatly limit upward fluid migration due to the presence of multiple layers of low permeability rock, the inherent tendency of the naturally occurring salty formation water (*i.e.*, brines) in these deep formations to sink below rather than mingle with or rise above less-dense fresh water (density stratification), and other factors, as demonstrated by the fact that the oil, gas, and brines in the formation have been trapped for millions of years. Moreover, the effects of the HF process itself will not cause changes in these natural conditions sufficient to allow upward migration to USDWs for the following reasons.

- During the HF process, elevated pressures are applied for a short duration (a matter of hours to days). This period of elevated pressure is far too short to mobilize HF constituents upward through thousands of feet of low permeability rock to overlying potable aquifers.
- Fluid migration to USDWs *via* induced fractures is also not plausible. An extensive database of measured fractured heights has been compiled from microseismic monitoring of over 12,000 HF stages. These data indicate that even the tallest fractures have remained far below USDWs.
- These same data were used to evaluate potential hydraulic fracture-fault interactions and the potential for fluid movement up natural faults. Our analysis shows that fault sizes activated by hydraulic fracturing are very small (typically < 30 ft in size) and are relatively unimportant for enhancing upward fluid migration.

Overall, there is no scientific basis for significant upward migration of HF fluid or brine from tight target formations in sedimentary basins. Even if upward migration from a target formation to a potable aquifer were hypothetically possible, the rate of migration would be extremely slow and the resulting dilution of the fluids would be very large. Such large dilution under this implausible scenario would reduce HF fluid constituent concentrations in the overlying aquifer to concentrations well below health-based standards/benchmarks. Given the overall implausibility and very high dilution factor, this exposure pathway does not pose a threat to drinking water resources.

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[5] Given the very low probability of a properly constructed well impacting shallow aquifers, we did not quantify potential health risks for such a scenario.

[6] We have prepared two scientific papers on these issues which have been submitted for publication. In addition, we had previously considered many of these issues in the context of an analysis submitted to the NYSDEC that focused on the Marcellus Shale (Gradient, 2012).

Various regulatory authorities have evaluated hypothetical upward migration of HF constituents during HF activities and come to similar conclusions. For example, based on its initial analysis in 2009, NYSDEC concluded that "groundwater contamination by migration of fracturing fluid [from the deep fracture zone] is not a reasonably foreseeable impact" (NYSDEC, 2009, p. 8-6). In its revised Draft Supplemental Generic Environmental Impact Statement (dSGEIS), NYSDEC (2011) reaffirmed this conclusion, indicating "…that adequate well design prevents contact between fracturing fluids and fresh ground water sources, and…ground water contamination by migration of fracturing fluid [from the deep fracture zone] is not a reasonably foreseeable impact" (NYSDEC, 2011, p. 8-29).

Thus, our analysis of hypothetical upward migration of HF constituents from tight formations across the US confirms that migration of HF fluid additives from target formations up through overlying bedrock to a surface aquifer is an implausible chemical migration pathway. The thickness of the overlying confining rock layers, and the effective hydraulic isolation that these overlying layers have provided for millions of years will sequester fluid additives within the bedrock far below drinking water aquifers. Neither induced fractures nor natural faults would provide a pathway for HF fluids to reach USDWs, as demonstrated by an extensive dataset on fracture heights and theoretical limits on fracture height growth. Even if such a pathway were hypothetically assumed, the slow rate of migration would lead to very large dilution and attenuation factors, thereby reducing HF fluid constituent concentrations in USDWs to levels that would be well below health risk-based benchmarks, and that would not pose a potential threat to human health even under such an implausible scenario.

ES.4 HF Fluid Accidental Spill Scenario Exposure Analysis

We also examined potential "unintended" fluid spill scenarios to assess whether such spills could lead to the presence of HF constituents in either groundwater or surface water that may be used as drinking water sources at levels that could pose possible human health risks. In this report, we use the term "spills" to encompass various types of accidental releases of fluids containing HF constituents, such as leaks from HF fluid containers, storage tanks, or pipe/valve ruptures during fluid handling, or even possibly cases of wellhead blowouts. As a conservative (*i.e.*, health protective) aspect of our assessment, we have assumed that potential spills are "unmitigated," meaning that any fluid spilled is not recovered, even though it is standard practice at well sites to have measures in place to mitigate spills. Instead, spills are assumed for purposes of this study to wash off of the well pad into nearby streams (assumed to exist in proximity to the pad)[7] and/or migrate into the soil and ultimately impact underlying groundwater resources.

ES.4.1 Overview of Approach to Surface Spill Analysis

We assessed the potential for human health impacts associated with drinking water as a result of potential surface spills of fluids containing HF chemical constituents (*i.e.*, HF fluids and flowback fluid). Our goal was to determine the concentrations at which the constituents of these fluids might be found in drinking water as a result of a spill and then compare those concentrations to concentration levels at which adverse health effects could start to become a possible concern. We also undertook an assessment of the likelihood that a spill of either HF fluids or flowback fluids would occur at a given well site.

The concentration of HF fluid or flowback fluid constituents that could possibly be found in drinking water as the result of a spill or release depends on a number of factors, beginning with the volume of fluid spilled. However, the concentration of the constituents in the fluid spilled would be reduced as a result of dilution in water or soil as it moves through the environment to reach a drinking water source. The extent of this dilution would depend on the conditions accompanying the spill. Therefore, a key part of our

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[7] We have not included any dilution that would inherently be provided by precipitation during the transport of material from the well pad to surface water.

analysis was determining the anticipated extent of dilution of constituent concentrations (expressed as "dilution factors" or "DFs").

Given the national scope of oil and gas production using HF, our analysis adopted methods that allow for assessing possible risks associated with a variety of potential spills spanning a wide range of environmental conditions. For example, depending on differences in climate and topography, regional streamflow varies substantially. In the event of a surface spill, such regional variations in streamflow would be expected to lead to variations in the possible HF constituent concentrations potentially impacting surface water – areas with low flows would likely experience higher HF concentrations (less dilution) than areas with higher flows (more dilution). Similarly, differences in local groundwater conditions (*e.g.*, depth to groundwater, differences in aquifer properties, *etc.*) will give rise to differences in the impacts of surface spills possibly impacting groundwater resources used for drinking water.

Given this natural variability, the results from "deterministic," or site-specific, assessment approaches can be constrained by the fact that the results can be difficult to extrapolate more broadly beyond the specific conditions evaluated. To address this limitation, we have adopted "probabilistic" methods that incorporate the wide range of variability that occurs in areas with active oil and gas plays in tight formations. Assessing the possible drinking water impacts associated with HF spills in a probabilistic framework is accomplished by examining a large number of possible combinations ("samples") from a range of conditions that might be encountered in nature. For example, one "sample" might combine a small spill volume with a discharge into a large stream; another "sample" might combine a small spill volume with a discharge into a small stream; while yet another sample could combine a larger spill volume into a small stream. By assessing a large number of repeated (random) "samples," the probabilistic analysis assesses the full range of possible conditions associated with a spill.

In order to use this approach, we needed to determine "probability distributions" for a number of key variables that reflect how likely a particular condition (such as spill size) is to occur. We then needed to combine the probabilities of different conditions occurring in a way that reflected the overall probability that a spill would result in a particular chemical constituent concentration in drinking water. To do this, we used a common simulation technique termed Monte Carlo sampling. The Monte Carlo sampling process involved selecting random samples from the underlying probability distributions that define variables relating to spill size and factors that affect chemical transport/dilution ("input variables"), and then using these random samples to estimate the resulting impacts (*e.g.*, resulting HF constituent concentration in either surface water or groundwater). This process was repeated many times (we selected a million samples) to generate the full range of possible combinations of outcomes spanning the full range of the input variables. The figure below illustrates the Monte Carlo process.

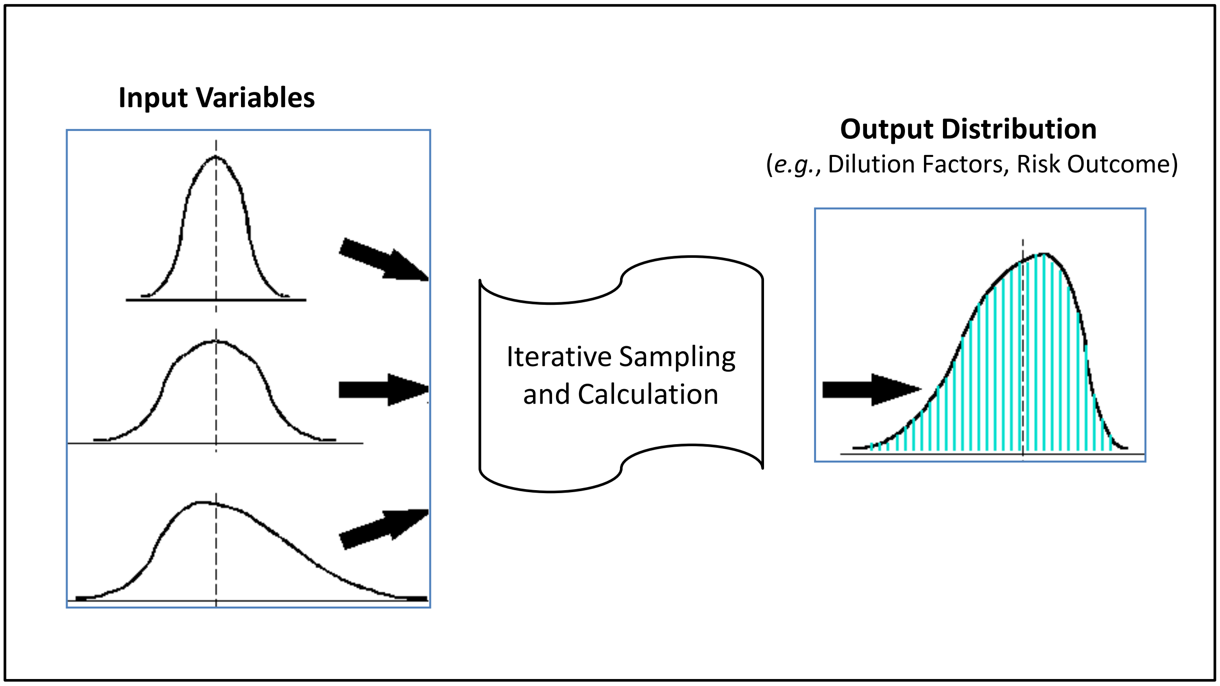

Figure ES.3 Illustration of Monte Carlo Sampling Method Used to Develop a Distribution of Outcomes (*e.g.*, DF values) to Assess Health Risks of HF Spills

Using this approach, we developed distributions of possible outcomes, *i.e.*, distributions of DFs, and resulting constituent concentrations in surface water and groundwater that might result from surface spills. We then assessed the likelihood of possible human health impacts by comparing the range of predicted constituent concentrations in surface water and groundwater with "risk-based concentrations" (RBCs) for drinking water (*i.e.*, concentrations below which human health impacts are not expected to occur) for various chemical constituents that may be found in HF or flowback fluids. Finally, we factored in the likelihood of a spill in order to determine an overall probability of human health impacts associated with spills of fluids containing HF chemical constituents.

Our analysis evaluated a wide range of HF constituents found in 12 typical HESI HF fluid systems used to develop oil and gas resources in tight formations. In addition, we extended our analysis to constituents that have been found in flowback fluid from wells that have been hydraulically fractured even though many of these constituents derive from the naturally-occurring formation water as opposed to the HF fluid pumped into the formation.

ES.4.2 Fluid Spill Distribution

As noted, our Monte Carlo sampling was based on probability distributions for key variables representing a range of conditions. The first of these variables is the possible range of volumes of surface spills during HF operations. The Pennsylvania Department of Environmental Protection (PADEP) Office of Oil and Gas Management (OGM) has compiled information specifically relating to spills during HF activities.[8] Spills associated with HF activities are reported in the PADEP "Oil and Gas Compliance Report" database, which is "designed to show all inspections that resulted in a violation or enforcement action assigned by the Oil and Gas program."[9] We downloaded all of the inspection data for wells tapping

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[8] http://www.portal.state.pa.us/portal/server.pt/community/office_of_oil_and_gas_management/20291. For reasons discussed later in this report, we did not use several other state databases because of difficulties in extracting information relating specifically to spills of HF fluid or flowback fluid.

[9] http://www.portal.state.pa.us/portal/server.pt/community/oil_and_gas_compliance_report/20299.

"unconventional" formations (primarily the Marcellus Shale, which is one of the tight formations covered by our analysis). From this information, we compiled all entries for inspections from 2009 through April, 2013 that indicated a fluid spill (with an associated volume, typically reported in gallons or barrels, but sometimes volumes as small as a cup or a quart). A total of 231 inspections reported spills from "unconventional" systems. A summary of the spill volumes associated with different probabilities (percentiles) for this distribution of spill data is provided below.[10]

Table ES.1 Spill Volume Percentiles

Percentile	Spill Volume (gal)
10%	1
25%	6
50%	38
75%	230
90%	1,152
95%	2,999

Note:
Cumulative percentiles based on fitting data to a lognormal distribution and selecting 1 million Monte Carlo samples. The percentiles represent the likelihood spill volumes are less than or equal to the volume at the reported percentiles.

The foregoing information provides a reasonable means to estimate the distribution of HF spill volumes *if a spill occurs*. The PADEP OGM also has compiled information on the number of wells installed each year. For the period 2009 through 2012, a total of 5,543 wells were installed in the Marcellus Shale in Pennsylvania. For this same period, there were 185 spills reflected in the PADEP database (for wells in unconventional formations). This suggests a spill frequency of 3.3% over this 4-year period. This spill frequency is likely a conservative (upper estimate) interpretation of the data, as it includes all spills in the PADEP database, even though some materials spilled were not identified as HF or flowback fluids (*e.g.*, hydraulic oil).[11]

For the purposes of our risk analysis, we have conservatively evaluated potential risks based on two scenarios: a 3.3% spill probability as well as a doubling of this rate to a 6.6% spill probability (*i.e.*, assuming hypothetically spills occur at double the frequency reported in the PADEP data) as a conservative measure. This range of spill probabilities is considered reasonable, if conservative, to use for our risk analysis.

ES.4.3 Surface Spill Impacts

If uncontrolled, HF constituents spilled to the surface could migrate overland *via* surface runoff/erosion to adjacent surface water resources; surface spills could also allow HF constituents to migrate through the soil and impact underlying groundwater resources under certain circumstances. For our exposure and risk analysis, we evaluated two bounding sets of hypothetical conditions, assessing the implications if: (1) 100% of the surface spill leaches to groundwater and (2) 100% of the surface spill impacts surface

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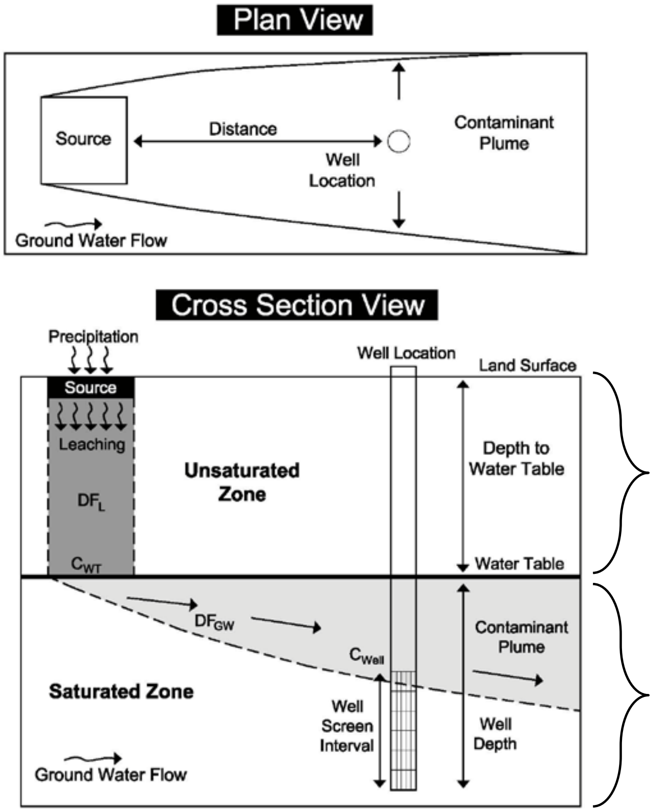
[10] The maximum spill reported was 7,980 gallons (Dimock, PA). Our analysis encompasses a spill of this size (it falls in the 99.6th percentile). In fact, because the distribution is unbounded at the upper tail, the largest spill volumes included in our analysis exceeded even this spill size and were well over 100,000 gallons, such that the range included could even account for such events as wellhead blowouts.

[11] Moreover, the way we have conducted this part of the analysis may result in an underestimation of the number of "unconventional" wells drilled to which the number of spills at "unconventional" well sites should be compared – leading to a potential overestimation of the rate of spills at these well sites.

water. These hypothetical scenarios bound the possible fate of surface spills, because the entirety of any given spill could not migrate to both groundwater and surface water (as our worst case analysis assumes), and therefore this approach, adopted solely for the purposes of this study, is considered quite conservative. More likely, even if spills escaped containment measures at the well pad, a portion of the spilled fluid would almost certainly be retained in the soil on or adjacent to the pad such that only a portion would potentially reach any nearby surface water bodies. Similarly, it is unlikely that 100% of the spill volume would leach to groundwater, as we have conservatively assumed. We discuss the development of probability distributions for the key variables with respect to these scenarios, below.

ES.4.3.1 Surface Spill Impacts to Groundwater

As one possible scenario for this study, surface spills of HF fluids or flowback fluids along with their constituents could spread out and soak into the ground in a shallow zone at the soil's surface. The fluid constituents in this surface zone could then be subject to leaching downward through unsaturated soils (herein referred to as the "unsaturated zone") as rainfall percolates into the ground, carrying the HF constituents downward with the percolating water. Given sufficient time, if the constituents in the fluid do not adsorb to soil and/or degrade (both processes are likely to occur), the constituents could reach a shallow aquifer beneath the area of the spill. The process of leaching downward through the soil would lead to spreading of the constituents within the unsaturated zone (dispersion) and mixing of the HF constituents in the leaching water over time. Similarly, if the constituents leach sufficiently and reach shallow aquifers, they could mix within the underlying groundwater ("saturated zone") and potentially migrate with groundwater to drinking water wells. This process would also cause the concentration of the fluid constituents to diminish, or be diluted, as they mix with the groundwater. To account for these inherent dilution mechanisms, we have adopted well-established modeling approaches to provide estimates of the degree of dilution that would likely occur between the point of the surface spill and a downgradient drinking water well. These modeling approaches are outlined below.



Overall DF = $DF_L \times DF_{GW}$

Unsaturated Zone (DF_L):
Dispersion only (no adsorption or degradation).

Saturated Zone (DF_{GW}):
Relied upon US EPA modeling results where DF probabilities are reported as a function of different spill areas (source area).

Figure ES.4 Schematic of Groundwater Pathway DF Development

For the saturated zone groundwater exposure analysis, we developed "dilution factors" ("DFs") based upon those developed by US EPA (1996). The US EPA derived groundwater DFs when it developed risk-based chemical screening levels in soil that are protective of groundwater resources (in its Soil Screening Guidance).[12] In its analysis, the US EPA modeled a wide range of possible hydrologic conditions, variable distances to nearby drinking water wells (including wells immediately adjacent to contaminated source areas), and variable well depths (from 15 feet to a maximum of 300 feet). Using a Monte Carlo probabilistic modeling approach to incorporate these types of variable conditions, US EPA determined groundwater DFs as a function of the size of contaminated "source areas."[13] US EPA did not report the full range of percentiles (*e.g.*, probability distribution) associated with their Monte Carlo modeling (US EPA only reported the 85th, 90th, and 95th percentile DFs). Thus, we extended the US EPA analysis to extrapolate a complete distribution of DFs to use in our probabilistic modeling.

In its derivation of groundwater DFs, US EPA adopted simplifying and conservative assumptions that underestimate chemical attenuation in the soil and groundwater; these assumptions included that chemicals do not adsorb to soil, and that chemicals do not degrade, both of which are "attenuation" processes that lead to additional reduction in constituent concentrations. In addition, in deriving the groundwater DFs, the chemical source was assumed to be "infinite." The US EPA adopted these assumptions as conservative measures. While indeed conservative, clearly such assumptions are not realistic if applied to a surface spill of fluids containing HF constituents. In particular, the assumption of an infinite source effectively assumes "steady state" conditions have been reached such that a constant/uniform constituent concentration exists in the unsaturated zone. This assumption thereby does not account for chemical dilution of a finite source within the unsaturated zone that is caused by dispersion. For a finite source, such as a single spill of HF or flowback fluid, the chemical concentration will diminish over time and as a function of depth within the soil as constituents are leached down through the unsaturated zone.

In this assessment, we have not assumed an infinite source because the spill volumes used in our analysis are finite (limited) volumes, based on the spill distribution described above. Consequently, we have accounted for dilution of chemical concentrations in the unsaturated zone before reaching the groundwater table due to chemical spreading (dispersion) within the unsaturated zone.[14] We used well-established, standard techniques (*i.e.*, a chemical advection-dispersion equation) to model constituent dilution within the unsaturated zone.

Using this approach, we calculated an overall DF for the soil-to-groundwater pathway by combining the saturated-zone DFs developed from the US EPA values with the Gradient-derived unsaturated-zone DFs. We emphasize that the soil-to-groundwater pathway DFs used in this analysis are more likely to underestimate than overestimate dilution because both the saturated- and unsaturated-zone DFs were derived assuming no chemical adsorption or degradation. This assumption leads to the conservative result that 100% of the chemicals spilled ultimately migrate to and mix within the drinking water aquifer – an unrealistic premise that adds further conservatism to our exposure analysis. The DFs we used to assess the potential surface spill impacts to a shallow drinking water aquifer are summarized below.

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[12] US EPA referred to them as "dilution attenuation factors" (DAFs). We use the term "dilution factors" because in our analysis, as was also the case in US EPA's DAF development, we have not accounted for "attenuation" processes such as chemical-soil adsorption or biodegradation. These attenuation processes would further reduce the chemical concentrations in the environment in the event of a spill (*i.e.*, leading to larger dilution factors if included).

[13] For example, US EPA determined that a chemical constituent originating from a small source area (~0.1 acre), and migrating in groundwater to a nearby drinking water well would be expected to be diluted at least 55,400-fold in 85% of scenarios, and at least 2,740-fold in 90% of scenarios. For a larger source area of 1 acre, the US EPA-derived groundwater DFs decrease to 668-fold in 85% of scenarios and 60-fold in 90% of scenarios.

[14] A chemical spill at the surface does not migrate downward as a uniform "pulse" but rather spreads out and disperses within the unsaturated zone. This process of dispersion causes a reduction of the chemical concentration within the soil.

Table ES.2 Summary of Spill to Groundwater DFs

Percentile	Unsaturated Zone (DF_L)	Saturated Zone (DF_{gw})	Overall DF
50%	101	1.1×10^{26}	1.1×10^{28}
75%	51	3.0×10^{14}	3.2×10^{16}
90%	28	4.9×10^{7}	5.3×10^{9}
95%	19	17,788	1.9×10^{6}

Notes:

Based on 1 million Monte Carlo samples. The percentiles represent the likelihood of equaling or exceeding the associated DF values.

For any given Monte Carlo sample, the overall DF is the product of the respective values of the unsaturated and saturated zone DFs. However, given that independent random variables govern each component DF, the percentiles of the overall DF are not given by the product of the respective unsaturated- and saturated-zone DFs at the same percentiles.

The saturated zone DFs presented above are not directly comparable to the US EPA-reported values (US EPA, 1996), since the US EPA percentiles are associated with a corresponding spill area, whereas the above values correspond to a range of spill areas, which are a function of the potential spill volume.

ES.4.3.2 Surface Spill Impacts to Surface Water

As another exposure scenario, we also considered the potential impacts of hypothetical surface spills affecting surface water resources. For the surface water exposure analysis, we developed surface water DFs conservatively assuming "low flow" mixing conditions in streams potentially impacted by surface spills.

As noted earlier, the national scope of this assessment extends across regions characterized by differences in climate and topography that in turn affect the distribution of stream flows. In order to account for these regional variations, we based our analysis on the distribution of low-end stream flow values for streams within the major sedimentary basins in the US. Stream flow was obtained from the national database of USGS stream gauging information (see Figure ES.5).

We selected the lowest average daily streamflow for each year of record at each gauging station.[15] From this data set of lowest average daily streamflow measurements (for each year of record), we then took the lowest average daily flow over all years of record at each station to develop the distribution of low-end streamflows for our assessment (low flows yield higher exposure concentrations).

Based on a statistical comparison of the low-end streamflow data, the data for the arid and semi-arid regions of the country were not statistically different, and the data for the temperate and semi-humid regions are also not statistically different. Thus, for the probabilistic analysis we evaluated the possible impacts of HF spills impacting surface waters for two separate climatic regions: arid/semi-arid, and temperate/semi-humid.

As noted previously, our surface water exposure analysis assumed that 100% of the HF fluid or flowback fluid chemical constituents spilled on the well pad reach a surface water body *via* overland runoff. This assumption ignores mitigation measures such as possible well setbacks and spill containment practices. In addition, many well pads will be located too far from streams for this pathway to be possible. Thus, the use of low-end stream flow, coupled with the assumption that 100% of any spilled fluid containing HF additives reach the surface drinking water source, results in a conservative approach that yields "high-

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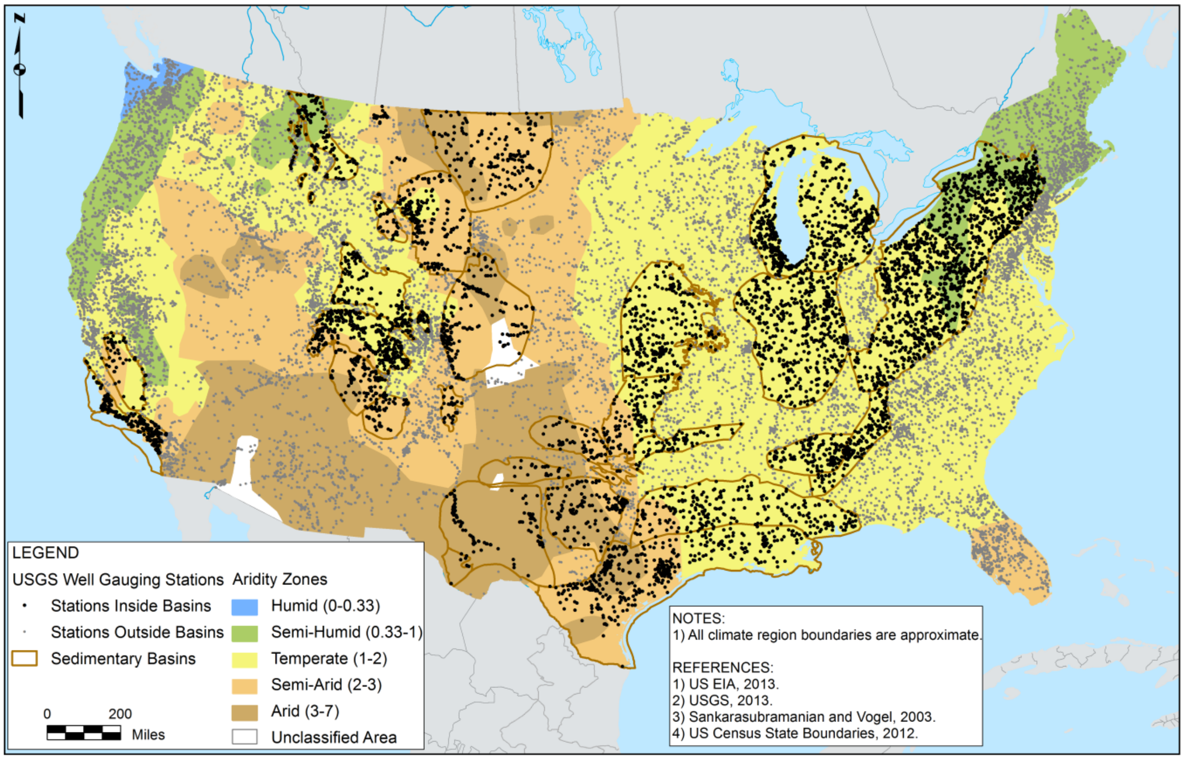
[15] As summarized in our report, we selected stations with a minimum of 5 years of gauging data as one criteria to ensure a reasonable minimum period over which to select "low flow" conditions.

end" estimates of potential human exposure for the surface water exposure pathway that are likely to over predict actual conditions in the event of a spill. Moreover, we have conservatively assumed that all the streams in the database could be used directly as drinking water sources (*i.e.*, with drinking water being taken directly from the stream as opposed to a downstream reservoir), regardless of whether a stream is large enough to serve as a drinking water source.



NOTES:
1) All climate region boundaries are approximate.

REFERENCES:
1) US EIA, 2013.
2) USGS, 2013.
3) Sankarasubramanian and Vogel, 2003.
4) US Census State Boundaries, 2012.

Figure ES.5 USGS Monitoring Stations, Sedimentary Basins, and Aridity Zones

One factor in our surface water exposure analysis was the period over which constituents in potential spills might migrate to and mix into a stream. In selecting the appropriate period for mixing to occur, we considered the likelihood of spill events having direct (immediate/short term) *versus* indirect (longer term) impacts on a nearby stream, and the physical processes that might convey HF constituents from the location of a surface spill to a nearby surface water body.[16]

Based on available data, spills associated with HF activities that directly impact surface water, which might raise concerns regarding short-term impacts, are rare. For example, based on the information in the PADEP OGM violation database (discussed earlier, see also Section 5), only about 6 out of every 10,000 wells (0.06%) experienced a spill that had a direct impact on a stream.[17] The rarity of these events is partly due to the fact that well pads are located some distance from nearby streams and there are only a very limited number of unlikely scenarios in which a spill might migrate quickly over such distances to a stream.

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[16] For the groundwater pathway, no mixing period was explicitly included both because groundwater travel would likely have timescales of years or decades, and because for the unsaturated zone component we conservatively selected the "peak" plume concentration (which may not occur for decades), rather than specifying a specific time-frame for the analysis.

[17] This is based on 4 of 234 spills (1.7%) in the PADEP OGM database that indicate direct impacts to a stream. When combined with the overall spill frequency (3.3%), this gives 0.06% probability that HF activities could result in an HF spill directly impacting a stream.

Given the low probability of incidents that might lead to short-term impacts, it was more relevant to focus our analysis on potential long-term effects, *i.e.*, effects that might be caused by (still infrequent) spills that do not reach streams quickly (and that, in reality, may never reach streams at all).[18] From a human health perspective, long-term effects (chronic impacts) are generally defined by exposure periods of seven years,[19] or in some instances one year, or longer.[20] From this perspective, selecting a mixing period that matches the exposure period for potential long term health effects is consistent with risk assessment methodology.

An appropriate mixing period can also be derived from an assessment of physical processes that could transport HF constituents from an area of spill-impacted soil (well pad) to a stream. These include direct overland runoff (*i.e.*, constituents carried with water and/or eroding soil particles that runs over the land surface) and slower migration underground (*i.e.*, movement with groundwater that then discharges into a stream). Direct overland runoff and soil erosion are episodic processes (*i.e.*, not "continuous") that are influenced by the frequency and magnitude of rainfall events. In order for 100% of spilled constituents to migrate to a stream as we have assumed, the surface runoff/erosion process is more likely to occur over timescales on the order of years (rather than days or months). If the migration to surface water is *via* groundwater flow, the timescales could be even longer – in many cases decades or more (Winter *et al.*, 1998). Thus, a time period on the order of years is considered to be a conservatively short transport timescale for all the constituents in a spill area to be transported to a stream.

Based on the foregoing considerations, we selected an averaging period of 1 year as a conservative (*i.e.*, health protective) approach.[21]

Using the spill volume distribution described earlier, and the foregoing methods for developing a distribution of surface water mixing volumes, the range of surface water dilution factors derived in this analysis is summarized below.

Table ES.3 Summary of Spill to Surface Water DFs by Aridity Regions

Percentile	Arid/Semi-Arid DF	Temperate/Semi-Humid DF
50%	1.4×10^8	4.9×10^8
75%	1.5×10^7	5.1×10^7
90%	2.0×10^6	6.7×10^6
95%	592,480	2.0×10^6

Note:
Results are Based on 1 million Monte Carlo samples. The percentiles represent the likelihood of equaling or exceeding the associated DF values.

ES.5 Toxicity Characterization

As reflected in the HESI HF fluid systems, a wide variety of additives and their associated constituents could be used in hydraulic fracturing. A number of these constituents are used as food additives, are present in a wide variety of household/personal care products, or occur naturally in the environment.

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[18] We also note that concentrations of chemical constituents which might give rise to possible health concerns due to long term exposure are generally lower (more restrictive) than their corresponding benchmarks based on short-term exposures.

[19] US EPA, 2002.

[20] ATSDR "Minimum Risk Levels" (MRLs) define chronic exposures as 365 days or more. http://www.atsdr.cdc.gov/mrls/index.asp.

[21] Note also that we have not accounted for the additional dilution that would occur due to direct rainfall, nor have we included any dilution if the transport to surface water is *via* groundwater.

Nonetheless, as part of this risk analysis, we evaluated the potential human toxicity of these constituents, regardless of other uses or origin.

We adopted established regulatory methodologies to evaluate the toxicity of constituents of HF fluid and flowback fluid. We used agency-established toxicity criteria (*e.g.*, drinking water standards, or risk-based benchmarks) when these were available. For constituents lacking these agency-established drinking water or health benchmarks, we developed risk-based concentrations (RBCs) for drinking water, based on published toxicity data (when available), toxicity benchmarks for surrogate compounds, or additional methods as described in this report. Use of tiered hierarchies for defining constituent toxicity is a standard risk assessment practice (US EPA, 2003, 2012a).

ES.6 Surface Spill Risk Evaluation Conclusions

As described in Section ES.4, we used the distribution (*e.g.*, percentiles) of groundwater and surface water pathway DFs to derive a distribution of possible HF fluid and flowback fluid constituent "exposure point concentrations" that might be found in drinking water in the event of a surface spill. We compared this distribution of exposure point concentrations to the chemical RBCs and expressed the ratio as a "Hazard Quotient" (HQ).[22] An HQ value less than 1.0 indicates the exposure concentration of a chemical constituent is below a concentration at which adverse health effects are not expected. We also summed the HQs for all chemicals used in particular HESI HF systems to calculate the "Hazard Index" for the entire HF system.

The results of our analysis indicate that potential human health risks associated with exposure to drinking water (derived from surface water or groundwater) potentially affected by spills of typical HESI HF fluids, or flowback fluids, are expected to be insignificant as defined by agency-based risk management guidelines. Our analysis yields this result even though it is based on a number of assumptions, highlighted below, that collectively result in a substantial overestimation of potential risk.

Key Conservative Assumptions

No containment or mitigation measures were included

100% of spill assumed to impact both surface water and groundwater

Distribution of low-end stream flow used for surface water dilution

All streams assumed to be direct sources of drinking water

Selected groundwater dilution factors based on US EPA's methodology which assume continuous and infinite sources (whereas HF spills are more appropriately characterized as short term, singular events)

Adsorption and degradation of chemicals was ignored

Human health risks associated with potential surface spills of fluids containing HF constituents are expected to be insignificant with respect to both impacts to USDWs and impacts to surface waters due to dilution mechanisms which are expected to reduce concentrations in potable aquifers and surface waters to levels below health-based drinking water concentrations in the event of surface spills. Based on the probabilistic analysis presented here, spanning an enormous range of conditions, HQs were below 1.0 even at the upper tails (high percentiles) of the distribution of dilution factors.

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[22] Note, the HQ value in our analysis is an indicator of whether the computed exposure concentration exceeds the health-based RBC, regardless of the constituent's toxicity end point or mode of action.

We have summarized the HQ results below for the central tendency (50th percentile) DF values, as well as upper percentiles (*e.g.*, HQs associated with 90th and 95th percentile DF values). For example, at the 95th percentile DF, the highest HQ for surface water in arid/semi-arid regions was 0.04. This means that in 95% of the Monte Carlo simulations, the highest HQs were less than or equal to this value.

When considering the results from this probabilistic analysis, it is important to understand what the results reported for any particular DF percentile represent. The DF percentiles are based on the presumption that a spill has occurred (that is, they are a function of spill volume and other environmental variables). However, as discussed earlier, the likelihood of spills occurring during HF activities, based on the experience in Pennsylvania, is conservatively estimated to be about 3.3%. Using this spill frequency, there is a 96.7% likelihood (probability) that there would be no release of HF constituents at a given well site, and thus 96.7% of the HQs would be zero (no exposure). In order to determine the overall likelihood, or probability, of any particular HQ outcome, the spill probability, and cumulative probability of any particular DF, must be combined using the following expression:

Overall HQ Occurrence Probability = (100% - Spill Frequency) + (Spill Frequency × DF Percentile/100)

For example, at a spill rate of 3.3%, given a typical (50th percentile) amount of dilution there is a 98.4% probability that the HQ for impacts to surface water associated with the use of HF fluids at a well site in an arid or semi-arid region would be less than 0.0002, or several orders of magnitude less than an HQ that would indicate that adverse health effects might be a concern. Even for a low dilution factor – one that would be exceeded in 95% of instances where a spill occurred (*i.e.*, the 95th percentile) – there is a very high (99.84%) likelihood that a well site even in an arid area would not experience an HQ greater than 0.04, which is still at a level where adverse health effects would not be expected to occur.

Table ES.4 Percentiles of Chemical HQs for Maximum Wellhead Chemical Concentrations for HESI HF Fluid Systems

DF Percentile[a]	Surface Water Arid/Semi-Arid	Surface Water Temperate/Semi-Humid	Groundwater	Spill Frequency 3.3%	Spill Frequency 6.6%
	Highest HQ at Associated DF Percentile			Overall HQ Occurrence Probability at Associated Spill Frequency[b]	
50%	0.0002	0.00005	2×10^{-24}	98.4%	96.7%
90%	0.01	0.003	4×10^{-6}	99.7%	99.3%
95%	0.04	0.01	0.01	99.84%	99.67%

Notes:

[a] The DF percentiles represent the cumulative probability associated with a particular DF (see Tables ES.2 and ES.3) in the event of a spill.

[b] The overall HQ percentile at any particular DF percentile is: (100% - Spill Frequency) + (Spill Frequency x DF Percentile/100).

ES.7 Overall Conclusions

Based on the foregoing analysis, we conclude that when used in their intended manner in tight oil and gas formations, *i.e.*, pumped into a subsurface formation to induce fractures in the target formation, HF fluids are not expected to pose adverse risk to human health because wells are designed and constructed to prevent HF fluids in the well from coming in contact with shallow aquifers and it is implausible that the fluids pumped into the target formation would migrate from the target formation through overlying bedrock to reach shallow aquifers. Even in the event of surface spills, inherent environmental dilution mechanisms would, with a high degree of confidence (based on our probabilistic analysis covering wide-ranging conditions), reduce concentrations of HF chemical constituents in either groundwater or surface water below levels of human health concern (RBCs), such that adverse human health impacts are not expected to be significant. Our conclusions are based on examining a broad spectrum of conditions spanning HF operations in tight oil and gas formations across the country. By extension, these conclusions would apply more broadly under environmental conditions (including geologic formations) in other parts of the world that are similar to those we have examined in the US.

1 Introduction

Oil and natural gas exploration and production – and natural gas in particular – have received increased attention nationally due to improvements in techniques to enhance the extraction of oil and gas from low permeability geologic formations from which production had previously proven infeasible. One of the key technologies that has unlocked the development potential of these formations is hydraulic fracturing (HF) – a well stimulation technique in which water, sand, and chemical additives are introduced into the target formation to open fractures and to keep them open using proppants (*e.g.*, sands) to enhance the flow of oil and gas to the well.

While it is beyond the scope of this report to cover all oil/gas-bearing formations which use hydraulic fracturing to develop the resource, we have examined a broad range of current oil/gas "plays" across the country, focusing predominantly on low permeability formations, specifically those that occur in deep shales, tight sands, and tight carbonate formations (hereafter "tight formations"). Such tight formations are estimated to contain significant oil and gas reservoirs in the US, as well as globally. Oil and gas exploration activities are expanding production from these formations, thereby attracting interest from multiple stakeholders, including the public, regulators, scientific community, and industry. As oil and gas development proceeds, concerns have been expressed over the potential for exposure to HF additives (and the chemicals found in the additives) that might impact drinking water resources. In response to these concerns, the United States Environmental Protection Agency (US EPA) is conducting a Congress-mandated study evaluating the potential impacts of HF on drinking water resources (US EPA, 2012b). This US EPA study focuses "primarily on hydraulic fracturing of shale for gas extraction" (US EPA, 2012b, p. 6).

This report, which has been prepared on behalf of Halliburton Energy Services, Inc. (HESI), contains Gradient's evaluation of the potential for human health risks associated with the use of HF fluids that might affect drinking water. We assessed the risks relating to drinking water associated both with the intended use of HF fluids, as well as unintended accidental releases of fluids containing HF constituents. In the first instance, we considered the steps that are taken to keep the fluids in a well from coming into contact with the surrounding formations (including drinking water aquifers) the well passes through above the formation targeted for oil and gas production ("zonal isolation") and the very low probability of HF fluids escaping from the well. We then examined the possibility that HF fluids pumped into the underlying tight formations might hypothetically migrate upward through the overlying bedrock strata into shallow overlying aquifers. This is an issue both Gradient (2012) and the New York State Department of Environmental Conservation (NYSDEC) (2011) have addressed for the Marcellus Shale formation in New York. Based on these respective analyses, we and NYSDEC both concluded this was an implausible migration pathway. To further assess whether HF fluids could migrate upward to reach drinking water aquifers, in this study we have examined a broader range of geologic conditions that encompass the range of tight formations in the US where HF might be used.

In addition, we examined possible unintended spills of HF fluids during the HF process and the potential for human health risks associated with such spills in the event that HF constituents were to migrate to surface water or drinking water aquifers. Our evaluation addressed the chemical constituents in typical HF fluid systems developed by HESI that may be used in a range of black shales, tight sands, and other tight formations around the country.

We also evaluated health risks associated with potential surface spills of flowback fluid (fluid recovered from the fracture zone after fracturing) using data primarily for flowback fluid samples collected from the Marcellus Shale formation in Pennsylvania and West Virginia, and supplementing this with limited available flowback fluid data from other shale and tight sand formations. We also considered available data for "produced" water (*i.e.*, fluids produced from gas wells later in the life cycle) as a surrogate of flowback fluid quality.

We provide an overview of the HF process in Section 2. An overview of the geological and hydrological conditions for important tight oil/gas plays throughout the US is provided in Section 3. Section 4 presents the conceptual model for our risk analysis, discusses the potential migration pathways that were evaluated in this report and sets forth the HF fluid and flowback fluid constituents we have considered in our analysis. In Section 5, we describe the modeling framework we used to estimate potential exposure concentrations in drinking water for the migration pathways and spill scenarios evaluated (our "conceptual site model"). Section 6 provides an overview of the chemical toxicity data and the procedures used to determine risk-based concentrations (RBCs) for drinking water that we used in our risk analysis. We summarize our risk analysis results in Section 7, followed by the conclusions from our analysis in Section 8.

2 Well Installation and Hydraulic Fracturing

Hydraulic fracturing is a multi-step process aimed at opening up fractures within oil and natural gas-bearing geologic formations to maximize the production of oil and natural gas from a production well. The HF process involves pumping a fluid and proppants (*e.g.*, sand) into the target hydrocarbon-bearing formation. The fluids generally consist mostly of water with small amounts of chemical additives, typically comprising about 0.5% by weight of the fluid, to enhance the efficiency of the fracturing process. The pumping of fluid under high pressure causes fractures to form in the target formation, and proppants (typically sand) "prop" the fractures open so that, after the fluid pressure is removed, the fractures remain open allowing the gas to be extracted from the formation. After the fracturing stage is complete, all readily recoverable portions of the HF fluid (mixed with naturally occurring fluids from the formation), referred to as "flowback fluid", are then pumped out.[23] Every step in the process – well installation, fracturing, fluids management, and well operation – is carefully planned, managed, and monitored to minimize environmental impacts and maximize gas yield. A detailed description of the HF process can be found in a variety of documents (*e.g.*, NYSDEC, 2011; CRS, 2009; API, 2009; US EPA, 2011a; GWPC and ALL Consulting, 2009).[24] A brief overview is provided in this section, including information on the role of chemical additives in HF fluid systems.

2.1 HF Well Pad Installation and Spacing

HF operations occur on "well pads," which are graded areas designed to store all the equipment and materials needed to drill and complete the well and to support subsequent oil and gas production. Many installations for production now utilize multiple horizontal wells (especially for developing shales) drilled at a common well pad in order to maximize oil and gas production and minimize the amount of land disturbance when developing the well network to extract the oil and/or natural gas. Well pads for multi-well installations may vary somewhat in size, depending on the number of wells installed and whether the operation is in the drilling or production phase. Typical well pads for multiple well installations are approximately 3.5 acres during the drilling phase, and approximately 1.5 acres during the oil/gas production phase (NYSDEC, 2011). One industry estimate for the Marcellus shale indicated that up to four horizontal wells would be drilled per year for a multi-well installation (NYSDEC, 2011).

2.2 Well Design and Installation

Oil and gas production wells are drilled using methods designed to prevent drilling fluids, HF fluids, or oil and natural gas from leaking into permeable aquifers. Production wells may be standard vertical wells or, increasingly, wells may incorporate horizontal drilling techniques to maximize the well's capture zone for oil/gas withdrawal. Most deep shale oil or gas wells and many other wells in tight formations today

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[23] The composition of the fluid that flows out of the well once the HF process has concluded and production begins changes over time. Initially the fluid is generally a mixture of the fluid used to hydraulically fracture the well and water and other constituents that are naturally present in the formation (sometimes referred to as "formation water"). Over time the proportion of HF fluid in the fluid flowing out of the well declines, and after a period of time the fluid flowing out is almost entirely formation water. As a matter of convenience, industry generally refer to the fluid that flows out of the well for the first several weeks as "flowback," "flowback water," or "flowback fluid," and the fluid that continues to flow from the well over the longer term production period as "produced water," although there is no bright line separating the two.

[24] See also web resources: http://www.halliburton.com/public/projects/pubsdata/hydraulic_fracturing/fracturing_101.html; http://fracfocus.org/hydraulic-fracturing-process.

are horizontal wells. In the case of a horizontal well, the upper portion of the well (*i.e.*, overlying the target zone) is drilled using vertical drilling techniques. As it approaches and enters the target zone, the drill is then turned horizontally to follow the target formation. The drilling phase for a single horizontal well typically lasts 4 to 5 weeks, including drilling, casing, and cementing the well, whereas the gas production phase lasts for years to decades.

Care is taken in the design and installation of wells to protect drinking water aquifers and to isolate the oil/gas producing zone from overlying hydrogeologic units. In addition to minimizing environmental impacts, it is critical for the well to be completely isolated from drinking water aquifers and other non-potable aquifer units (referred to as "zonal isolation") in order to economically produce oil/gas from the well (API, 2009). The American Petroleum Institute (API) has developed guidance that provides a detailed description of typical practices followed in the design and installation of wells (API, 2009). Similarly, well design/installation best practices are described in the Marcellus Shale Coalition, Recommended Practices: Site Planning Development and Restoration (Marcellus Shale Coalition, 2012).

The following elements are included in the design and installation of oil/gas wells to ensure well integrity, *i.e.*, that the internal conduit of the well is only in communication with the hydrocarbon-bearing unit and not with other overlying units. These well installation and design elements reflect the current state of the art in well installation technology that have evolved, based on over 75 years of oil and gas well installation experience (API, 2009).

2.2.1 Multiple Well Isolation Casings

The design and selection of the well casing is of utmost importance. Well casings are designed to withstand forces associated with drilling, formation loads, and the pressures applied during hydraulic fracturing. The design of deep oil/gas wells, such as those installed in deep shales and other tight formations, can include up to four protective casings to ensure well integrity, as shown on Figure 2.1:

- Conductor casing. This outermost casing, which is installed first, serves to hold back overburden deposits, isolate shallow groundwater, and prevent corrosion of the inner casings, and may be used to structurally support some of the wellhead load (API, 2009). The casing is secured and isolated from surrounding unconsolidated deposits by placement of a cement bond, which extends to ground surface (Figure 2.1).
- Surface casing. After the conductor casing has been drilled and cemented, the surface casing is installed to protect potable aquifers. The typical depth of the surface casing can vary from a few hundred to 2,000 feet. Similar to the conductor casing, the surface casing is also cemented in-place to the ground surface. API recommends that two pressure integrity tests be conducted at this stage:
    - Casing pressure test. This tests whether the casing integrity is adequate for meeting the well's design objectives (*i.e.*, no leaks or zones of weakness); and
    - Formation pressure integrity test. After drilling beyond the bottom of the surface casing, a test is performed to determine whether any formation fluids are "leaking" into the borehole.

  These tests help assess the adequacy of the surface casing/seal integrity and determine the need for remedial measures, if any, prior to proceeding to the next step.
- Intermediate casing. The purpose of the intermediate casing is "to isolate subsurface formations that may cause borehole instability and to provide protection from abnormally pressured subsurface formations" (API, 2009). The need to install an intermediate casing typically depends on the hydrogeologic conditions at a site. The intermediate casing is cemented either to the

ground surface or at a minimum to above any drinking water aquifer or hydrocarbon bearing zone. Similar to the surface casing, casing pressure and formation pressure integrity tests are performed to ensure the adequacy of the casing and seal integrity.

- Production casing. The final step in the well installation process consists of advancing the production casing into the natural gas producing zone. The production casing isolates the natural gas producing zone from all other subsurface formations and allows pumping the HF fluids into the target zone without affecting other hydrogeologic units; the production casing also provides the conduit for oil/natural gas and flowback fluid recovery once fracturing is completed. The production casing is cemented either to ground surface (if an intermediate casing has not been installed) or at least 500 feet above the highest formation where HF will be performed. Finally, the production casing is pressure tested to ensure well integrity prior to perforating the casing within the gas-bearing zone and initiating the hydraulic fracturing process.

The multiple well casings, cement bonds, and pressure tests at each stage of the well installation process ensure that the well casings have adequately isolated the well from subsurface formations.[25]

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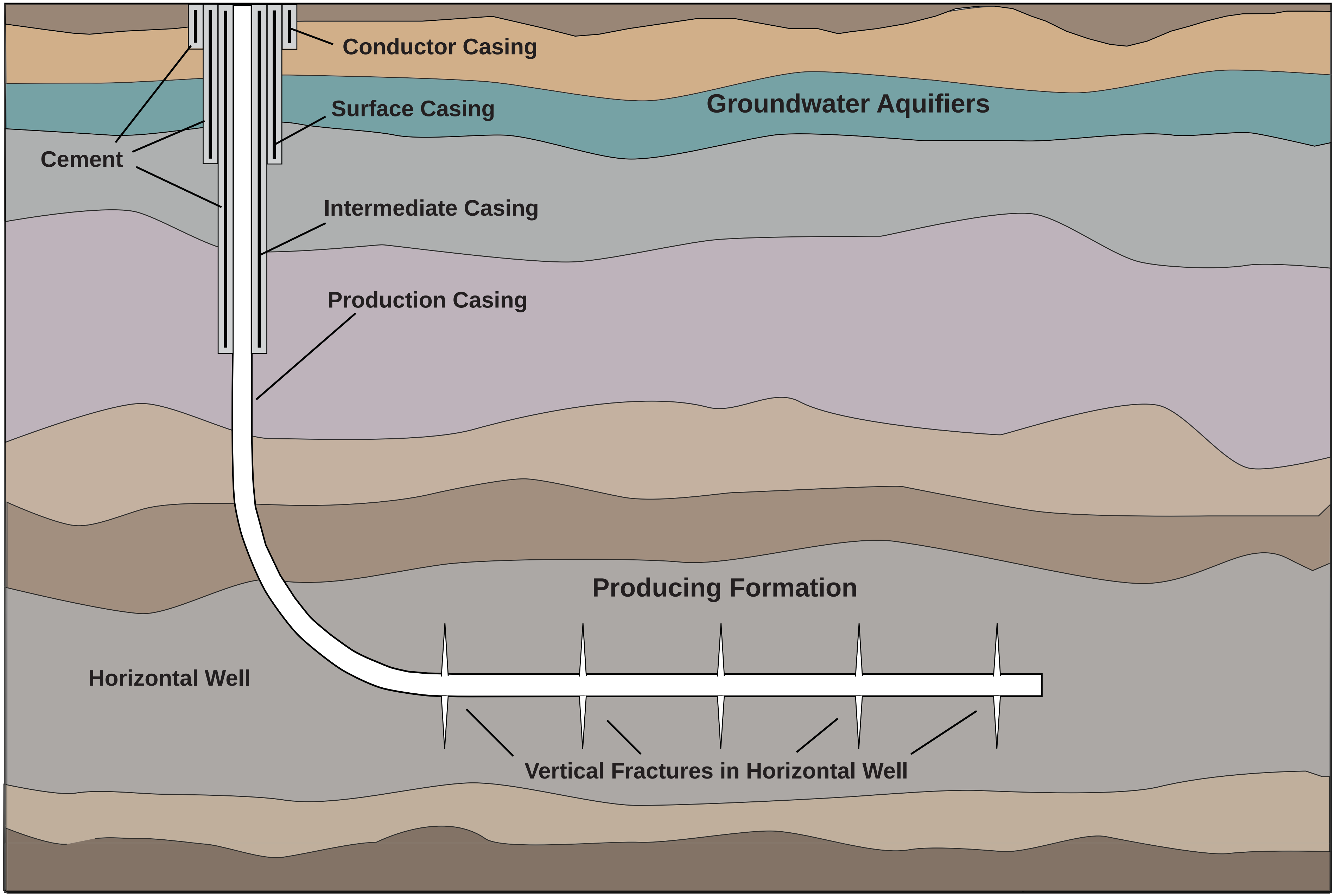
[25] Oil/gas well installation and production procedures are also governed by state regulations which are often quite detailed and extensive. State regulatory programs and the provisions they include that help to protect drinking water resources are discussed in GWPC and ALL Consulting (2009).



REFERENCE: API, 2009.

GRADIENT

Typical Horizontal
Well Design

FIGURE
2.1

Date: 4/25/2013

File Path:G:\Projects\210116_HESI\Graphics\NonCAD\Figure_2.1.ai

2.2.2 Well Logging

Cement bonds play a critical role in isolating the oil/gas well from other subsurface formations, including water-bearing formations. Monitoring of these seals, referred to as cement bond integrity logging, is conducted to confirm the presence and the quality of the cement bond between the casing and the formation. Such logging is typically conducted using a variety of electronic devices for each cement bond associated with the well (API, 2009).

By following these well installation and testing best practices, wells are carefully constructed, with a number of key design and monitoring elements (*e.g.*, multiple well casings/cement bonds, logging to ensure the adequacy of cementing, and pressure integrity testing). These practices protect drinking water aquifers by achieving full zonal isolation of the well from overlying formations.

2.2.3 Perforation

After the well has been installed and its integrity has been tested, the last step in the process prior to hydraulic fracturing is the perforation of the portion of the well in the hydrocarbon production zone (the horizontal section in the case of a horizontal well). Depending on the length of the portion of the well to be perforated, the perforation process may proceed in phases. The perforations are required because they will serve not only as the means for the HF fluid to be pumped into the formation and enable it to be hydraulically fractured, but also as the means of capturing the oil/natural gas during the production phase.

2.3 Hydraulic Fracturing Process

After well installation and integrity testing have been completed, the HF process commences. Because each oil and gas zone may have different characteristics, the specific hydraulic fracturing steps taken and the fluids used are tailored to the particular conditions of the formation being fractured. The selection of site-specific fracturing steps and fluids is determined during an HF planning phase. Therefore, while the HF process outlined below applies generally, the sequencing of a particular HF operation may change depending upon specific local conditions. We describe a typical sequence of fracturing steps along with a description of typical HF additives used and their purpose. Not all of the additives are used in every hydraulically fractured well as the exact "blend" and proportions of additives will vary based on the site-specific depth, thickness and other characteristics of the target formation.

2.3.1 HF Planning and Monitoring

Similar to well design and installation, the HF process is carefully planned and monitored to ensure that the induced fractures are contained within the target formation to the extent possible, and, if there are any indications of abnormal conditions (*e.g.*, abnormal pressure drop), immediate actions can be taken to halt the HF process. The key HF planning and monitoring elements are described below (API, 2009):

2.3.1.1 HF Planning

The following steps are typically undertaken for each HF job:

- The required HF treatment (*e.g.*, the fracturing pressure, the additive mix and sequencing, duration) is designed by experts. In some cases, these experts will utilize state of the art computer models to ensure that the HF treatment being applied is appropriate for the job and results in fractures that are contained within the target zone. In other cases, experts may rely on prior experience in hydraulically fracturing other wells in the area, the designs for which may have been based in part on models.

- Prior to commencing HF treatment, the well casing and all equipment to be used in the process (*e.g.*, pumps, high pressure lines) are pressure tested to ensure that they can withstand the pressure to be applied during HF. Any leaks observed during such testing are addressed.
- In some cases, a "mini-frac" treatment, utilizing a small volume of HF fluid, is initially conducted to collect diagnostic data, which are then used to refine the prior computer modeling results and to finalize the HF execution plan.

These planning measures and data help refine the HF execution, and the pressure testing of equipment helps to minimize the likelihood of any fluid spills during the HF process.

2.3.1.2 Monitoring During HF Treatment

Data are continuously collected during HF to monitor operating conditions and to ensure that fractures are propagating in the subsurface consistent with the design.

- Pressure monitoring. Pressure data are collected at several key locations: the pump, wellhead, and intermediate casing annulus (if the intermediate casing has not been cemented to the surface). Typically, pressure variations are minimal and only slight adjustments are required during the HF process. Unusual pressure changes during the HF process are typically a sign of a problem, *e.g.*, a surface spill, or a subsurface leak from the production to the intermediate casing. In such cases, HF pumping operations are immediately shut down.
- Pressure relief mechanisms. In addition to pressure monitoring, pressure relief mechanisms are also included in the production wells. For example, API (2009) recommends that the intermediate casing annulus should be equipped with a pressure relief valve, with the line from such a valve leading to a lined pit. Such a pressure relief mechanism ensures that if there is a leak from the production casing, any released HF fluid is contained within the intermediate casing annulus, and removed before it migrates into the subsurface.
- Fracture geometry monitoring. During the HF process, real time computerized monitoring is often undertaken to ensure that facture geometry in the subsurface is consistent with the HF job design. Two monitoring techniques – tilt meter and microseismic monitoring – are utilized to collect such data. These data help determine the vertical and lateral extent, azimuth, and complexity of fractures.

These planning and monitoring procedures are implemented to ensure the HF process proceeds according to design and to minimize the potential for spills of HF fluids. Spill mitigation measures, including containment berms, protective barriers (plastic barriers), *etc.*, are additional measures implemented at the well pad to contain spills, should they occur (API, 2011).

2.3.2 HF Phases and the Role of Chemical Additives

Generally, the process of pumping the HF fluids down the well to create fractures in the formation involves the following three phases:

1. Pre-frac acid flush phase prior to fracturing consisting of water and an acid, such as hydrochloric acid, in order to clean out debris in the well, after it has been drilled, cased, cemented, and perforated in the oil- or gas-bearing zone.
2. Fracturing phase, during which the fractures are induced in the target formation and proppants are pumped into the fracture network to "prop" the fractures so that they remain open.
3. Flush phase to clean out the well after fracturing, including removing excess proppant materials.

Hydraulic fracturing may be conducted in stages, with discrete sections of the well "fractured" at a time; in the case of horizontal wells, hydraulic fracturing generally proceeds in this fashion. HF fluid properties may be adjusted during each phase with the use of additives to enhance the effectiveness of the HF process.

HF additives serve many functions and are needed to ensure that the HF job is effective and efficient—from limiting the growth of bacteria to preventing corrosion of the well casing. The HF additives used in a typical fracture treatment depend on the geologic conditions of the formation being fractured.

As summarized in Table 2.1, HF fluid is predominantly water (~ 90% by weight), with proppants (*e.g.*, sand, ceramic beads, *etc.*) comprising approximately 9% and the HF additives comprising the remainder (~ 0.5%). Each HF additive serves a specific, engineered purpose. For example, the addition of friction-reducing constituents to HF fluids (called slickwater) allows fracturing fluids, as well as sand or other solid materials called proppants, to be pumped to the target zone at a higher rate and reduced pressure than if water alone were used. Cross-linking agents are sometimes used to enhance the ability of gelling agents to transport proppants. The following types of additives are also commonly included: biocides to prevent microorganism growth and to reduce biofouling of the fractures; oxygen scavengers and other stabilizers to prevent corrosion of metal pipes; and acids that are used to remove debris from the well that may have accumulated during the well construction. A description of these and other typical HESI HF additives that might be used in tight formations is given in Table 2.1.

Table 2.1 Example HF Fluid Components for Tight Formations

Additive Type	Description of Purpose	HF Fluid Composition (% by weight)
Water	Main fracturing fluid used for typical HF development	90.23
Proppant	"Props" open fractures and allows gas/fluids to flow more freely to the well bore	9.11
Acid	Cleans up perforation intervals of cement and drilling mud prior to fracturing fluid pumping, and provides accessible path to formation	0.4
Breaker	Reduces the viscosity of the fluid in order to release proppant into fractures and enhance the recovery of the fracturing fluid	0.00006
Bactericide/ Biocide	Inhibits growth of organisms that could produce gases (particularly hydrogen sulfide) that could contaminate methane gas; also prevents the growth of bacteria which can reduce the ability of the fluid to carry proppant into the fractures	0.02
Corrosion Inhibitor	Reduces rust formation on steel tubing, well casings, tools, and tanks (used only in fracturing fluids that contain acid)	0.0008
Friction Reducer	Allows fracture fluids to be pumped at optimum rates and pressures by minimizing friction	0.08
Gelling Agent	Increases fracturing fluid viscosity, allowing the fluid to carry more proppant into the fractures	0.001
Iron Control	Prevents the precipitation of metal oxides which could plug off the formation	0.02
Scale Inhibitor	Prevents the precipitation of carbonates and sulfates (calcium carbonate, calcium sulfate, barium sulfate) which could plug off the formation	0.02
Surfactant	Reduces fracturing fluid surface tension thereby aiding fluid recovery	0.1

Source: NYSDEC, 2011, Figure 5.4. See also US EPA (2011a) for similar information.

Specific HF chemical additives found in typical HESI HF formulations used for hydraulic fracturing in tight formations are discussed in Section 4.2.

2.4 Flowback

Upon completion of the hydraulic fracturing process, HF fluids pumped into the target formation together with naturally occurring fluid within the fractured formation, are recovered as "flowback fluids." Flowback fluid is distinguished from "produced water," which more generally refers to water brought to the surface along with oil and gas in a producing well which is not specifically related to hydraulic fracturing (Veil *et al*., 2004).

Much of the flowback fluid is produced in the first few weeks after the fracturing treatment. In the Barnett, Fayetteville, and Marcellus Shales, 10 to 15% of the injected HF fluid flows back in the first 10 days; in the Haynesville Shale about half as much returns to the surface in that time (Mantell, 2011). The total amount of HF fluid that is ultimately returned to the surface as part of the flowback fluid varies depending on the characteristics of the formation and other factors. For the Marcellus Shale, estimates are that 9 to 35% of the HF fluid will flow back; recovery rates in other formations may differ.

Once the well is placed in production, water continues to be produced along with the desired natural gas and petroleum resources targeted by the well. This water is generally called "produced water," "coproduced water," or "brine" and is a common feature of all types of wells, including conventional oil and gas wells. During longer term production, the amount of produced water per well varies significantly between shale formations. For example, the Barnett Shale has high water production (> 1,000 gallons per MMCF natural gas produced), the Marcellus Shale has low water production (< 200 gallons per MMCF natural gas), and the Eagle Ford, Haynesville and Fayetteville Shales fall somewhere in the middle (Mantell, 2011).

Flowback fluid is either recycled for re-use in subsequent HF operations, or disposed off-site by HF operators. Depending on local conditions and regulations, flowback fluid disposal options may include deep well injection or treatment either at a publicly-owned treatment works (POTWs) or at a private treatment facility.

Specific chemicals that have been found in flowback fluids are discussed in Section 4.2.

3 Environmental Setting for Tight Oil/Gas Reservoirs

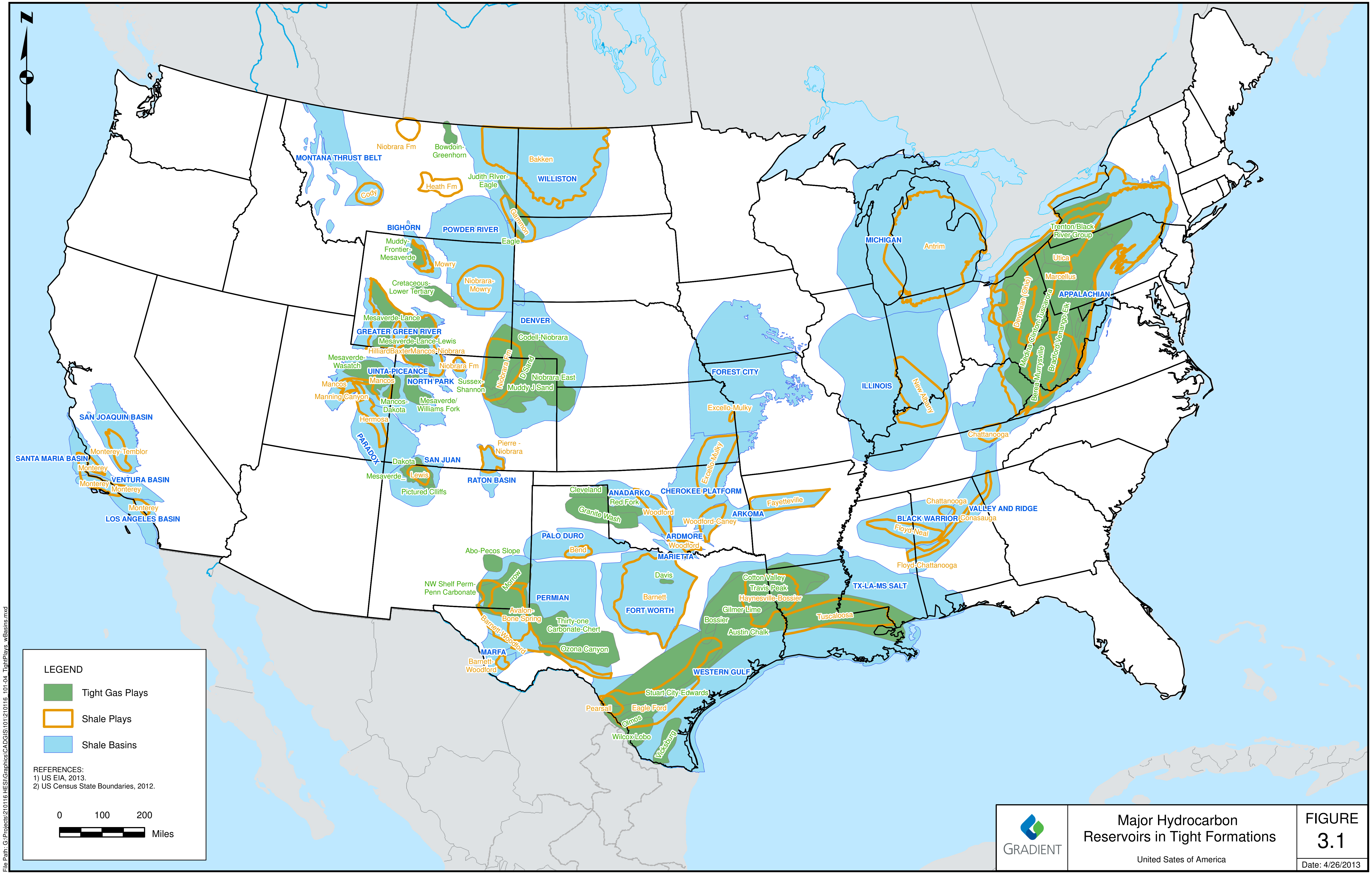
This section discusses characteristics of the environmental setting, specifically geology, hydrogeology, and hydrology, of the tight formations evaluated in our risk analysis. These characteristics were examined since they govern the fate and transport of HF constituents from the target formation into overlying formations (if any) and from unintended surface releases during the HF process.

3.1 Sedimentary Basins and Tight Formations

The tight formations considered in our risk analysis (shales, sands, and carbonates) are located in sedimentary basins. A sedimentary basin is a low area of the Earth's crust where sediment has accumulated. Basins form in areas where the earth's crust undergoes extension (*e.g.*, as the result of plate tectonic activity), which causes the crust to stretch, thin, and subside. As sediment accumulates, it creates an additional load, which may contribute to subsidence and ongoing evolution of the basin. Over time, the sediment becomes lithified into rock types associated with sedimentary basins (*e.g.*, sandstone, shale). Basins have formed in this manner over geologic time and are distributed around the globe, including approximately 144 in the US (Coleman and Cahan, 2012). The thickness of sediment in US basins varies depending on their history of formation, uplift, and subsequent erosion. For example, in some cases, sediment thicknesses in excess of 10 km accumulated during periods of deposition, such as portions of the Appalachian basin during the Permian period circa 300 to 250 million years ago (Ma) (Garven *et al*., 1993; Rowan, 2006).

All sedimentary basins have layered structures, although sediment thickness and stratigraphy may vary within and between basins (Miall, 2008). Major rock types of sedimentary basins include sandstone, shale, conglomerate, carbonate, and salt formations. The layered structure has a major influence on fluid migration, as higher permeability layers (*e.g.*, sandstone) serve as dominant migration pathways and low permeability layers (*e.g.*, shale) confine flow (see Section 3.2). Historically, oil and gas production has occurred from higher permeability formations such as sandstone and carbonate rocks (conventional reservoirs); however, advancements in directional drilling and hydraulic fracturing have allowed for economical production from tight formations. Figure 3.1 shows the distribution of tight oil and gas formations throughout the contiguous US.

Of the tight formations, black shales are perhaps the most widely targeted for HF stimulations. Black shales consist of very fine-grained, organic-rich sediment that was typically deposited in marine environments. Conditions favoring the deposition of shale and other low permeability fine grained rocks such as siltstone and mudstone were pervasive throughout geologic time, and as a result, these are the most common rock types in sedimentary basins (Prothero and Schwab, 1996). For example, Figure 3.2 is a cross section of the Appalachian Basin (adapted from Ryder *et al*., 2009), and it shows that the rocks are dominated by siltstone, mudstone and shale. In this cross section, the black shales most commonly targeted for HF stimulation in the Appalachian Basin are found at depths of 3,000 feet or greater (*e.g.*, Utica and Marcellus formations). In fact, it is generally the case that tight oil and gas formations are overlain by thick sequences (typically thousands of feet) of predominantly fine grained rocks with inherently low permeabilities that restrict vertical fluid migration (discussed in Section 3.2 below).



REFERENCES:
1) US EIA, 2013.
2) US Census State Boundaries, 2012.

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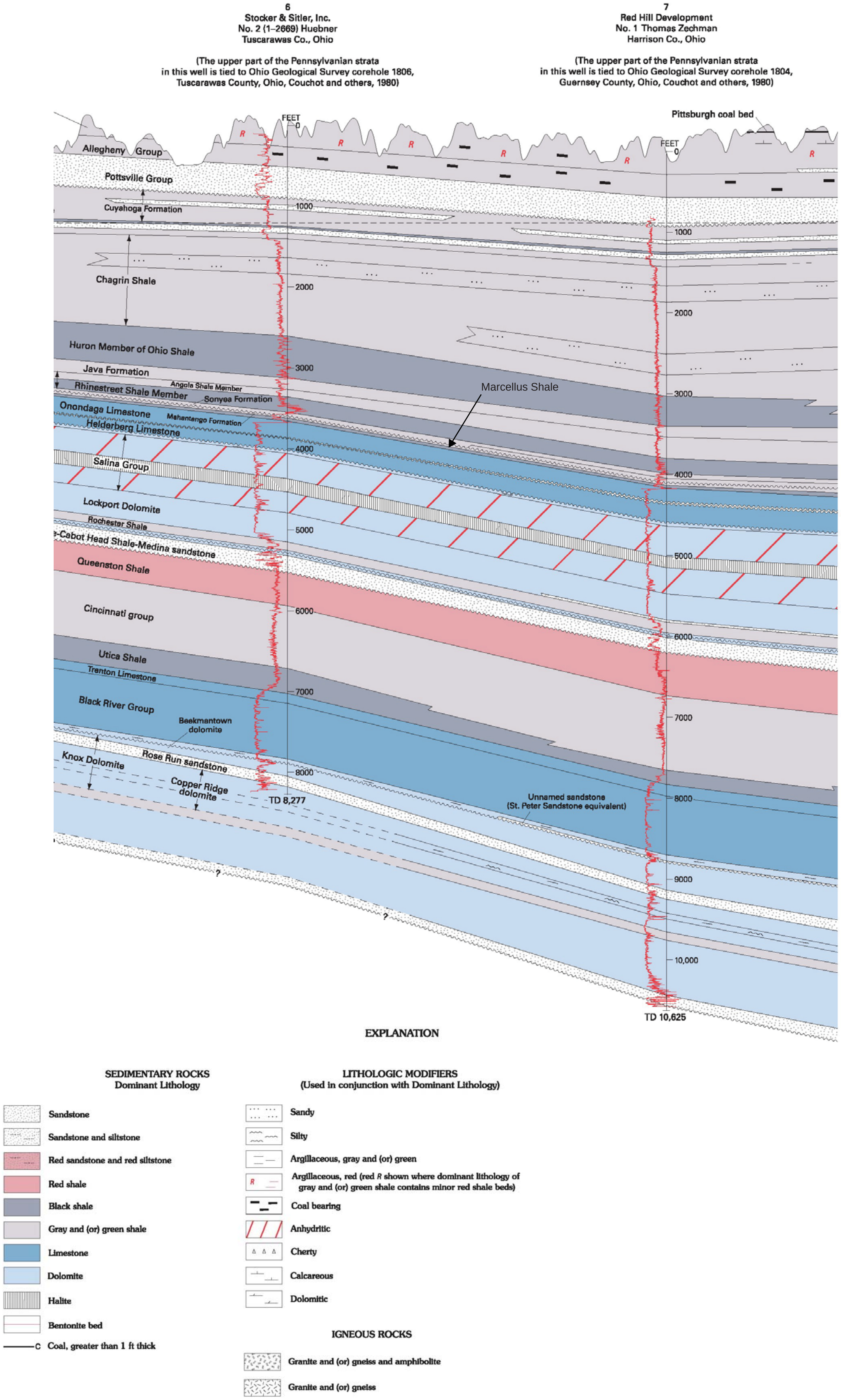
GRADIENT

Major Hydrocarbon Reservoirs in Tight Formations

United Sates of America

FIGURE 3.1

Date: 4/26/2013



REFERENCE: Adapted from Ryder *et al.* (2012).

Cross Section of
the Appalachian Basin

FIGURE
3.2

Date: 4/25/2013

Another example of a tight formation is the Bakken Shale, located in the Williston Basin of North Dakota, South Dakota, and Montana at depths ranging from 8,000 to 10,000 feet below ground surface (bgs). The Williston Basin is a sag basin, unbounded by large scale structures such as faults, where sediment accumulated from the Cambrian (550 Ma) to the Quaternary (2 Ma) in a different depositional setting than the Marcellus (Sandberg, 1962). The cross sections of Sandberg (1962), Meissner (1978), and Baird and Dyman (1993) show that this long-term sediment accumulation resulted in the formation of approximately 16,700 feet of sedimentary rocks near the basin's center, most of which consist of low-permeability formations (*e.g.*, shale, siltstone, mudstone). Thus, despite differences in geography, depositional and tectonic history between the Appalachian and Williston basins, both contain thick sequences of low permeability rocks that overlie tight oil and gas reservoirs targeted for production. Similar examples of black shale reservoirs at depth can be found in sedimentary basins throughout the US (see Figure 3.1) and abroad.

Advancements in HF and directional drilling have led to increased production not only in black shale formations, but also from other tight reservoirs. These formations are similar to black shales in that they are low-permeability layers of limited vertical, and often areal extent, and production from them was previously uneconomical. On the other hand, these reservoirs are different from black shales in their lithology (sandstone or carbonate *vs*. fine-grained shale) and often in depositional environment (*e.g.*, tight sands typically derive from river deposits of fluvial origin). Nevertheless, these reservoirs are classified as low permeability formations (< 1 millidarcy) and must be hydraulically fractured in order to produce an economical amount of natural gas or oil. One example of a tight sand reservoir is the Williams Fork formation located in the Piceance Basin in northwest Colorado. The Williams Fork ranges in thickness from 1,200 to 5,000 feet (Aschoff and Edwards, 2013) and gas-bearing units are located at depths from 4,000 to 9,000 feet (Johnson and Roberts, 2003). As a result of their fluvial origin, the gas-bearing deposits of the Williams Fork are often laterally discontinuous and limited to the size of the river deposits during past periods of deposition (Pranter and Sommer, 2011). Similar to the black shales of the Appalachian and Williston Basins, the discontinuous strata of the Williams Fork tend to be bounded by overlying lower permeability rocks.

Aside from the Piceance Basin, other tight sand reservoirs targeted for hydrocarbon production in the US include the Berea Sandstone (Appalachian Basin), Morrow Sandstone (Anadarko Basin), and Star Point Sandstone (Mesaverde Group – Uinta Basin) among others (see Meckel and Thomasson (2008) for a more detailed review). There are also several examples of tight carbonate gas plays, such as the Trenton/Black River group (northern Appalachian Basin) and the Austin Chalk formation (western Texas Gulf Coast Basin). Although each of these formations differ in geographic location and depth, all are overlain by thick sequences of shale, siltstone and other fine-grained rocks with low permeability.

3.2 Hydrogeology of Sedimentary Basins

The hydrogeology of sedimentary basins is complex due to the inherent layered structure and presence of multiple fluids. At all depths (beginning typically within 300 ft of the surface), the sedimentary column is saturated with fluid. Near the surface (typically < 600 feet depth) this fluid is freshwater and is a source of potable water for domestic wells (Focazio *et al*., 2006). Aquifers tapped for potable water supplies are referred to as Underground Sources of Drinking Water (USDWs) as defined by the US EPA (US EPA, 2012c) and contain less than 10,000 mg/L of Total Dissolved Solids (TDS). USDWs are typically less than several hundred feet deep, although some may be as deep as 1,200 feet (*e.g.*, in the Forth Worth Basin, Texas – US EPA, 2011a). With increased depth beneath the ground surface, TDS levels increase significantly resulting in more saline conditions (often saltier than seawater, *i.e.*, ≥ 35,000 mg/L) and groundwater is not potable. Saline fluids, often referred to as brine, are also present to some extent in oil and gas-bearing formations at depth (both tight and conventional oil/gas formations).

Brine is present down to the maximum depth of fluid underground, up to 10 to 15 km or deeper, *i.e.*, the entire vertical extent of the sedimentary column (Nur and Walder, 1990). As a result of high TDS, brine is denser than freshwater. The presence of brine at depth creates a density stratification and generally prevents saline water from mixing with overlying freshwater (*i.e.*, freshwater floats on top of the dense brine layer). Flow in the deeper portions of basins does occur, although the amount of deep circulation is negligible relative to the flow rate of freshwater through shallow aquifers (Toth, 1962, 1963). Deep circulation is limited by the low permeability of rock formations, the suppression of vertical flow by density stratification (Senger and Fogg, 1987), and frictional energy dissipation along long flow paths (Phillips, 2003). These effects generally result in very low flow rates at depth (Toth, 1962, 1963) and basin-scale travel times that may be millions of years or longer (Kreitler, 1989; Hogan *et al*., 2007). As a consequence of this combination of factors, upward fluid migration from the depths at which black shale and other tight oil and gas plays occur (typically thousands of feet below ground surface) is extremely restricted.

Of all the factors that limit upward flow rates, the low vertical permeability of sedimentary rocks is generally the most important. Permeability is a property of sedimentary rocks that controls the rock's capacity to transmit fluid. Higher permeability layers serve as dominant migration pathways, whereas low permeability layers confine flow. In the layered structure of sedimentary basins, vertical flow (upward or downward) is approximately perpendicular to the direction of bedding, which causes the least permeable layer to control overall permeability (Kreitler, 1989). In most of the basins depicted in Figure 3.1, sedimentary rocks above tight reservoirs are dominated by fine-grained (*e.g.*, shale, mudstone) or mixtures of fine-grained and coarse-grained rocks such as shaly sandstone (Baird and Dyman, 1993; Kiteley, 1978; Ryder *et al*., 2008, 2009, 2012; Sandberg, 1962; Swezey, 2008, 2009). These rocks tend to have low permeability and therefore, multiple, often thick, low-permeability layers limit vertical flow and hydraulically isolate hydrocarbon reservoirs from overlying potable aquifers. Any vertical fluid migration that might occur does so over very long periods, typically millions of years or longer (Law and Spencer, 1998).

Several studies have hypothesized that upward HF fluid migration through open, permeable faults (*e.g.*, Myers, 2012) or hydraulic fractures (Rozell and Reaven, 2012) to overlying potable groundwater might occur. The idea of upward HF fluid migration along thousands of feet of a continuous permeable fault plane is inherently paradoxical and physically implausible. For example, hydrocarbons cannot accumulate in subsurface areas where permeable pathways to the surface exist, otherwise buoyant oil and gas would leak upward. Thus, the occurrence of permeable faults and significant hydrocarbon accumulations are mutually exclusive (*i.e.*, do not co-exist). We discuss the implausibility of upward fluid migration from tight formations along natural faults later in Section 5.2.

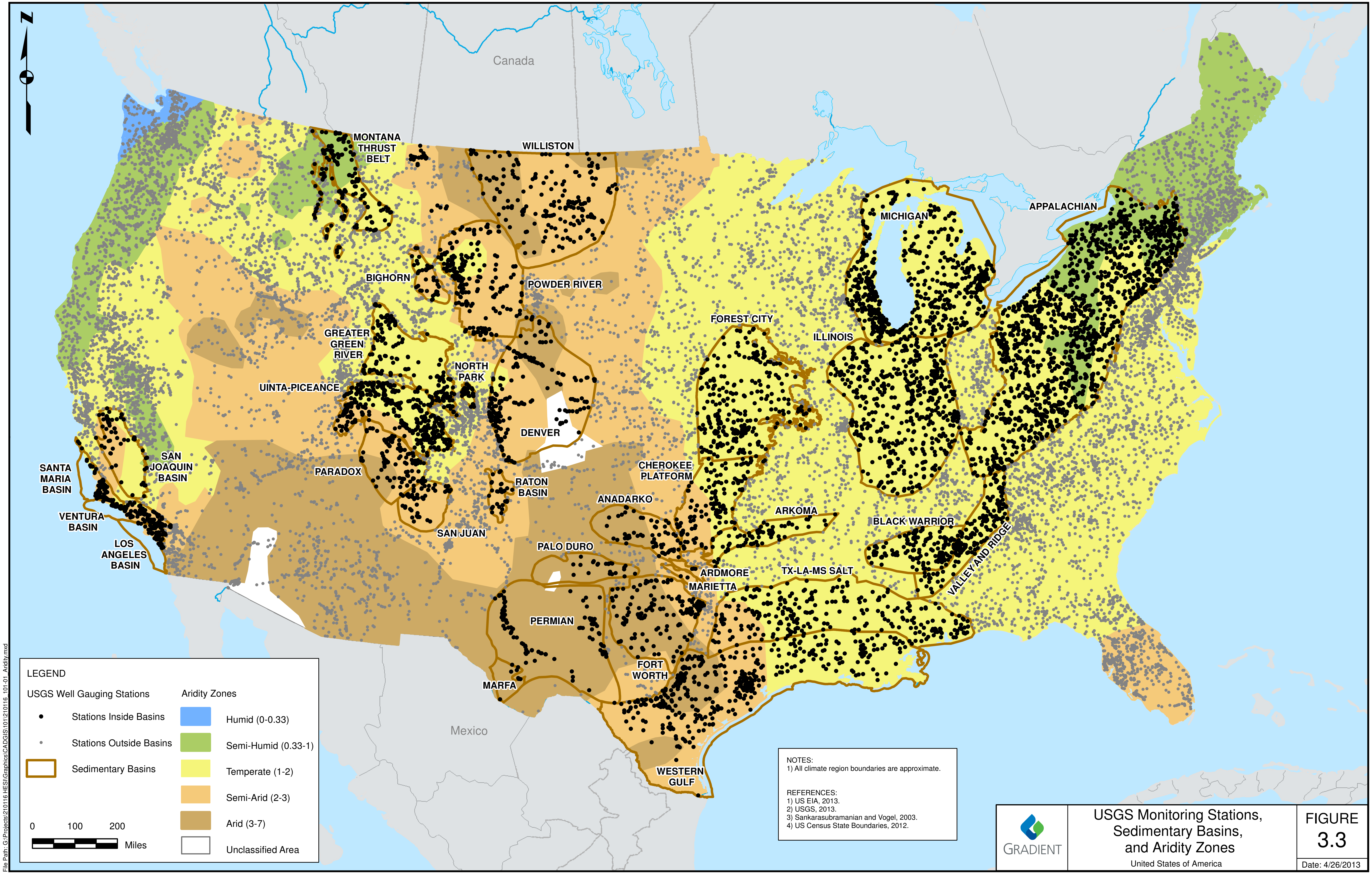
3.3 Surface Water Hydrology

For this study we have reviewed and compiled information relating to regional-scale surface water resources. Surface water is an important source of drinking water, especially in urban areas around the country. One component of our risk evaluation examines possible impacts of HF-related spills that could potentially impact such surface water resources, and therefore, we examined stream flow information that is collected and maintained by the United States Geological Survey (USGS). The USGS maintains and monitors an extensive network of stream gauges throughout the country (USGS, 2013). We obtained the USGS database and evaluated data for gauging stations located within the oil/gas basins of interest for this study. There are 3,459 stations that fall within these basins, with average monitoring periods ranging from approximately 20 to nearly 30 years of record (see Figure 3.3 and Table 3.1).

Not surprisingly, streamflow varies regionally, with lower flows found typically in more arid regions and higher flows in more temperate and humid regions. In our analysis of the USGS streamflow data, we grouped the gauging stations based on hydroclimatological regions, after Sankarasubramanian and Vogel (2003). The hydroclimatological regions are defined in terms of an "aridity index," which is the ratio of mean annual potential evapotranspiration to mean annual precipitation. In simpler terms, the aridity index is related to the quantity of water that is available to supply streamflow in a given region. Table 3.1 summarizes the available stream flow data in each hydroclimatological zone in terms of the total number of gauging stations and average period of record. Basins containing major tight oil and gas plays span four climatic regions: arid, semi-arid, temperate, and semi-humid. These data are used in subsequent analyses of potential surface spills, as described in more detail in Section 5.3.

Table 3.1 Summary of USGS Gauging Stations in Tight Formation Basins by Hydroclimatic Zones

Aridity Index	Number of Stations	Average Years of Record
Arid (3-7)	199	21.8
Semi-arid (2-3)	560	22.7
Temperate (1-2)	2,316	26.8
Semi-humid (0.33-1)	384	27.9



NOTES:
1) All climate region boundaries are approximate.

REFERENCES:
1) US EIA, 2013.
2) USGS, 2013.
3) Sankarasubramanian and Vogel, 2003.
4) US Census State Boundaries, 2012.

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USGS Monitoring Stations,
Sedimentary Basins,
and Aridity Zones
United States of America

FIGURE
3.3

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4 Conceptual Model for Risk Analysis

The process of hydraulic fracturing typically requires the handling of large volumes of HF fluid or flowback fluid containing HF constituents. Questions have been raised as to whether HF constituents could migrate upward from the target formations (the fracture zones) and contaminate shallow groundwater aquifers. In addition, although many controls and best management practices are established to reduce the likelihood and minimize the potential impacts of spills, it is possible that some surface spills or releases of HF fluids or flowback fluids may occur. For example, spills/releases could occur due to failures at pipe/pump fittings during HF fluid handling or pumping, or while flowback fluid is being recovered and stored for disposal or reuse. We outline below the conceptual model for our human health risk analysis that evaluates potential impacts on drinking water related to the HF process and potential spills.

4.1 Exposure Pathway Scenarios

Our exposure and risk analysis examines the potential human health consequences associated with HF constituents potentially impacting drinking water resources. We first consider the potential for HF fluids to reach drinking water aquifers as they are pumped down the well. As discussed in Section 2.2, gas production wells are carefully constructed, with a number of key design and monitoring elements to protect and to fully isolate the well from drinking water aquifers. In addition, the HF process includes rigorous monitoring and contingency measures to immediately detect and contain a casing release before it can enter the aquifer. As we discuss later in Section 5.1, based on an API study, consultants to New York State Department of Environmental Conservation estimated the risk of a properly constructed well contaminating a potable groundwater supply to be less than one in 50 million (NYSDEC, 2011, p. 6-41). Therefore, human health risks associated with this exposure scenario were not quantified as this exposure pathway is expected to be *de minimis*.

We next address the plausibility of upward migration of HF constituents once they reach the fracture zone and whether such a scenario could impact overlying shallow drinking water aquifers during the fracturing and post-fracturing periods. Questions have been raised concerning this hypothetical migration pathway and our analysis in Section 5 indicates that the inherent geologic factors common to the tight sedimentary formations targeted for HF preclude this possibility and it is not a plausible exposure pathway.

We also evaluate possible impacts to drinking water resources associated with potential surface spills of fluids containing HF constituents, *i.e.*, HF fluids and flowback fluid, including the following spill scenarios:

- Surface spills during HF fluid handling or flowback fluid recovery which potentially allow HF constituents to runoff the well pad and impact surface water used for drinking water; and
- Surface spills during HF fluid handling or flowback fluid recovery that possibly lead to HF constituents migrating downward through soil and impacting shallow aquifers and nearby drinking water wells.

Each of the migration/exposure pathways outlined above is identified on Figure 4.1, which depicts the conceptual model for the drinking water exposure pathways in our risk analysis. For the surface spill analysis, in order to be conservative (*i.e.*, health-protective), we have not taken into account any best management practices, institutional controls, or mitigation measures. For this reason, our analysis addresses "uncontrolled" or "unmitigated" surface spills of HF fluids and flowback fluid, even though it is standard practice to have measures in place at well sites to mitigate the effects of spills.[26]

If HF constituents in hypothetically uncontrolled surface spills migrate overland *via* surface runoff/erosion or through the shallow subsurface, they potentially could affect adjacent surface water resources. In addition, HF constituents in surface spills could leach through the unsaturated zone (soil above the groundwater table) and potentially affect shallow aquifers, a potential source of drinking water. For our exposure and risk analysis we have evaluated two sets of extreme conditions, assessing the hypothetical implications if: (1) 100% of the surface spill leaches to groundwater; and (2) 100% of the surface spill impacts surface water. These are bounding scenarios because the entirety of any given spill could not migrate to both groundwater and surface water (as our worst case analysis assumes). More likely, even if spills escaped containment measures at the well pad, a portion of the spilled fluid would almost certainly be retained in the soil on or adjacent to the pad such that only a portion would potentially reach any nearby surface water bodies. Similarly, it is unlikely that 100% of the volume of a spill would leach to groundwater, as we have conservatively assumed.

We also considered potential subsurface release of HF constituents to potable aquifers due to a potential well casing failure during the HF fluid pumping phase. As discussed in Section 2.2, gas production wells are carefully constructed, with a number of key design and monitoring elements to protect and to fully isolate the well from drinking water aquifers. In addition, the HF process includes rigorous monitoring and contingency measures to immediately detect and contain a casing release before it can enter the aquifer. As we discuss later in Section 5.1, based on an API study, consultants to New York State Department of Environmental Conservation estimated the risk of a properly constructed underground injection well contaminating a potable groundwater supply to be less than one in 50 million (NYSDEC, 2011, p. 6-41). Using this analogy, it is extremely unlikely that a properly constructed well subject to HF would allow contamination of a potable aquifer. Therefore, human health risks associated with this exposure scenario were not quantified as this exposure pathway is expected to be *de minimis*.

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[26] These measures may include berms and other forms of secondary containment (API, 2011).

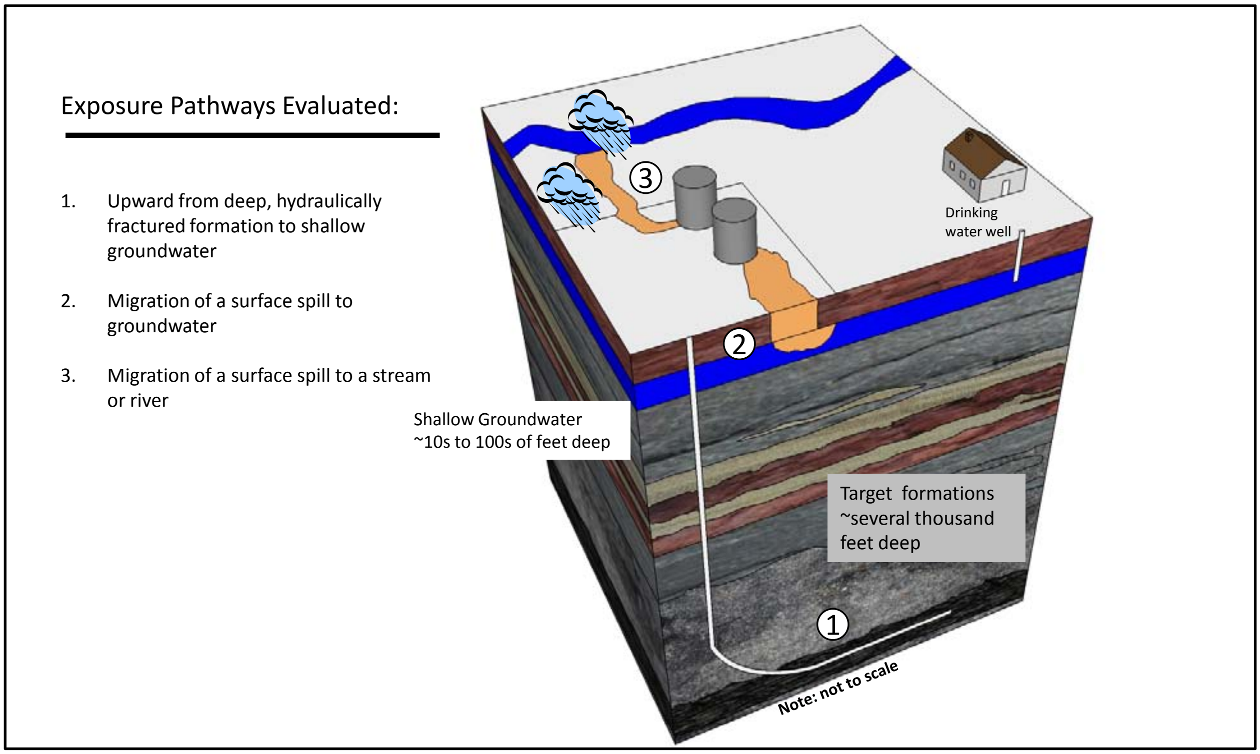

Figure 4.1 Conceptual Model of Exposure Pathways Evaluated in Health Risk Analysis

4.2 HF Chemicals Evaluated

As summarized in the following sections, our risk analysis included HF chemical additives found in typical HF systems used by HESI for hydraulic fracturing in tight oil and gas-bearing formations. We also evaluated chemical constituents that have been found in flowback fluids.

4.2.1 HESI HF Fluid Systems and Constituents

HESI has developed HF fluid systems for fracturing tight formations in all regions of the US. These fluid systems include a range of different types and volumes of fluids. Distinguishing features of the different HESI HF fluid systems are noted below in Table 4.1.

Table 4.1 Features of Different Types of HF Fluid Systems

Fluid System	Description
Water Frac	A fracturing treatment performed using a water-based fluid formulation in which the friction pressure is reduced when pumping fluid volumes through several thousand feet of casing. This increases the amount of hydraulic pressure imparted on the oil or natural gas-bearing formation. These formulations also have a very low viscosity, which encourages the development of many small interconnected cracks to improve production.
Foam Frac	High-viscosity fracturing fluids that use less polymer loading than conventional, non-foamed fluids. In addition, the gas in the foam expands after HF treatment improving fluid recovery while providing good fracture conductivity and regained permeability. These formulations allow the use of smaller fluid volumes for hydraulic fracturing.
Gel Frac	A fracturing fluid composed mostly of water with a gelling agent added to make the fluid thicker and slicker.
Hybrid Frac	A fracturing treatment that relies upon a combination of the Water Frac and Gel Frac systems.
Pre Frac Acid	A mixture of water and an acid, such as hydrochloric acid, is used prior to introducing subsequent HF fluids in order to clean out debris in the well after it has been drilled, cased, cemented, and perforated in the oil- or gas-bearing zone.

According to HESI, in tight formations, a typical well is anticipated to use approximately 5,000 to 73,000 gallons of fluid for the total pre-frac acid phase, and one hundred thousand to several million gallons for the combined fracturing/flush phases – with the fracturing phase comprising the vast majority of the fluid volume (see Table 4.2). We also note that one of the HESI formulations that may be used in some formations is a "foam frac" fluid. This HF system uses far smaller fluid volumes (less than 30,000 gallons for the frac and flush stages) compared to other HF systems – see Table 4.2.

The chemical constituents of the HF additives contained within these typical HESI HF fluid systems are listed in Table 4.3.

Table 4.2 Typical HESI HF Fluid Systems

Formulation Name	Fluid Stage Designation	Fluid Volume (gal)
Pre-frac Acid 01	Acid prior to HF	34,000
Pre-frac Acid 02	Acid prior to HF	73,000
Pre-frac Acid 03	Acid prior to HF	5,000
Foam frac 01	TW	5,340
	XLF	22,082
	TW + XLF (total)	27,422
Gel frac 01	XLF	1,915,000
Hybrid frac 01	LF	170,000
	WF	4,500,000
	LF + WF (total)	4,670,000
Hybrid frac 02	TW	816,750
	XLF	2,329,000
	TW + XLF (total)	3,145,750
Hybrid frac 03	LF	29,203
	XLF	97,000
	LF + XLF (total)	126,203
Hybrid frac 04	TW	393,700
	Flush	461,993
	XLF	2,154,500
	TW + XLF + Flush (total)	3,010,193
Hybrid frac 05	TW	849,000
	XLF	1,247,100
	TW + XLF (total)	2,096,100
Hybrid frac 06	TW	7,000
	LF	175,680
	XLF	1,179,324
	LF + XLF + TW (total)	1,362,004
Water frac 01	WF	4,500,000
Water frac 02	WF	4,500,000
Water frac 03	WF	7,310,000
Water frac 04	Flush	204,600
	LF	502,200
	LF + Flush (total)	706,800

Notes:

Abbreviations are defined as follows: Treated Water (TW) recycled/treated water, Linear Fluid (LF) such as polymer gels, Cross-Linked Fluid (XLF) often borate or organometallic components to link polymers, Water Frac (WF) water-based system not including LF or XLF components.

Table 4.3 Constituents in Typical HESI HF Fluid Systems

CAS No	Chemical
95-63-6	1,2,4 Trimethylbenzene
CBI	Olefin
CBI	Olefin
CBI	Olefin
CBI	Olefin
CBI	Quaternary ammonium salt
52-51-7	2-Bromo-2-nitro-1,3-propanediol
64-19-7	Acetic acid
108-24-7	Acetic anhydride
CBI	Surfactant mixture
68551-12-2	Alcohols, C12-16, ethoxylated
68951-67-7	Alcohols, C14-C15, ethoxylated
68439-57-6	Alkyl (C14-C16) olefin sulfonate, sodium salt
CBI	Fatty acid tall oil
61791-14-8	Amines, coco alkyl, ethoxylated
631-61-8	Ammonium acetate
12125-02-9	Ammonium chloride
7727-54-0	Ammonium persulfate
7722-76-1	Ammonium phosphate
12174-11-7	Attapulgite
121888-68-4	Bentonite, benzyl(hydrogenated tallow alkyl) dimethylammonium stearate complex
3468-63-1	C.I. Pigment Orange 5
10043-52-4	Calcium chloride
CBI	Guar gum derivative
CBI	Ethoxylate fatty acid
15619-48-4	Chloromethylnaphthalene quinoline quaternary amine
7758-19-2	Chlorous acid, sodium salt
CBI	Aldehyde
94266-47-4	Citrus, extract
71-48-7	Cobalt acetate
14808-60-7	Crystalline silica, quartz
111-46-6	Diethylene glycol
111-40-0	Diethylenetriamine
64-17-5	Ethanol
78330-21-9	Ethoxylated branched C13 alcohol
111-76-2	Ethylene glycol monobutyl ether
CBI	EDTA/Copper chelate
CBI	Ethoxylated fatty acid
61791-08-0	Fatty acids, coco, reaction products with ethanolamine, ethoxylated
9043-30-5	Fatty alcohol polyglycol ether surfactant
50-00-0	Formaldehyde
CBI	Oxylated phenolic resin
CBI	Oxylated phenolic resin
56-81-5	Glycerine
9000-30-0	Guar gum
7647-01-0	Hydrochloric acid

Table 4.3 Constituents in Typical HESI HF Fluid Systems

CAS No	Chemical
64742-94-5	Heavy aromatic petroleum naphtha
9012-54-8	Hemicellulase enzyme
64742-47-8	Hydrotreated light petroleum distillate
67-63-0	Isopropanol
CBI	Carbohydrate
7791-18-6	Magnesium chloride hexahydrate
67-56-1	Methanol
CBI	Fatty acid tall oil
64742-48-9	Naphtha, hydrotreated heavy
91-20-3	Naphthalene
68410-62-8	Naphthenic acid ethoxylate
127087-87-0	Nonylphenol ethoxylated
Mixture	Organic acid salt
CBI	Organic phosphonate
CBI	Polyacrylamide copolymer
CBI	Surfactant mixture
CBI	Cured acrylic resin
61791-26-2	Polyoxylated fatty amine salt
584-08-7	Potassium carbonate
590-29-4	Potassium formate
1310-58-3	Potassium hydroxide
13709-94-9	Potassium metaborate
71-23-8	Propanol
107-19-7	Propargyl alcohol
CBI	Quaternary ammonium compound
68953-58-2	Quaternary ammonium compounds, bis(hydrogenated tallow alkyl) dimethyl, salts with bentonite
68527-49-1	Reaction product of acetophenone, formaldehyde, thiourea and oleic acid in dimethyl formamide
CBI	Proprietary
112926-00-8	Silica gel
7631-86-9	Silica, amorphous – fumed
CBI	Fatty acid ester
144-55-8	Sodium bicarbonate
9004-32-4	Sodium carboxymethyl cellulose
7647-14-5	Sodium chloride
CBI	Inorganic salt
2836-32-0	Sodium glycolate
1310-73-2	Sodium hydroxide
7681-52-9	Sodium hypochlorite
7681-82-5	Sodium iodide
10486-00-7	Sodium perborate tetrahydrate
7775-27-1	Sodium persulfate
7757-82-6	Sodium sulfate
7757-83-7	Sodium sulfite
7772-98-7	Sodium thiosulfate
CBI	Fatty acid ester ethoxylate
CBI	Fatty acid tall oil amide

Table 4.3 Constituents in Typical HESI HF Fluid Systems

CAS No	Chemical
CBI	Terpenoid
CBI	Terpenoid
81741-28-8	Tributyl tetradecyl phosphonium chloride
101033-44-7	Triethanolamine zirconate
1319-33-1	Ulexite
CBI	Borate salt
68909-34-2	Zirconium, acetate lactate oxo ammonium complexes

Notes:
CBI – Confidential Business Information.
Gradient was provided chemical-specific CAS and chemical names and used this information to evaluate chemical-specific toxicity for these CBI constituents.

4.2.2 Constituents in Flowback Fluid

The chemical composition of flowback fluid may be influenced by the fluids used to fracture the well, the composition of naturally occurring brines and hydrocarbons in the target formation, and chemical reactions such as precipitation and dissolution. As a conservative measure, we have included all the constituents of flowback fluid in our analysis even though many of these constituents are not related to HF operations and would be found in the produced water from a well even if it had not been hydraulically fractured.

In order to identify the chemical constituents of flowback fluid to use for purposes of our analysis, we considered two types of data sources. First, we considered data reported from analyses of flowback fluid samples. However, such data are limited. To supplement these data, the chemistry of produced water may serve as a surrogate for the portion of flowback fluid chemistry that consists of constituents naturally occurring in the brine. According to US EPA, "the concentration of contaminants in produced water varies from region to region and depends on the depth of the production zone and the age of the well, among other factors. Since most contaminants found in produced water are naturally occurring, they will vary based on what is present in the subsurface at a particular location" (US EPA, 2000).

To identify potential sources of flowback fluid chemistry data, we searched the scientific literature, US government reports, and industry white papers. We identified and reviewed over 30 different documents that included some data on flowback fluid or produced water chemistry. We evaluated whether the sources were reliable and relevant based on the following criteria:

- Relevance of analytes to risk assessment (*e.g.*, stable isotopes were excluded, major ions were mainly excluded);
- Whether the methods for sample collection and analysis were defined;
- Whether the number of samples was available; and
- Whether the data are redundant with other datasets already reported (many studies cite and reanalyze previously published data).

Using these criteria, we compiled a database of concentration statistics for flowback fluid (*e.g.*, number of samples, minimum, median, and maximum concentrations) from seven different datasets (Appendix A, Table A.1). A total of 82 different flowback fluid-related constituents were considered in this risk evaluation. An additional 48 analytes were compiled in the database, but were excluded from this evaluation because they are unlikely to be a human health concern (*e.g.*, major ions common in aqueous samples, some of which are nutrients) or were infrequently detected (*e.g.*, fewer than 3 detections in a data set).

The highest median flowback fluid constituent concentrations reported in the seven data sources were utilized our risk evaluation (Table 4.4). The most comprehensive data set of flowback fluid chemistry is available for the Appalachian Basin (Hayes, 2009). As part of the Hayes study, flowback fluid samples from 19 Marcellus shale wells were collected on days 1, 5, and 14 after well completion, and produced water samples were collected 90 days after the wells began operating. The majority of chemical concentrations identified for use in the risk assessment are from the Hayes (2009) study.

Brines produced in the Appalachian Basin are among the most concentrated in the entire US (USGS, 2002), so concentrations of most inorganic chemicals in the Marcellus Shale are expected to be higher than in other formations. For organic constituents, it is difficult to assess whether data from the Marcellus Shale are representative of other tight formations, as very little additional data exists.

Table 4.4 Flowback Fluid Constituent Concentrations

CAS	Parameter	Highest Median (µg/L)	Flowback Data Source
7429-90-5	Aluminum-DISS	227	Hayes, 2009
7440-36-0	Antimony-DISS	5	Hayes, 2009
7440-38-2	Arsenic-DISS	13	Hayes, 2009
7440-39-3	Barium-DISS	496,000	Hayes, 2009
7440-42-8	Boron-DISS	12,400	Hayes, 2009
24959-67-9	Bromide	607,000	NYSDEC, 2011
7440-43-9	Cadmium-DISS	3	Hayes, 2009
7440-47-3	Chromium	82	NYSDEC, 2011
7440-47-3	Chromium (VI)	5	NYSDEC, 2011
7440-47-3	Chromium (VI)-diss	539	NYSDEC, 2011
7440-47-3	Chromium III	25	Hayes, 2009
7440-47-3	Chromium-DISS	7	Hayes, 2009
7440-48-4	Cobalt-DISS	250	Hayes, 2009
7440-50-8	Copper-DISS	13	Hayes, 2009
57-12-5	Cyanide, Total	5	Hayes, 2009
57-12-5	Cyanide, Total	5	Hayes, 2009
7439-92-1	Lead-DISS	13	Palmerton Group, 2008-2009
7439-93-2	Lithium-DISS	61,350	NYSDEC, 2011
7439-96-5	Manganese-DISS	2,975	NYSDEC, 2011
7439-97-6	Mercury-DISS	0	Hayes, 2009
7439-98-7	Molybdenum-DISS	84	Hayes, 2009
7440-02-0	Nickel-DISS	20	Hayes, 2009
7782-49-2	Selenium-DISS	3	Hayes, 2009
7440-22-4	Silver-DISS	3	Hayes, 2009
7440-24-6	Strontium-DISS	1,300,000	Hayes, 2009
14808-79-8	Sulfate	500,000	Benko and Drewes, 2008
7440-28-0	Thallium-DISS	5	Hayes, 2009
7440-31-5	Tin-DISS	500	Hayes, 2009
7440-32-6	Titanium-DISS	250	Hayes, 2009
7440-66-6	Zinc-DISS	147	Hayes, 2009
105-67-9	2,4-Dimethylphenol	5	Hayes, 2009
91-57-6	2-Methylnaphthalene	3	Palmerton Group, 2008-2009
95-48-7	2-Methylphenol	5	Hayes, 2009
108-39-4/106-44-5	3/4-methylphenol	5	Hayes, 2009
83-32-9	Acenaphthene	1	Hayes, 2009
98-86-2	Acetophenone	5	Hayes, 2009
100-51-6	Benzyl alcohol	5	Hayes, 2009
117-81-7	Bis(2-ethylhexyl)phthalate	5	Hayes, 2009
218-01-9	Chrysene	1	Hayes, 2009
84-66-2	Diethyl phthalate	5	Hayes, 2009
84-74-2	Di-n-butyl phthalate	5	Hayes, 2009
117-84-0	Di-n-octyl phthalate	5	Hayes, 2009
206-44-0	Fluoranthene	1	Hayes, 2009
86-73-7	Fluorene	1	Hayes, 2009
85-01-8	Phenanthrene	1	Hayes, 2009
108-95-2	Phenol	1	Hayes, 2009
64743-03-9	Phenols	18	Hayes, 2009
129-00-0	Pyrene	1	Hayes, 2009
110-86-1	Pyridine	14	Hayes, 2009
87-61-6	1,2,3-Trichlorobenzene	3	Hayes, 2009
95-63-6	1,2,4 trimethylbenzene	5	Palmerton Group, 2008-2009
108-67-8	1,3,5-Trimethylbenzene	5	Palmerton Group, 2008-2009
107-06-2	1,2-Dichloroethane	5	Palmerton Group, 2008-2009
78-93-3	2-Butanone	3	Hayes, 2009

Table 4.4 Flowback Fluid Constituent Concentrations

CAS	Parameter	Highest Median (µg/L)	Flowback Data Source
99-87-6	4-Isopropyltoluene	5	Palmerton Group, 2008-2009
67-64-1	Acetone	37	Palmerton Group, 2008-2009
71-43-2	Benzene	480	NYSDEC, 2011
75-15-0	Carbon Disulfide	3	Hayes, 2009
100-41-4	Ethyl Benzene	54	NYSDEC, 2011
98-82-8	Isopropylbenzene (cumene)	3	Hayes, 2009
75-09-2	Methylene Chloride	3	Hayes, 2009
91-20-3	Naphthalene	3	Hayes, 2009
103-65-1	n-Propylbenzene	5	Palmerton Group, 2008-2009
108-88-3	Toluene	833	NYSDEC, 2011
1330-20-7	Xylenes	444	NYSDEC, 2011
95-47-6	o-Xylene	5	Palmerton Group, 2008-2009
64-19-7	Acetic acid	116,300	Connolly *et al* ., 1990b
64-17-5	Ethanol	5,000	Hayes, 2009
107-21-1	Ethylene glycol	25,000	Hayes, 2009
67-63-0	Isopropanol	5,000	Hayes, 2009
67-56-1	Methanol	5,000	Hayes, 2009
71-36-3	n-Butanol	5,000	Hayes, 2009
79-09-4	Propionic Acid	28,600	Connolly *et al* ., 1990b
64-18-6	Formic acid	1,200	Connolly *et al* ., 1990b
NORM		**pCi/L**	
	RA 228	504	Rowan *et al* ., 2011
	RA 226	611	Palmerton Group, 2008-2009
	Uranium 238	0.061	NY Times, 2011
	Uranium 235	0	NY Times, 2011
	PB 214	174	Palmerton Group, 2008-2009
	PB 212	60	Palmerton Group, 2008-2009
	Gross alpha [a]	6,845	Rowan *et al* ., 2011
	Gross beta [a]	1,170	Rowan *et al.* , 2011

Notes:

"-DISS" suffix indicates dissolved results.

"Highest Median" = highest median from multiple data sets (see Appendix).

[a] Rowan *et al* . (2011) reports that gross alpha and gross beta are likely dominated by RA-226 and RA-228 sources.

5 Exposure Analysis

This section describes the methods we used to evaluate the potential migration of chemicals in HF and flowback fluids in order to address the exposure pathways outlined in the preceding section. We first examine the risks possibly posed by the "intended" use of HF fluids – pumping the fluids into the target formation in order to create fractures. For this analysis, we examine the potential for fluids pumped down the well to reach drinking water aquifers, particularly the plausibility of HF fluids pumped into tight formations migrating upward from those formations. We specifically addressed this issue in our prior analysis in the context of the Marcellus Shale. Following that analysis, we evaluate the fate of potential "unintended" surface spills of HF and flowback fluids. For the surface spill scenarios, we developed dilution factors for each exposure pathway (surface water and shallow groundwater) to assess the degree to which the HF and flowback fluid constituents will be diluted from the point of the spill to the point at which a potential drinking water exposure might occur. Using these dilution factors, we determined "exposure-point concentrations" for the constituents of HF and flowback fluids, *i.e.*, concentrations that might hypothetically be found in a drinking water source as a result of a spill.

5.1 Protection of Drinking Water Aquifers Through Zonal Isolation

We began our exposure analysis by considering the potential for HF fluids to escape as they are being pumped down the well and thereby reach drinking water aquifers. As discussed in Section 2, wells are carefully designed, incorporating a number of key elements to protect drinking water aquifers and to fully isolate the natural gas producing zone of the well.[27] In addition, the HF process includes rigorous monitoring and contingency measures to immediately detect and contain a casing release before it can enter the aquifer. Specifically, the well design, monitoring, and contingency measures that minimize the likelihood of HF constituents from entering a potable aquifer include the following (API, 2009):

- All components of the HF operations are carefully planned and controlled. For example, key elements of an HF operation, such as gas well design, fracturing pressure required, and duration of fracturing, are determined by highly specialized professionals.
- Oil and gas wells are constructed with up to four protective casings, carefully designed to ensure that the well is only in communication with the oil and gas bearing zone and to isolate the fluids in the interior of the well from hydrogeologic units – and any accompanying groundwater – that overlie the gas producing zone, a process referred to as "zonal isolation." Each of these casings is secured by placing a cement seal, thereby completely vertically isolating the interior of the well from the subsurface (Figure 2.1).
- During well installation, monitoring is conducted to ensure that the casings have been properly sealed and can withstand the anticipated pressures. This is accomplished by monitoring the thickness/bond quality of the cement seal. In addition, pressure tests are conducted to ensure that the casing can withstand the anticipated pressures (*i.e.*, there are no zones of weaknesses or leaks) and that there is no leakage from the bottom of the bore hole (*i.e.*, at the base of the seal).

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[27] State agencies also regulate oil and gas exploration and production activities to require sound practices to minimize potential environmental impacts.

- Prior to initiation of HF, the well is again pressure tested to ensure that the well can withstand the pressures experienced during the HF process and that there are no leaks in the production casing.
- During the HF process, pressure is continuously monitored in real time to watch for any abnormal pressure variations, and to immediately shut down the HF process in the event of an unusual response (*e.g.*, sudden drop in pressure).
- Gas wells contain pressure relief and release containment mechanisms within the annulus of the intermediate casing (*i.e.*, immediately beyond the production casing), that provide both a warning mechanism and a means to contain and recover any HF fluid that may escape beyond the production casing (see Section 2).

For the above-listed reasons, the likelihood of HF constituents entering a potable aquifer as a result of a leak from a properly constructed well is extremely low.

Information from underground injection wells also provides further evidence that potential releases from properly constructed wells are highly unlikely. Based on an API study, NYSDEC (2011, p. 6-41) quantified the probability of a properly constructed underground injection well contaminating a potable aquifer to be 2×10^{-8} (less than 1 in 50 million wells). Because oil/gas wells are subjected to positive pressures for an extremely short duration (one to two days of HF stimulation) compared to underground injection wells used to inject wastes into the subsurface, the probability of a gas well casing leakage affecting a potable aquifer is expected to be even lower. In addition, "regulatory officials from 15 states have recently testified that groundwater contamination from [the] hydraulic fracturing procedure is not known to have occurred despite the procedure's widespread use in many wells over decades" (NYSDEC, 2011, p. 6-41). Given the extremely low probability of casing leakage affecting potable aquifers, exposures and risks for this scenario were not quantified in this risk evaluation.

5.2 Implausibility of Migration of HF Constituents from Target Formations

Having considered the steps taken to ensure that HF fluids do not escape from the well as they move through the well to the formation being hydraulically fractured, we next considered whether drinking water sources could be affected by the HF fluids once they are pumped into the target formation. As described earlier, a portion of the HF fluid injected into the formation will be recovered after fracturing as flowback fluid. Any fluid not recovered will remain in the target formation (along with additives in the fluid). Some have hypothesized that residual HF constituents in the fractured target formation might migrate upward and potentially contaminate overlying potable aquifers (*e.g.*, Myers, 2012; Rozell and Reaven, 2012; Warner *et al.*, 2012). Whether this is plausible or not depends on the manner in which fluids are sequestered in the target formation, the ability of the overlying formations to transmit water, and whether there is a driving force (head gradient) sufficient to induce water (and chemicals) to migrate upward from the target formation. These factors were previously evaluated by NYSDEC (2011), which concluded that this migration pathway was not plausible in the Marcellus Shale formation. Our examination of this transport pathway more broadly in tight formations across the US is described in this section and indicates similarly that migration of HF constituents from the target formation to overlying shallow aquifers is physically implausible.

We divided our evaluation of potential upward fluid migration into two phases or periods:

1. The period prior to the HF process ("Baseline Period"); and
2. The period when fluid is pumped into the target formation to create fractures (the "HF Period").

There is also a "Production Period" when oil and gas are being produced from the well, however, as discussed in this section, the potential for upward migration is even lower during the Production Period than during the Baseline Period. Therefore, it is not considered separately.

The Baseline Period is used as a point of comparison for evaluating the potential changes to fluid and chemical migration brought about by HF, including effects related to fracture propagation, faults, and short term elevated pressures at depth. Our analysis incorporates an extensive literature review on the geological conditions where tight oil and gas reservoirs occur and the migration of fluids and chemicals at the depths at which these reservoirs are found. We also analyze an extensive dataset of measured fracture heights and seismicity associated with HF from over 12,000 individual fracture stages in more than 25 sedimentary basins across the US and Canada.

Our analyses clearly demonstrate that hydraulic fractures and potential fault interactions are constrained to the vicinity of target formations and that it is not physically plausible for induced fractures or faults to create hydraulic connections to USDWs. In the absence of these pathways, upward migration of fluid (and chemicals carried with fluid) through intact bedrock is extremely slow (typically requiring millions of years or longer to traverse overlying rocks) if the direction of vertical flow is even upward at all. Low upward flow rates through intact bedrock coupled with attenuation of chemicals over such long flow paths and timescales *via* a range of natural processes (*e.g.*, biodegradation, adsorption, ion exchange) will result in insignificant upward migration of chemical constituents. Therefore, from a potential human exposure standpoint, this migration pathway is not "complete." Despite the exposure pathway being incomplete, as a hypothetical (but quite unrealistic) scenario, we evaluated the amount of dilution if upward fluid migration were to occur. Our results indicate that even if we were to consider this hypothetical unrealistic pathway, the DFs would be extremely high and would be such that chemicals would be attenuated (diluted) to well below health protective drinking water benchmarks.

5.2.1 Baseline Period

Tight oil and gas deposits have been hydraulically isolated from overlying formations for long periods, ranging from tens to hundreds of millions of years (Law and Spencer, 1998). For example, brine and natural gas have been trapped for almost 400 million years in the Marcellus Shale formation (Garven *et al.*, 1993). As discussed in Section 3.2, tight oil- and gas-bearing formations are typically found at depths of several thousand feet and lie beneath numerous layers of low permeability rocks. There are many factors that create the hydraulic isolation of oil and gas formations – and that would effectively preclude the upward migration of any HF fluids introduced into the formation – and a few of the most important are discussed here.

In order to evaluate the constraints on upward fluid migration, one must first understand the conditions that allow for upward flow to occur. As a rule, the necessary conditions required for fluids at depth to flow upward are: (1) a permeable pathway for fluid to migrate; and (2) a driving force to cause fluid to flow upward.

Permeable pathways can occur in coarse-grained high permeability rocks (*e.g.*, sandstone) or in open fractures and faults.[28] As discussed in Section 3.2, sedimentary basins have multiple layers of different types of rocks, many of which are low permeability rocks such as shale, mudstone and siltstone.[29] Even if there are some high permeability layers, upward flow must also traverse these low permeability layers. In this physical setting, the overall permeability of the layered series of rocks is controlled by the least

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[28] Note, if fractures or faults are "closed," then these are not expected to serve as significant migration pathways.

[29] For example, as shown in Figure 3.2, the Marcellus Shale is overlain by multiple layers of rock that are predominantly shale and that are collectively several thousand feet thick.

permeable layer (Kreitler, 1989), and this will not allow for a permeable pathway to exist in intact (*i.e.*, unfractured) rock in these layered sedimentary basins. Therefore, the only way in which meaningful upward fluid migration might potentially occur is through fractures or faults that cut across multiple low-permeability rock layers.

In general, fractures and faults are considered the primary pathways that allow for vertical fluid migration through the deeper portions of the earth's crust (Nur and Walder, 1990; Townend and Zoback, 2000). However, even if such migration were to occur, the time required for fluid to migrate from great depths is very long (*e.g.*, millions of years) (Kreitler, 1989; Hogan *et al*., 2007). Furthermore, the driving force for fluid migration (called the upward head gradient) is inherently related to the permeability of bedrock. For example, when a basin actively accumulates sediment, the weight of newly accumulated material would normally cause underlying rocks to compact and therefore, expel water from the pore space (Plumley, 1980). If the permeability of rocks is too low to allow water to escape freely, then a portion of the overlying weight will be borne by the trapped fluid and will result in increased fluid pressure. In such cases, the elevated fluid pressure can provide the driving force for upward fluid flow (*i.e.*, an upward head gradient). Other factors can also lead to increased fluid pressure, such as the conversion of organic matter to oil and gas. However, a common feature necessary to allow the buildup of elevated pressure at depth is that there must be inherently low permeability layers of overlying rocks. Elevated pressures generated by these mechanisms constitute the primary large scale driving forces for upward head gradients that would be prerequisite to inducing any upward flow.

Physical relationships can be used to estimate the effective permeability of the sequence of rock layers overlying an oil/gas-bearing formation where upward flow could potentially occur. One approach is to calculate the permeability that would be required for elevated pressures in oil and gas formations to persist after pressure generating processes ceased (*e.g.*, rapid sedimentation or oil and gas generation that occurred tens to hundreds of millions of years ago). The following equation, which is a 1-dimensional solution to the governing equation for pressure diffusion (Deming, 1994), can be used for this purpose:

$$k = z^2 \alpha \mu / 4t \tag{5.1}$$

where:

k = Effective permeability of rocks overlying an oil/gas-bearing formation;
z = Thickness of overlying rocks;
α = Compressibility of bedrock;
t = Timescale for diffusion of pressure; and
μ = Viscosity of water.

For timescales of 10 million to 100 million years, overburden thicknesses of 3,000 to 15,000 ft (1,000 to 3,000 m - the depth range of most tight oil and gas formations), $\alpha = 7 \times 10^{-6}$ psi^{-1} (10^{-9} Pa^{-1}) (a typical value for shale; Deming, 1994), and $\mu = 10^{-5}$ lb-f s ft^{-2} (0.0005 Pa-s), the permeability that would allow elevated pressure ranges from 10^{-22} ft^2 (10^{-23} m^2) to 10^{-19} ft^2 (10^{-20} m^2).[30] Similar approaches have been used by others to evaluate the permeability that would be required to prevent pressure build up over geologic time (Townend and Zoback, 2000; Zoback, 2007). These results give the upper bound permeability as approximately 10^{-17} to 10^{-16} ft^2 (10^{-18} to 10^{-17} m^2). Thus, the range of permeability over which upward flow might occur ranges from approximately 10^{-22} to 10^{-16} ft^2 (10^{-23} to 10^{-17} m^2). Such low

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[30] Note that this range of permeabilities is at the extreme low-end of values reported in most standard groundwater hydrology texts (*e.g.*, Freeze and Cherry, 1979), but is consistent with the low permeability shales that are commonly found at depth (*e.g.*, Kwon *et al*., 2001 and references therein; Corbet and Bethke, 1992; Neuzil, 1986).

permeability values lead to insignificant upward fluid flow (if upward flow even occurs). The impermeability of these layers is demonstrated by the fact that they have trapped buoyant fluids (*i.e.*, oil and natural gas) over timescales of tens to hundreds of millions of years (Thornton and Wilson, 2007; Stueber and Walter, 1991; Connolly *et al*., 1990a,b).

Another limit on upward flow is fluid density stratification. The dominant fluid at depth in sedimentary basins is brine, which can be over 25% more dense than freshwater in many cases (Batzle and Wang, 1992). A dense brine layer at depth creates a stable fluid layer which is overlain by fresh water that "floats" on top as a less dense liquid. (Any HF fluids mixed with the brine would also be subject to these same forces.) As a result, these natural density gradients must be accounted for when evaluating the potential for vertical fluid flow, because failing to do so could lead to predictions of upward flow when the direction of flow is actually downward (Senger and Fogg, 1987). For example, a brine with density of 74.9 lb ft^{-3} (1,200 kg/m^3) would create a downward head gradient of 0.2 for a typical freshwater density of 62.4 ft^{-3} (1,000 kg/m^3) (Flewelling and Sharma, Submitted). This is a large downward head gradient and conditions that could overcome this degree of stratification could only be found in highly pressurized strata, which are inherently associated with very low permeability overlying rocks (as discussed previously).

To summarize, large upward head gradients are needed to overcome the natural density stratification in sedimentary basins and to cause brine (and other constituents associated with it) to flow upward. The situations that can potentially create large enough upward head gradients (*e.g.*, rapid sedimentation or the conversion of organic matter to oil and gas with corresponding increases in fluid pressure) are inherently associated with low permeability overlying rocks. Thus, there are natural constraints that cause upward flow rates to be insignificant during the Baseline Period (prior to hydraulic fracturing). The presence of concentrated brine and significant reserves of trapped oil and gas at depth are a clear demonstration of the effectiveness of the hydraulic isolation of hydrocarbon-bearing formations from overlying potable groundwater, isolation that has persisted for millions of years.

5.2.2 Impact of Hydraulic Fracturing on Fluid Migration

As discussed in Section 2, the HF process typically undertaken in these tight formations is completed in a relatively short time interval (typically minutes to hours per operation or stage). HF fluids (water and additives) and proppants are pumped into a well at pressures that may range from slightly above hydrostatic to slightly above lithostatic pressure (Flewelling and Sharma, Submitted). The entire HF process is typically completed at a single well within one to two days. After the HF treatment has been completed, pumps begin pulling material out of the well, first to remove HF fluid and naturally-occurring brine (if any) from the formation, and then to commence oil and gas production. During oil and gas production, pressure in the well is lower than ambient pressure in the formation, causing all fluids (oil, gas, brine, and residual HF fluid) to migrate toward the well. Thus, high fracturing pressures are only applied for a short duration (days), whereas subsequent gas production is conducted over the long-term (years).[31]

The following three processes during the period when hydraulic fracturing is being conducted could potentially affect fluid migration:

- Application of elevated pressures during the HF stimulation;
- Opening of induced fractures in the target formation as a result of the elevated pressures; and

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[31] The fractures induced in the target formation by HF and the open wellbore create a preferential pathway and hydraulic conditions that inherently cause any gas and fluids to migrate into the well during the production period.

- Potential interactions among HF fluid, induced fractures, and naturally occurring faults.

The effect of each of these processes on potential upward fluid migration is discussed in the following subsections.

5.2.2.1 Effect of Elevated Pressures During HF Stimulations

Elevated pressures at depth could potentially displace natural formation brines or cause HF fluid to flow outward from the target formation. However, as is the case during the Baseline Period, the extent of potential migration depends on physical constraints on fluid flow. Beyond the fracture network (*i.e.*, just beyond the fracture face or at the outermost limits of fracture propagation), changes in fluid pressure depend on rock and fluid properties that control pressure propagation. The following equation can be used to predict the distance (s) from the fracture network at which a change in fluid pressure would occur in response to HF:

$$s = \sqrt{\frac{4kt}{\alpha\mu}} \tag{5.2}$$

where all variables are the same as previously defined. For a typical HF stage lasting 1-2 hours, with k values ranging from 10^{-19} to 10^{-15} ft^2 (10^{-20} to 10^{-16} m^2) (typical values for shale; Freeze and Cherry, 1979), $\alpha = 7 \times 10^{-6}$ psi^{-1} (10^{-9} Pa^{-1}), and $\mu = 10^{-5}$ lb-f s ft^{-2} (0.0005 Pa-s) at 120 ºF (50 ºC), s ranges only from about 1 inch to 10 feet (0.017 to 2.4 m). Thus, beyond the fracture network, the pressure disturbance in bedrock is likely to be localized, extending less than ten feet from the fractures. Therefore, the short term application of HF pressures is unable to significantly affect potential upward fluid migration (if the direction of flow is even upward).

The short duration and localized pressure pulse associated with HF stimulations is in sharp contrast with the long duration and large scale depressurization brought about by hydrocarbon production. For example, Equation 5.2 predicts that pumping from an oil or gas well for 10 years would cause a pressure disturbance 16 to 1,600 ft (5 to 500 m) from the edge of the fracture network. Large scale depressurization has been observed in oil and gas reservoirs, for example, in the Frio and Woodbine formations in Texas (Kreitler *et al*., 1987, as cited in Kreitler, 1989). In the Palo Duro Basin, one analysis suggests that it would take approximately 10,000 years before pressures would recover to 90% of pre-production levels (Senger *et al*., 1987). In formations where hydrocarbon production has caused large-scale depressurization (*e.g.*, the Frio formation), it is not known how long it might take for such an expansive area to return to pre-production pressures (Kreitler, 1989).

Our analysis and these examples suggest that the HF pressure pulse is short lived and localized. Moreover hydrocarbon production (*i.e.*, pumping) will cause fluids to flow toward the fracture network over the long term, even after hydrocarbon production has ceased, thereby eliminating any short-term localized pressure effects of HF.

5.2.2.2 Effect of Induced Fractures

Others have questioned whether induced fractures during the HF process might be able to extend upward to depths of potable groundwater and thereby create a pathway for potential upward fluid migration (*e.g.*, Rozell and Reaven, 2012). An extensive data set of hydraulic fracture heights determined from microseismic monitoring was presented by Fisher and Warpinski (2011). These data indicated that hydraulic fractures have remained far below potable groundwater in a range of sedimentary basins in the US and Canada.

To extend this analysis further, we have developed a bounding relationship for maximum fracture height and compared it to measurements from over 12,000 HF stages, where fracture networks were mapped with microseismic sensors. This extensive dataset spans more than 25 sedimentary basins throughout the US and Canada (see Figure 5.1) and encompasses more broadly the range of basin characteristics encountered throughout the world.

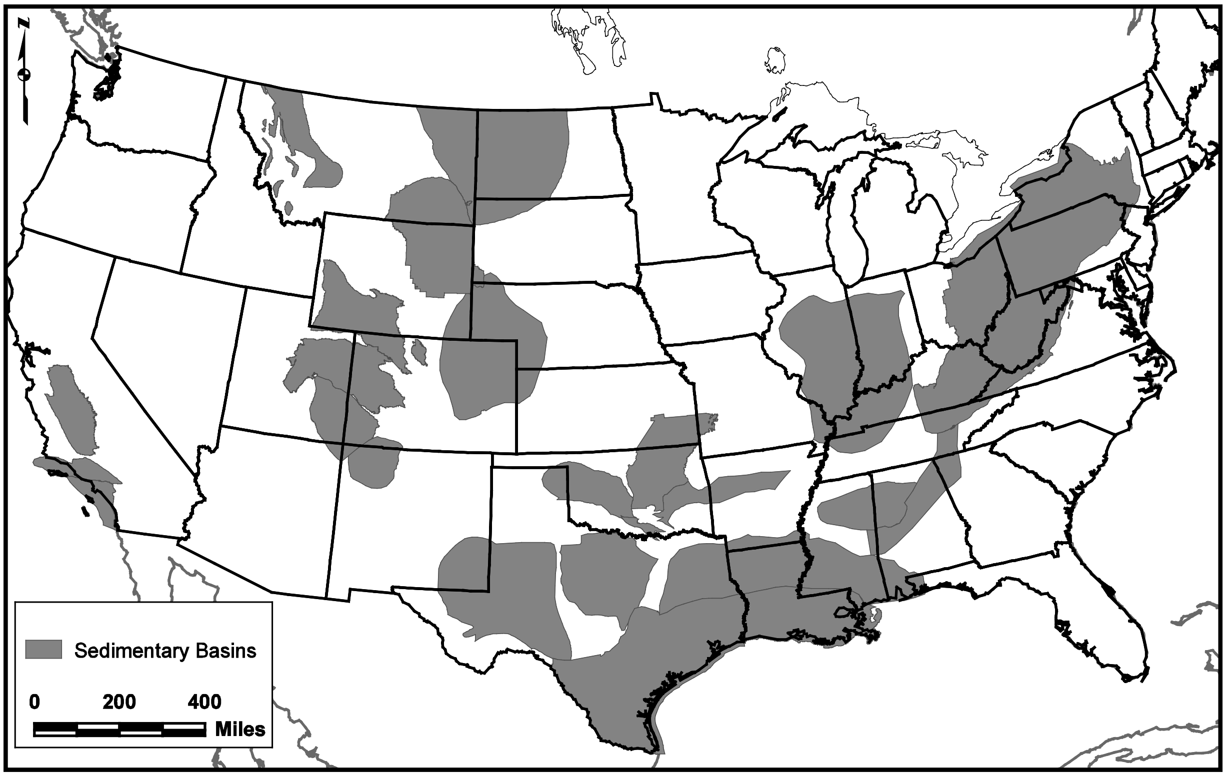

Figure 5.1 Locations of Basins with Microseismic Data (gray regions) in the US

The maximum height of an induced fracture is a function of HF fluid volume as well as physical characteristics of the target formation and HF process. The following equation describes this relationship (Flewelling *et al*., Submitted):

$$H = \left[\frac{2VE}{\pi a P_n (1-\nu^2)}\right]^{\frac{1}{3}} \tag{5.3}$$

where H is the maximum fracture height, V is the fluid volume, E is Young's modulus, a is a shape factor related to fracture geometry, P_n is the net pressure in the fracture, and ν is Poisson's ratio. This relationship represents a simplified bounding limit because it incorporates the following assumptions that lead to maximum predicted fracture heights:

- The entire volume of fluid pumped into the formation is used to open a single vertical fracture and none leaks into bedrock pore spaces;

- The entire volume of fluid pumped into the formation is used to open a single vertical fracture and none leaks into bedrock pore spaces;
- The rock being fractured is homogenous (*i.e.*, no changes in rock properties inherent to the layered structure of sedimentary basins);
- The in-situ stresses acting on the rock being fracture do not change with depth; and
- There is no energy lost to fracture the rock (analogous to hydraulic fracture propagation up a pre-existing favorably oriented joint or fault).

Predicting maximum fracture heights is important for defining an upper limit, but most induced fractures are expected to be much shorter due to a variety of natural fracture containment mechanisms that were purposefully not included in the derivation of our maximum height relationship. For example, *in situ* stress contrasts across different rock layers are common in sedimentary basins and these contrasts are widely regarded as one of the most important controls on vertical fracture growth (van Eekelen, 1982; Warpinski *et al.*, 1982). Fluid leakage into bedrock pore spaces and the propagation of complex fracture networks (*e.g.*, the propagation of multiple fractures simultaneously) also limit fracture height by detracting from the amount of fluid available to open a single tall fracture (Geertsma and De Klerk, 1969; Nordgren, 1972; Pollard and Aydin, 1988). Overall, there are many natural mechanisms that can limit fracture height and that would cause the bounding relationship (Equation 5.3) to overestimate fracture height in most cases. Instances where fractures attain the theoretical maximum limit are therefore, expected to be rare.

An examination of actual fracture data demonstrates that the theoretical fracture height limit represented by Equation 5.3 (a function that depends on the volume of pumped fluid) accurately predicts the upper limit of fracture height and, as expected, generally overestimates fracture height growth for the majority of HF stimulations monitored. Figure 5.2 shows a comparison of Equation 5.3 to an extensive dataset of fracture heights for a range of reasonable upper bound parameters (E/P_n = 30,000 and a = 1/6 for the upper curve; E/P_n = 6,000 and a = 2/3 for the lower curve; in both cases ν = 0.2) (Flewelling *et al*., in review). The tallest fracture height observed was about 2000 ft (600 m). These data also show a general decrease in fracture height with fluid volume above about 400,000 gallons (1,500 m^3). The data points at higher fluid volumes are in reservoirs where there is good fracture height containment, due to site-specific geological factors (*e.g.*, *in situ* stress contrasts that limit fracture height) (van Eekelen, 1982; Warpinski *et al.*, 1982). In these cases, pumping larger volumes results in fractures that are long (*i.e.*, grow horizontally) and short. Where this occurs, larger fluid volumes are intentionally pumped because these long fractures create greater contact with the target formation and therefore enhance production. Stated another way, higher fluid volumes do not necessarily result in greater fracture height. Instead, a variety of factors – including the design of the HF stimulation and natural constraints (*e.g.*, *in situ* stress contrasts) – combine to limit fracture height growth.

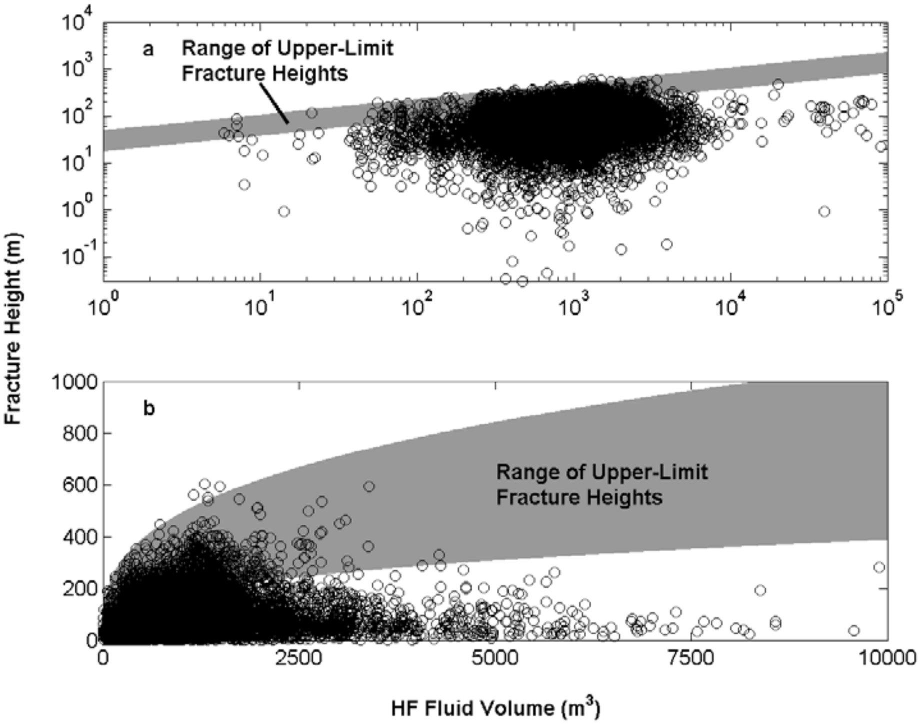

Figure 5.2 Observed Fracture Heights *versus* Hydraulic Fracture Fluid Volume in (a) Log and (b) Linear Space

Furthermore, at shallow depths, the orientation of principal stresses changes, such that fracture propagation becomes horizontal rather than vertical (Brown and Hoek, 1978; Sheorey, 1994), as demonstrated with recent tiltmeter data (Fisher and Warpinski, 2011). Given the limits on fracture height at depth imposed by fluid volume and other factors and the tendency for fractures to grow horizontally at shallow depths, it is not plausible for induced fractures to create hydraulic communication between tight oil and gas formations and shallow potable aquifers, as has been speculated by others (*e.g.*, Myers, 2012; Rozell and Reaven, 2012).

The limitations to fracture height are also apparent when looking at the depth range of induced fractures (see Figure 5.3). Note that in all cases, there is at least about 1,600 ft (500 m) of intact bedrock above the tallest fractures, however, it is more typical for fractures to be overlain by more than 3,300 ft (1,000 m) of intact bedrock. For comparison, typical depths of potable groundwater are several hundred feet or less (Focazio *et al.*, 2006). Thus, fractures have remained below the typical depths of potable groundwater for all HF stages monitored in this extensive dataset. Another important consideration is that enhanced fluid migration through fractures is limited to the extent of proppant transport. For example, investigation of HF data from the Inglewood oil field in the Los Angeles basin suggested that proppant did not reach the ends of induced fractures and thus, the outer limits of fractures would have closed back up once the pressure from the HF job was released (Cardno ENTRIX, 2012). In such cases, the maximum extent of fracture propagation may over predict the actual extent of long term hydraulic communication. Overall, these findings demonstrate that induced fractures are not a plausible pathway for upward migration of HF constituents from the target formation to overly USDWs.

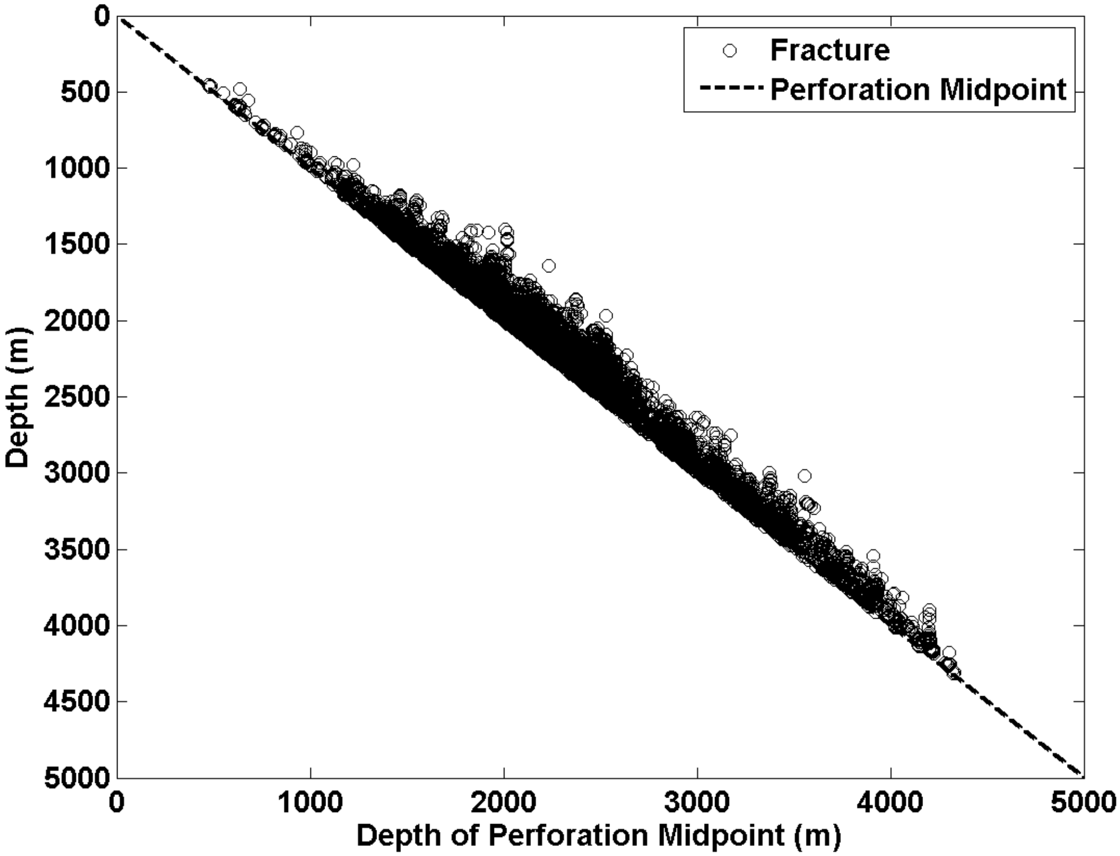

Figure 5.3 Depth Range of Perforation Midpoints and Tallest Fractures

5.2.2.3 Effect of Natural Faults

Faults are naturally occurring cracks in the earth that are naturally stressed by large-scale forces (*e.g.*, plate tectonics). Faults can range in size from very small (*e.g.*, several meters) to very large (*e.g.*, hundreds of kilometers). In some cases, large faults may cut across multiple rock layers, including oil and gas formations and overlying potable groundwater. Others have raised concerns about potential fluid migration associated with interactions between induced fractures and large naturally occurring faults (*e.g.*, Myers, 2012). As discussed below, there is no evidence that maximum fracture heights or potential upward fluid migration are controlled by natural faults.

The data presented previously in our discussion of fracture height growth can also be used to evaluate the potential role of faults in fluid migration. Fracture heights were determined by finding the difference in elevation between the perforated section of each monitored HF stage and the shallowest (*i.e.*, furthest from the wellbore) microseismic event (also called microseisms). Microseisms are small shock waves that are created when a rock cracks or a fault moves. Thus, the way in which fracture heights were determined in the previous section inherently included any potential fracture-fault interactions and the results (presented in Figure 5.2) depict the maximum height of fracture-fault interactions. As shown in Figure 5.2, the vertical extent of microseismicity is contained within the predicted fracture height limit (upper bound of the shaded area in Figure 5.2). This finding is an indication that microseismicity (including potential slip along natural faults) is localized to the fractured rock volume. Stated differently, the extent of fracture propagation controls the extent of potential fault movement, both of which have remained below potable groundwater (Figure 5.3). Others have predicted this outcome based solely on geomechanical theory (Shapiro *et al*., 2011), and therefore, there is strong evidence from physical theory and the extensive dataset presented here that natural faults do not play a significant role in upward fluid migration in the context of HF activities.

The notion of upward fluid migration, as discussed in this section, assumes that naturally occurring faults are sealed and that upward fluid migration can only occur through induced fractures and fault-slip areas. We made this assumption because significant reservoirs of oil/gas can only accumulate where faults are sealed (*i.e.*, essentially impermeable over geologic time – millions of years or longer), otherwise the buoyant fluids would have leaked upward long ago (Bradley and Powley, 1994). Not all faults are sealed, however, and other analyses have focused on potential upward migration through open, permeable faults (Myers, 2012). There is an inherent paradox regarding permeable faults and upward migration, in that hydrocarbons cannot accumulate where there are permeable pathways for buoyant oil and gas to leak upward. Thus, the occurrence of permeable faults and significant hydrocarbon accumulations are mutually exclusive. For this reason, the issue of potential upward HF fluid and brine migration is only relevant where sealed faults are present (*i.e.*, possible locations of hydrocarbon accumulation) and in these cases, fracture height growth and fault slip are the primary mechanisms to consider. As we have shown, in these situations neither fracture growth nor fault movement is capable of creating hydraulic connections between tight oil and gas formations and overlying potable groundwater.

5.2.3 Overall Evaluation of Pathway

The following conclusions can be drawn from our analysis of the fate of HF constituents pumped into the target formation:

- Tight oil and gas formations are set in very restrictive environments that inherently limit fluid migration. As a result, HF fluid pumped into the target formation – like the oil and gas and associated brines that have been trapped for millions of years – is not able to migrate far from the induced fracture network. The HF pressure pulse is only able to propagate outward from the fracture network (*e.g.*, beyond the induced fractures) on the order of meters, *i.e.*, is not large enough to affect upward fluid migration through intact bedrock.
- Monitoring data from over 12,000 HF stages indicate that fractures have remained below the depths where potable groundwater occurs (Focazio *et al*., 2006). Furthermore, the volume of HF fluid inherently limits the maximum height that a fracture can attain. A number of natural mechanisms (such as *in situ* stress contrasts) further serve to limit fracture height growth. Based on typical HF volumes, the depth range of tight oil and gas formations, and the tendency for fractures to grow horizontally rather than vertically at shallow depths, it is not physically plausible for induced fractures to create hydraulic connections between tight oil and gas formations and overlying potable aquifers.
- Potential fracture-fault interactions are limited to the fracture network and hence, ultimately controlled by HF fluid volume. Thus, the limits on fracture heights are also limits on potential fault movement. The fracture monitoring data also provide clear evidence that natural faults have not enhanced upward fluid migration beyond the fracture network and theoretical calculations (as described by Shapiro *et al*., 2011) indicate that large fault movements are not expected.

Overall, upward fluid migration from tight oil and gas formations to overlying potable aquifers is not physically plausible. Therefore this exposure pathway is not complete.

Our findings are fundamentally at odds with several studies that have hypothesized that there are potential risks associated with fluid migration from target formations (*e.g.*, Myers, 2012; Rozell and Reaven, 2012). Such unrealistic and unsupportable conclusions presented by these studies are the result of fundamentally flawed analyses. These studies fail to properly characterize the environmental setting of tight oil and gas formations, the HF process, and the physics that constrain fracture growth and fluid migration.[32] In contrast, others from around the world who have reached conclusions similar to ours when these considerations are appropriately taken into account. For example, the Royal Society and the Royal Academy of Engineering (2012) concluded that a variety of factors constrain fracture height growth and that, ultimately, the volume of fluid injected is insufficient by orders of magnitude to induce fractures that are tall enough to reach shallow potable groundwater. They also found that the upward flow of fluids from the target formation to overlying aquifers *via* natural fractures in the intervening strata is highly unlikely and that it is hard to conceive how such flow might occur given the restrictive hydrogeological conditions. These conclusions, and our own, are further supported by the observation that there is no confirmed evidence that potential fluid migration from target formations has contaminated groundwater (NYSDEC, 2011, Appendix 15; US GAO, 2012; Kresse *et al.*, 2012; NZ PCE, 2012). In fact, Kresse *et al.* (2012) recently sampled 127 domestic wells to look specifically for potential HF impacts to groundwater in the Fayetteville Shale area and determined that there were "no systematic, regional effects on shallow groundwater quality from shale gas production." Our analyses, as well as those of others, clearly demonstrate that fluid migration from target formations to shallow potable groundwater is not physically plausible and therefore, this pathway is not complete.

5.2.4 DF Calculation for Hypothetical Migration

Despite the lack of a mechanism to drive upward flow from tight oil and gas formations to overlying USDWs, we nonetheless evaluated this implausible pathway. In order to create a hypothetical scenario of upward flow, we applied extreme (high) values of the upward head gradient to rock layers overlying tight oil and gas formations. Under this assumption and by taking into consideration the low permeability of rocks associated with conditions of upward flow, we estimated the DF for this hypothetical pathway (see Appendix B for details). Using an approach analogous to the groundwater and surface water dilution assessments, the concentration of HF constituents in an aquifer (C_{gw}) under the influence of upward seepage from tight oil and gas formations is given by the following equation:

$$C_{gw} = \frac{C_{OG}}{DF_{OG}}$$

Where DF_{OG} is the dilution factor for upward migration from the target oil and gas formation and C_{OG} is the concentration of HF constituents in the fracture network. The dilution factor (DF_{OG}) should be comprised of two components—one to account for dilution of constituents into the bedrock pore space and another to account for mixing based on the hypothetical rate of upward flow (from the target formation) relative to the groundwater flow rate in the overlying aquifer.[33] Note, however, that we have only accounted for the latter to keep this hypothetical analysis as simple as possible. As indicated below, the DF_{OG} values for this very conservative (*i.e.*, health protective) approach are extremely large and inclusion of other attenuation processes (*e.g.*, dilution into bedrock pore space, chemical degradation, adsorption) would lead to even larger DF_{OG} values.

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[32] The flaws in the modeling undertaken by Myers and others are discussed further in Appendix E.

[33] Note that this simplified (conservative) analysis does not account for additional dilution that would occur in the event multiple water-bearing zones intervene between the target formation and the shallow drinking water zone.

As described in Appendix B, the 95th percentile (*i.e.*, low end) value of DF_{OG} thus derived is 9,800,000. Considering that this DF is based on extreme assumptions (*e.g.*, assumed upward flow and high-end gradient) and does not account for dilution resulting from mixing of HF constituents with bedrock porewater, the DF is expected to be orders of magnitude higher than this computed value. In comparison to the surface spill scenarios, dilution for upward migration from the target formation is expected to be significantly greater (if upward migration occurs at all). Because greater dilution connotes lower potential risk, the risks for the hypothetical upward migration scenario would be orders of magnitude less than the surface spill scenario discussed below, and therefore, were not explicitly quantified in our risk analysis.

In summary, we have analyzed the potential for HF additive migration from tight oil and gas formations to overlying USDWs. Based on this analysis, we have concluded that the pathway is not complete and therefore should not be considered further in this human health evaluation. Although the exposure pathway is not complete, we nevertheless calculated DF values for this hypothetical upward migration scenario. These calculations show that even if upward migration were to occur, the DF values would be extremely high such that even under this implausible pathway, upward migration of HF constituents would pose at most *de minimis* risks to USDWs.

5.3 Surface Spills

In order to assess the potential for human health impacts associated with drinking water as a result of surface spills of fluids containing HF chemicals, we determine the concentrations at which the constituents of these fluids might be found in drinking water as a result of a spill ("exposure point concentrations") and then compare those concentrations to concentration levels at which adverse health effects would start to become a concern (the derivation of these "risk-based concentrations" is discussed in Section 6). We also took into consideration the likelihood that a spill of fluids containing HF constituents (*i.e.*, HF fluids or flowback fluid) (sometimes referred to herein as "HF spills") would occur in the first place.

In order to determine the exposure point concentrations at which constituents might be found in drinking water (either surface water or groundwater depending on the pathway being evaluated) as a result of a spill, we began with the concentrations of these chemicals in the HF fluid or flowback fluid (discussed in Section 4.2). However, the concentration of constituents in the fluid spilled would be reduced as a result of dilution in water or soil as it moves through the environment to reach a drinking water source. The extent of this dilution would vary depending on the conditions accompanying the spill. Therefore, a key part of our analysis was determining the anticipated extent of dilution of HF fluid or flowback fluid constituent concentrations (expressed as "dilution factors" or "DFs").

5.3.1 Overview of Probabilistic Approach for Evaluating Potential Impacts of Surface Spills

Given the national scope of oil and gas production using HF technologies, our analysis adopted methods that allow for assessing possible risks associated with HF spills spanning a wide range of spill volumes and environmental conditions. For example, depending on differences in climate and topography, regional streamflow varies substantially. In the event of surface spills of HF fluids or flowback fluid, such regional variations in streamflow would be expected to lead to variations in the possible constituent concentrations potentially impacting surface water – areas with low flows would likely experience higher constituent concentrations (less dilution) than areas with higher flows (more dilution). Similarly, differences in local groundwater conditions (*e.g.*, depth to groundwater, differences in aquifer properties, *etc.*) will give rise to differences in the impacts of surface spills possibly impacting groundwater resources used for drinking water.

Given this natural environmental variability, the results from "deterministic," or site-specific, assessment approaches can be constrained by the fact that the results can be difficult to extrapolate more broadly beyond the specific conditions evaluated. To address this limitation, we have adopted "probabilistic" methods that incorporate the wide range of environmental variability that occurs in areas with active oil and gas plays. In a probabilistic analysis, the range of environmental conditions is defined not by single "deterministic" variables, but instead is defined in terms of a probability distribution (*i.e.*, range of values and their associated likelihoods of occurring) of possible conditions (environmental variables). Assessing the possible drinking water impacts associated with HF spills in a probabilistic framework is accomplished by selecting repeated "samples" from the range of environmental conditions represented by the underlying probability distributions of environmental variables. These "samples" represent combinations of environmental conditions that might be encountered in nature. By assessing a large number of "samples," the probabilistic analysis inherently assesses the full range of environmental conditions.

In our probabilistic analysis, key variables for which we have defined probability distributions include the following:

- HF spill volume;
- Surface water streamflow;
- Depth to groundwater; and
- Aquifer characteristics.

Our analysis involved a commonly used probabilistic sampling method termed Monte Carlo sampling. The Monte Carlo sampling method involves selecting repeated samples (randomly) from the underlying probability distributions that define environmental variables affecting chemical transport/dilution, and then using these random samples to estimate the resulting impacts (*e.g.*, the resulting constituent concentration in either surface water or groundwater). This process is repeated many times (we selected a million samples to determine each distribution) to generate the full range of possible combinations of outcomes spanning the full range of the input variables.

The figure below illustrates the Monte Carlo process. Samples from the probability distributions of "input variables" (these would include variables such as spill volume, streamflow rate, *etc.*) are selected and used to assess the distribution of the "output" variable of interest (*e.g.*, dilution factors, risk estimates).

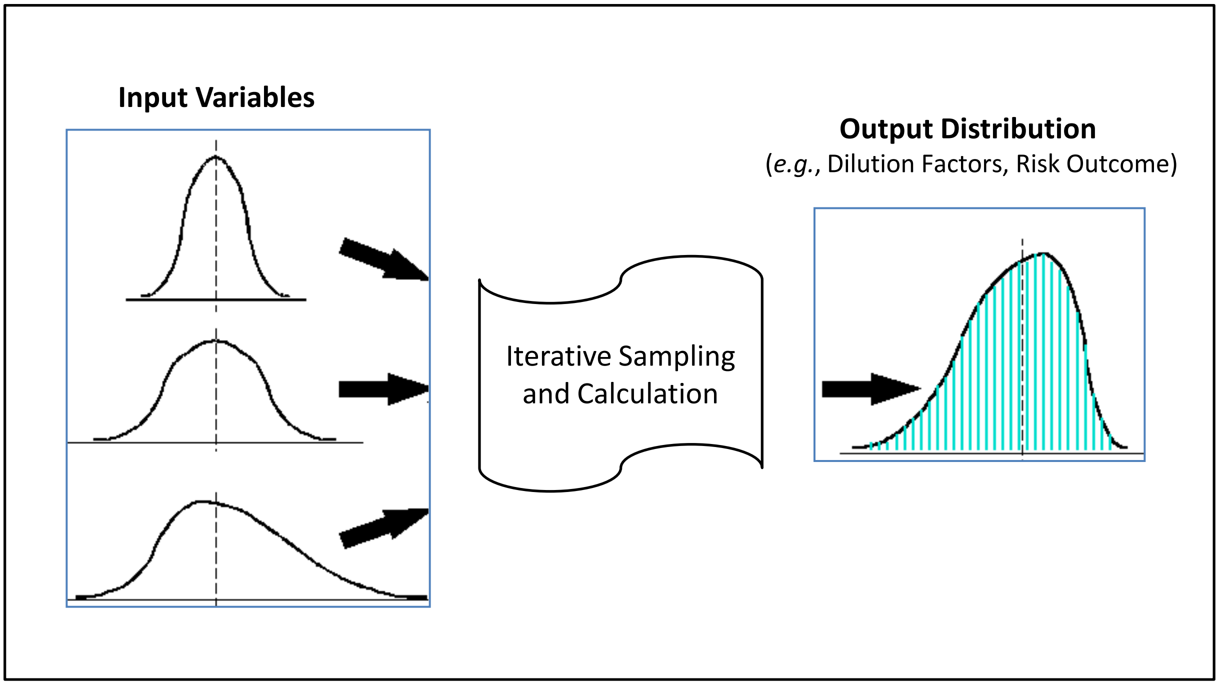

Figure 5.4 Illustration of Monte Carlo Sampling Method Used to Develop a Distribution of Outcomes (*e.g.*, DF values) to Assess Health Risks of HF Spills

In our analysis, we developed distributions for key variables such as spill volume and stream flow by using various data sources such as US EPA and state databases. Using this Monte Carlo approach, we derived distributions of dilution factors associated with possible spills of HF fluids or flowback fluids. We then applied these DF distributions to the concentrations of constituents in HF fluids and flowback fluids to determine potential constituent concentrations in surface waters and groundwater under a variety of conditions. Finally, we assessed the likelihood of possible human health impacts by comparing the range of predicted HF constituent concentrations in surface water and groundwater with "risk based concentrations" (RBCs) for drinking water. We also undertook an assessment of the likelihood that a spill of fluids containing HF chemicals (either HF fluids or flowback fluids) would occur at a given well site.

Our analysis evaluated a wide range of HF constituents found in 12 typical HESI HF fluid systems used to develop oil and gas resources in tight formations; these constituents (approximately 100) are listed in Table 4.3. In addition, we extended our analysis to constituents that have been found in flowback fluid from wells that have been hydraulically fractured even though many of these constituents are not associated with HF fluids but instead are found naturally in target formations (Table 4.4).

5.3.2 Surface Spill Volumes

The possible range in volumes of surface spills is one of the important input variables in our analysis. Several states, including West Virginia (WV), New Mexico (NM), and Colorado (CO), have compiled information relating to spill incidences during oil and gas exploration and production (US EPA, 2012b). Our review of the information compiled in these databases indicates that the majority of the information appears to be related to a wide range of oil extraction activities in general, including spills relating to distribution and storage facilities, while only a subset of the information appears to be pertinent to HF operations or even to well pad operations more generally.[34] As a result, use of these databases in our analysis could be misleading.

A more relevant database for purposes of our analysis is available from the Pennsylvania Department of Environmental Protection (PADEP) Office of Oil and Gas Management (OGM), which has compiled information specifically relating to spills during HF activities.[35] Spills associated with HF activities are reported in the PADEP "Oil and Gas Compliance Report" database, which is "designed to show all inspections that resulted in a violation or enforcement action assigned by the Oil and Gas program."[36] We downloaded all of the inspection data for "unconventional" wells. From this information, we compiled all entries for inspections from 2009 to up through April, 2013 that indicated a fluid spill (with an associated volume, typically reported in gallons or barrels, but sometimes volumes as small as a cup or a quart). A total of 231 inspections reported spills from "unconventional" systems. The distribution of spills (in gallons) fit a lognormal distribution with a $\log_{10}$ mean of 1.58 (*i.e.*, median value of 38 gallons), and $\log_{10}$ standard deviation of 1.15. A summary of the spill volumes associated with different probabilities (percentiles) for these lognormally distributed spill data is provided below.[37]

Table 5.1 Spill Volume Percentiles

Percentile	Spill Volume (gal)
10%	1
25%	6
50%	38
75%	230
90%	1,152
95%	2,999

Note:
Based on 1 million Monte Carlo samples.

The foregoing information provides a reasonable means to estimate the distribution of HF spill volumes *if a spill occurs*. The PADEP OGM also has compiled information on the number of wells installed each year. As summarized below, for the period 2009 through 2012, a total of 5,543 wells were installed in the Marcellus in Pennsylvania. For this same period, there were 185 spills reported (for unconventional installations).[38] This suggests a spill frequency of 3.3% over this 4-year period.[39]

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[34] Other than occasional "notes" associated with individual incidents, there are no fields in the respective databases that distinguish whether the spill was HF-related or not.

[35] http://www.portal.state.pa.us/portal/server.pt/community/office_of_oil_and_gas_management/20291

[36] http://www.portal.state.pa.us/portal/server.pt/community/oil_and_gas_compliance_report/20299

[37] The maximum spill reported was 7,980 gallons (Dimock, PA), which is covered by our spill distribution. In fact, because the distribution is unbounded at the upper tail, the largest spill volumes included in our analysis were well over 100,000 gallons, such that the range included could even account for such events as a wellhead blowout.

[38] A total of 231 spills were identified in the PADEP database. A total of 46 of these spills were reported in 2013, however, there was no corresponding information on the number of wells installed in 2013. We therefore relied on the number of spills (185) and number of installed wells from 2009 to 2012 to calculate spill frequency.

[39] The way we have conducted this part of the analysis may result in an undercounting of the number of "unconventional" wells drilled to which the number of spills at "unconventional" well sites should be compared, leading to a potential overestimation of the rate of spills at these well sites.

Table 5.2 Summary of PADEP Oil and Gas Wells Drilled and Spills

Formation/Type	2009[a]	2010[a]	2011[b]	2012[c,d]	Totals
Non Marcellus	1,765	1,397	954	1,025	5,141
Marcellus	795	1,446	1,937	1,365	5,543
Total	**2,560**	**2,843**	**2,891**	**2,390**	**10,684**
Spills (unconventional wells)	28	33	45	79	185
Spills (relative to Marcellus wells)	3.5%	2.3%	2.3%	5.8%	3.3%

Notes:
[a] PADEP, 2011.
[b] PADEP, 2012.
[c] PADEP, 2013.
[d] 2012 data was reported as "conventional" (1,025 wells) and "unconventional" (1,365 wells) (PADEP, 2013).

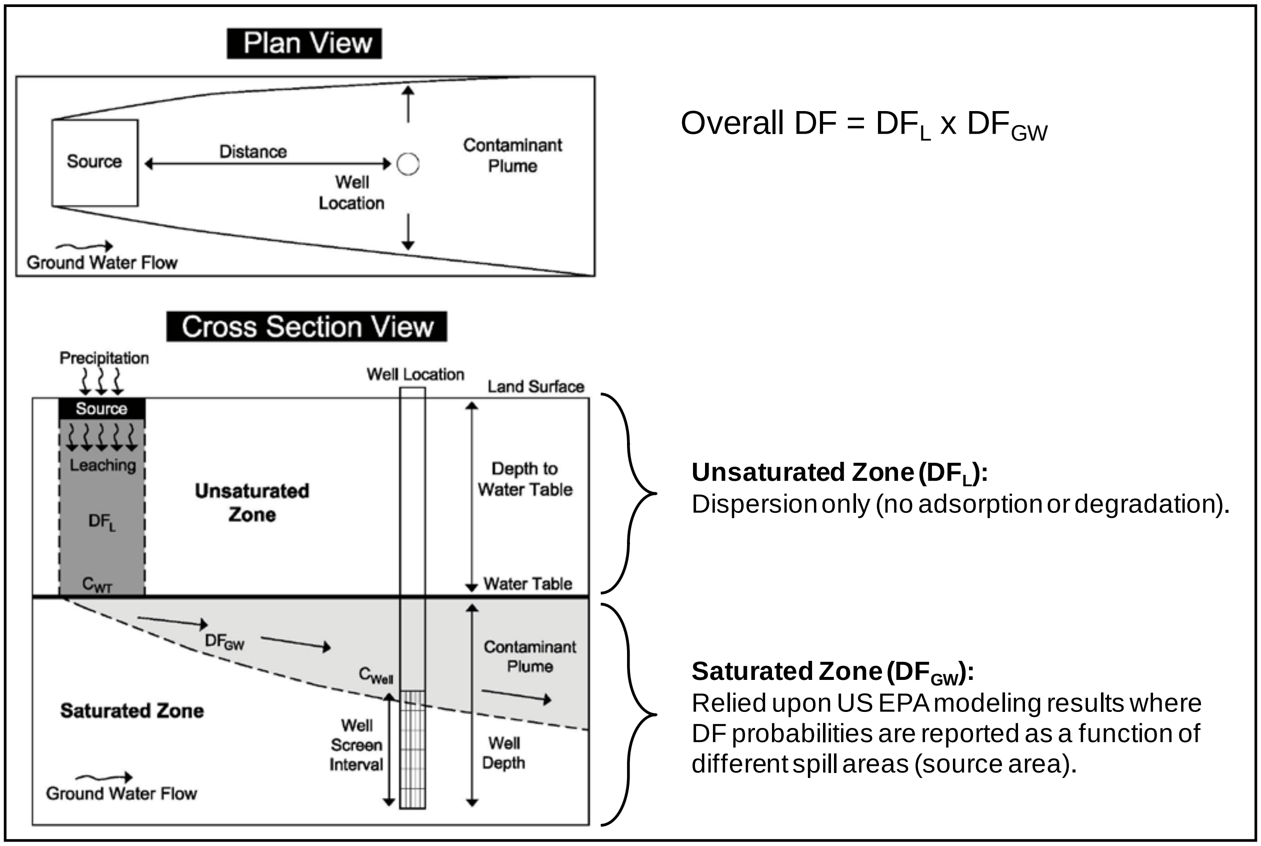
Given that the PADEP database includes spills of materials unrelated to HF fluids (*e.g.*, hydraulic oil), this estimate of spill frequency over predicts spills of HF fluids. Nevertheless, for the purposes of our risk analysis, we have evaluated potential risks based on two scenarios: a 3.3% spill probability as well as a 6.6% spill probability, or in other words assuming hypothetically spills occur at double the frequency reported in the PADEP data. These spill probabilities are considered conservative bounds for our analysis.

If HF constituents in hypothetically uncontrolled surface spills migrate overland *via* surface runoff/erosion, they potentially could affect adjacent surface water resources under certain circumstances. In addition, HF constituents in surface spills could leach through the unsaturated zone (soil above the groundwater table) and potentially affect shallow aquifers, a potential source of drinking water. For our exposure and risk analysis, we evaluated two bounding sets of hypothetical conditions, assessing the implications if: (1) 100% of the surface spill leaches to groundwater; and (2) 100% of the surface spill impacts surface water. These hypothetical scenarios bound the possible fate of surface spills, because the entirety of any given spill could not migrate to both groundwater and surface water (as our worst case analysis assumes), and therefore this approach, adopted solely for the purposes of this study, is considered quite conservative. More likely, even if spills escaped containment measures at the well pad, a portion of the spilled fluid would almost certainly be retained in the soil on or adjacent to the pad such that only a portion would potentially reach any nearby surface water bodies. Similarly, it is unlikely that 100% of the volume of a spill would leach to groundwater, as we have conservatively assumed.

5.3.3 Surface Spill Impacts to Groundwater

In this section, we set forth the approach we used to evaluate the potential impacts to shallow aquifers in the event 100% of the surface spill migrates to the groundwater. We adopt fundamental fate and transport methods widely used among scientists and US EPA/state regulatory agencies for establishing health-based soil and groundwater cleanup criteria at hazardous waste sites (*e.g.*, US EPA, 1996).

As noted in Section 4, our analysis focuses on the potential impacts to a domestic well used for drinking water. The migration of HF fluid and flowback fluid constituents from surface spills and their potential impacts to a drinking water well can be broken down into a two-step process: (1) constituents must first leach downward through the soil in the unsaturated zone to the top of the water table (groundwater aquifer or saturated zone); and (2) constituents must then migrate laterally in the saturated zone to a downgradient drinking water well (see the cross section view in Figure 5.5). During both steps in this process, the concentrations of chemicals in the spill fluids are diluted due to dispersion.



Overall DF = DF_L x DF_{GW}

Unsaturated Zone (DF_L):
Dispersion only (no adsorption or degradation).

Saturated Zone (DF_{GW}):
Relied upon US EPA modeling results where DF probabilities are reported as a function of different spill areas (source area).

Figure 5.5 Schematic of Spill to Groundwater Pathway

This step-wise process results in a chemical concentration at the drinking water well that is a function of the dilution in both the unsaturated zone and the saturated (groundwater) zone, as expressed mathematically below:

Step 1: Unsaturated Zone Leaching and Dilution at Water Table

$$C_{WT} = \frac{C_{HF}}{DF_L} \tag{5.4}$$

Step 2: Saturated Zone (Groundwater) and Dilution at Drinking Water Well

$$C_{well} = \frac{C_{WT}}{DF_{GW}} \tag{5.5}$$

Step 1 and Step 2 Combined

$$C_{well} = \frac{C_{HF}}{DF_L \times DF_{GW}} \tag{5.6}$$

where:

C_{well} = Concentration of HF fluid or flowback fluid constituent at well (µg/L)
C_{HF} = Concentration of constituent in fluid spilled at the surface (µg/L)

C_{WT} = Concentration of constituent entering water table at the bottom of the unsaturated zone (µg/L)
DF_L = Dilution factor due to leaching from the soil surface to the water table (unsaturated zone)
DF_{GW} = Dilution factor of leachate into groundwater (saturated zone)

Thus, determining the concentration at which a chemical might be found in a drinking water well as a result of a spill requires a determination of how much the spilled fluid is diluted at each step, which is addressed through the calculation of appropriate dilution factors ("DFs") for both the unsaturated zone and the saturated zone.

It is important to emphasize at this point that we adopted two simplifying assumptions in our analysis that are likely to over predict (lower DFs) the potential impacts to groundwater:

- Chemical adsorption is not considered, and;
- No degradation of HF constituents is included.

These are very conservative assumptions, as many chemicals adsorb to soil and biodegrade in the environment.[40] Both of these natural phenomena reduce chemical mobility and/or persistence in the soil and groundwater.

Determining the unsaturated and saturated zone DFs – and therefore the ultimate concentration of chemicals leaching from a surface spill into an underlying aquifer, and subsequently impacting a downgradient well – depends on a variety of parameters, including:

- Aerial extent of possible spills;
- Depth to groundwater;
- Groundwater flow rates;
- Drinking water well depth, and;
- Distance to well.

Our derivation of the respective unsaturated zone (DF_L) and saturated zone (DF_{gw}) dilution factors draws upon Monte Carlo modeling efforts and information compiled by US EPA (1996).[41] In establishing "soil screening levels" (SSLs), which represent chemical concentrations in soil deemed not to cause adverse impacts to groundwater, the Agency compiled a database of regional hydrogeological parameters relating to depth to groundwater resources and groundwater flow rates. The Agency itself used Monte Carlo modeling methods to evaluate the saturated zone dilution factors for chemicals that potentially could migrate from soils (and landfills) to nearby wells using a range of parameters governing groundwater transport. Using this Monte Carlo modeling framework, the US EPA derived a probability distribution of DFs (based on spill area and the regional variations in hydrogeologic factors). Drawing upon this

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[40] For example, alcohols (*e.g.*, methanol, propargyl alcohol, isopropanol) break down relatively rapidly in soil or groundwater. Hydrophobic organic compounds and most heavy metals are expected to be adsorbed within the target formation (or in soils in the event of a spill), thus greatly retarding their transport in the subsurface.

[41] US EPA used the term groundwater "dilution attenuation factor" (DAF). We use the term "dilution factor" because in our analysis, as was also the case in US EPA's DAF development, we have not accounted for "attenuation" processes such as chemical-soil adsorption, or biodegradation. These attenuation processes would further reduce the chemical concentrations in the environment in the event of a spill (*e.g.*, leading to larger dilution factors if included).

information, we describe the methods we used to derive the unsaturated zone and saturated zone DFs below.

5.3.3.1 Leachate Migration to Groundwater (Unsaturated Zone)

Assuming that no spill mitigation measures are implemented, a surface spill would give rise to an initial zone of surface soil contamination in the area affected by the spill. That is, chemicals in HF fluids would spread out over the area of the spill and potentially seep into the surface soil. The chemicals initially retained in the surface soil zone could subsequently leach to groundwater.

Chemical migration in soil *via* leaching (*e.g.,* leaching in the unsaturated zone) can be readily modeled using the principle of "advection and dispersion." The advection-dispersion equation (ADE) is a mathematical model describing the movement of chemicals in soil as a function of the flow of water and chemical dispersion. We present in Appendix C a mathematical description of the one dimensional ADE used in our analysis to derive the dilution factor for the unsaturated zone (DF_L).

As chemicals leach through the unsaturated zone (soil), the chemical "pulse" resulting from a surface spill gradually moves downward in the soil profile over time with percolating water. As chemicals move downward, chemical dispersion occurs within the soil profile due to variability in the rate of water movement through pores of different sizes and configurations within the soil profile. This dispersion reduces the concentration of the "chemical pulse" at any given point within the soil profile as illustrated in Figure 5.6. This figure shows the chemical concentration profile in the unsaturated zone at two different time periods following a spill – 50 days and 500 days after a spill (*e.g.*, this shows the "pulse" at two different periods in time, and the concentration at 500 days is lower than the concentration at 50 days). Note that the chemical concentration profiles shown in this figure represent the "normalized" concentration, which is the concentration at any particular time after a release, relative to the initial concentration of the chemical immediately following a release before any leaching occurs.[42]

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[42] Mathematically this normalized concentration is expressed as C/Co, where Co is the initial concentration at time t = 0 (immediately following a spill). Immediately following a spill, before any leaching has occurred, the ratio C(t)/C(t = 0) equals 1 (no dilution).

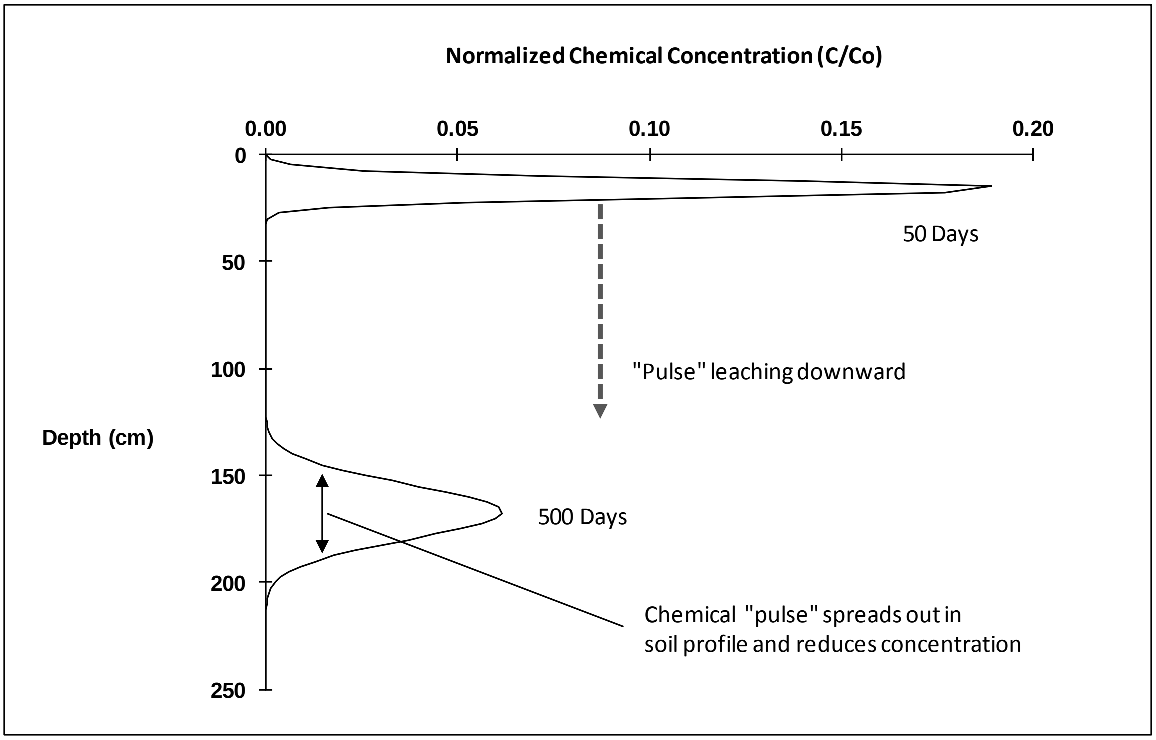

Figure 5.6 Example of Chemical Profile and Dilution in Unsaturated Zone

The unsaturated zone leaching dilution factor (DF_L), can be expressed by rearranging Equation 5.4 presented earlier:

$$DF_L = \frac{C_{HF}}{C_{WT}} \qquad (5\text{-}7)$$

The ratio C_{HF}/C_{WT}, is the initial concentration when spilled ($C_{HF,}$ or C_o in the ADE) relative to the chemical concentration at the bottom of the unsaturated zone entering the water table ($C_{WT,}$ or C(x,t) in the ADE where x is set to the depth of the water table). The derivation of the leaching dilution factor is presented in Appendix C.

As described in Appendix C, we calculate the unsaturated zone DF_L for the peak concentration, or in other words when the maximum concentration intercepts the water table. This is a conservative approach as it gives the lowest unsaturated zone DF. The DF_L for the peak concentration at the water table is a function of three variables:

1. The initial depth of contamination at the surface (proportional to initial spill depth),
2. The depth to the water table, and,
3. The dispersivity coefficient (a measure of hydrodynamic dispersion).

The initial depth of surface soil contamination was modeled based on the simulated spill volume (*e.g.*, each Monte Carlo iteration), and the depth or "thickness" of the liquid initially spilled. Immediately after a spill occurs, depending on the volume of liquid, the liquid may "pond" on the surface. For our analysis, we applied a uniform probability distribution for the initial thickness of this ponded liquid resulting from a spill ranging from 1 cm to 5 cm (approximately 0.4 inches to 2 inches).[43] A uniform distribution assigns equal probability to the possible range of spill thickness values between these two endpoints.

The depth to groundwater random variable was modeled based on a probability distribution derived from a database of nation-wide data developed by US EPA (1996). The dispersivity coefficient was modeled as a function of the depth to the water table (*e.g.*, the migration "length scale") as has been reported in the scientific literature. Appendix C provides a further discussion of these variables.[44]

As summarized later in this section, the Monte Carlo sampling approach combines these three random variables as parameters in the ADE to develop the probability distribution of the unsaturated zone DF.

5.3.3.2 Groundwater Dilution (Saturated Zone)

Just as dilution occurs in the unsaturated zone, chemicals are further diluted when leachate from the unsaturated zone enters the aquifer (the saturated zone) and mixes with groundwater. The chemical concentration in groundwater at a drinking water well that is downgradient (in the flow path) from a surface spill, is given by Equation 5.5 presented earlier:

$$C_{gw} = \frac{C_{WT}}{DF_{GW}}$$

where:

C_{gw} = Chemical concentration in groundwater at a drinking water well (μg/L)
C_{wt} = Chemical concentration in leachate at the water table just before entering groundwater (μg/L)
DF_{GW} = Groundwater dilution factor (unitless)

We developed probability distributions of groundwater (saturated zone) DF values based on DFs derived by US EPA (1996) in its Soil Screening Guidance. We chose this approach because the US EPA conducted an extensive groundwater modeling effort, using Monte Carlo methods to develop a range of groundwater (saturated zone) DF values that are considered by the US EPA sufficiently robust to be applied nation-wide. US EPA adopted a number of conservative assumptions in deriving the DF values:

- The Agency assumed an infinite (*i.e.*, continuous, unending) chemical source, with no chemical adsorption to soil, and no chemical degradation. In fact, as noted above many of the HF and flowback fluid constituents adsorb strongly and/or biodegrade. Excluding these processes significantly underestimates dilution and attenuation of these chemicals.
- The nearest drinking water wells were assumed to be as close as the downgradient edge of the spill footprint (*e.g.*, no "separation" or "setback" from the hypothetical spill), and located laterally within the dimensions of the spill (ignoring scenarios where a well is located beyond the edge of the spill and thus a chemical plume could "bypass" a well in such a scenario).

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[43] The spill area, which is needed to select the groundwater DF from the distribution developed by US EPA, is simply the spill volume divided by the initial ponded depth of the spill (*e.g.*, Volume = Area × Depth, or Area = Volume ÷ Depth).

[44] Interestingly, the unsaturated zone peak DF is independent of the infiltration rate. This is a consequence of the fact that we have conservatively calculated the DF when the peak concentration intercepts the water table. The infiltration rate simply influences the time required for the peak to arrive at the water table, but not the concentration.

- Wells were assumed to be screened within 15 to 300 feet beneath the water table, thus encompassing the unlikely possibility of very shallow groundwater use and little dilution (*i.e.*, a drinking water well drawing water from a depth only 15 feet below the water table). Conversely, in the more typical scenario involving a drinking water well drawing water from a greater depth,[45] the chemical plume would have to migrate deeper within the aquifer potentially across one or more confining layers to impact a drinking water well, resulting in greater chemical dilution.[46]

The US EPA derived DF values that vary as a function of source area. In US EPA's Monte Carlo groundwater modeling effort, variable values of infiltration rates, depths of drinking water wells, and saturated zone parameters (*e.g.*, groundwater flow rate, thickness of aquifer) were all modeled by US EPA. The Agency developed DF values for spill areas ranging from 0.02 acres up to 60 acres; DF values derived by US EPA for chemical source areas ranging from 0.1 acres up to approximately 2 acres are summarized in Table 5.3. As an example, the 90th percentile DF value of 60 for a 1.1 acre source area indicates that the groundwater dilution will be 60 *or greater* in at least 90 percent of cases involving a spill covering 1.1 acres; the 95th percentile DF is 3.1, meaning that the DF is 3.1 or more in 95 percent of the cases modeled by US EPA for a 1.1 acre source area.[47]

Table 5.3 Summary of Saturated Zone DF Values Derived by US EPA

Chemical Source Area (acres)	85th Percentile DF	90th Percentile DF	95th Percentile DF
0.1	55,400	2,740	44
1.1	668	60	3.1
1.8	350	33	2.3

Source: US EPA (1996, Table 5).

The US EPA reported only three percentiles (85th, 90th, and 95th) of the distribution of all the DFs generated by its modeling efforts. In order to develop the complete probability distribution from this information, we extrapolated from these three percentiles. Using the methods described in Appendix C (Section C.2), we derived the mean and standard deviation for the groundwater DF as a function of spill area. As the summary in Table 5.4 below indicates, our method of developing a complete distribution reproduced the US EPA reported percentiles with reasonable agreement.

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[45] As indicated by the Water Systems Council (WSC), most wells for household use range from 100 to 500 feet deep (WSC, 2003).

[46] Because the US EPA adopted an infinite source and no chemical adsorption to soil, the groundwater DFs the Agency derived implicitly exclude any dispersion/dilution within the unsaturated zone. Thus, the DF values represent solely the effects of mixing and dilution within the saturated aquifer, and do not account for dilution of a finite source within the unsaturated (soil) zone due to dispersion. As discussed above, in order to provide a more realistic estimate of constituent concentrations that might reach a drinking water well, we have taken into account some degree of dilution in the unsaturated zone, although our model still underestimates the impact that migration through the unsaturated zone would have on constituent concentrations because it ignores the attenuation that would occur as a result of adsorption and degradation.

[47] Note that while US EPA reports the DF values as "high end" percentiles of the probability distribution (*e.g.*, 85th, 90th and 95th percentiles), these statistics actually represent conservative DF values whereby the majority of values modeled by US EPA exceed these values. This is self evident from the fact that the 85th percentile DF values are larger than the 90th and 95th percentile values. Thus, the reported "90th percentile" values in fact represent the lowest 10th percentile DF value within the cumulative probability distribution function derived by US EPA – 90 percent of the DFs are larger than the reported 90th percentile.

Table 5.4 Comparison of Calculated Groundwater DFs with US EPA-reported DAF Percentiles

Percentile	Source Area = 0.02 acres		Source Area = 0.11 acres		Source Area = 1.1 acres		Source Area = 1.8 acres	
	US EPA Reported DAF	Calculated DF	US EPA Reported DAF	Calculated DF	US EPA Reported DAF	Calculated DF	US EPA Reported DAF	Calculated DF
10th	--	1.5E+23	--	6.4E+16	--	3.2E+12	--	8.4E+11
25th	--	9.6E+18	--	4.3E+13	--	9.4E+09	--	2.9E+09
50th	--	2.1E+14	--	1.3E+10	--	1.4E+07	--	5.5E+06
85th	14,200,000	13,757,122	55,400	51,282	668	689	350	353
90th	209,000	276,654	2,740	2,699	60	66	33	37
95th	946	847	44	35	3.1	3.0	2.3	2.2

5.3.3.3 Combined Leaching and Groundwater Dilution

The overall dilution factor due to leaching through the unsaturated zone and mixing with groundwater in the saturated zone is simply:

$$\text{Overall DF} = DF_L \times DF_{GW}$$

Based on the spill volume distribution described earlier, and the foregoing methods for developing groundwater pathway DFs, we derived a distribution of groundwater and unsaturated zone DFs – which combined to make an overall DF – in the event a surface spill occurs. The Monte Carlo sampling process for developing the distribution of DFs is shown schematically below (Figure 5.7). Random samples were successively drawn from the underlying probability distributions to generate spill volumes and parameters necessary to calculate each DF. Each iteration of random samples generated a single value of the calculated DF_L and DF_{gw}, as well as their product, or the overall DF for the groundwater pathway. Based on repeated samples (1 million total) a probability distribution of DF values was generated that considers the wide range of environmental conditions across the entire country. A summary of selected percentiles of this groundwater pathway DF distribution is given in Table 5.5.

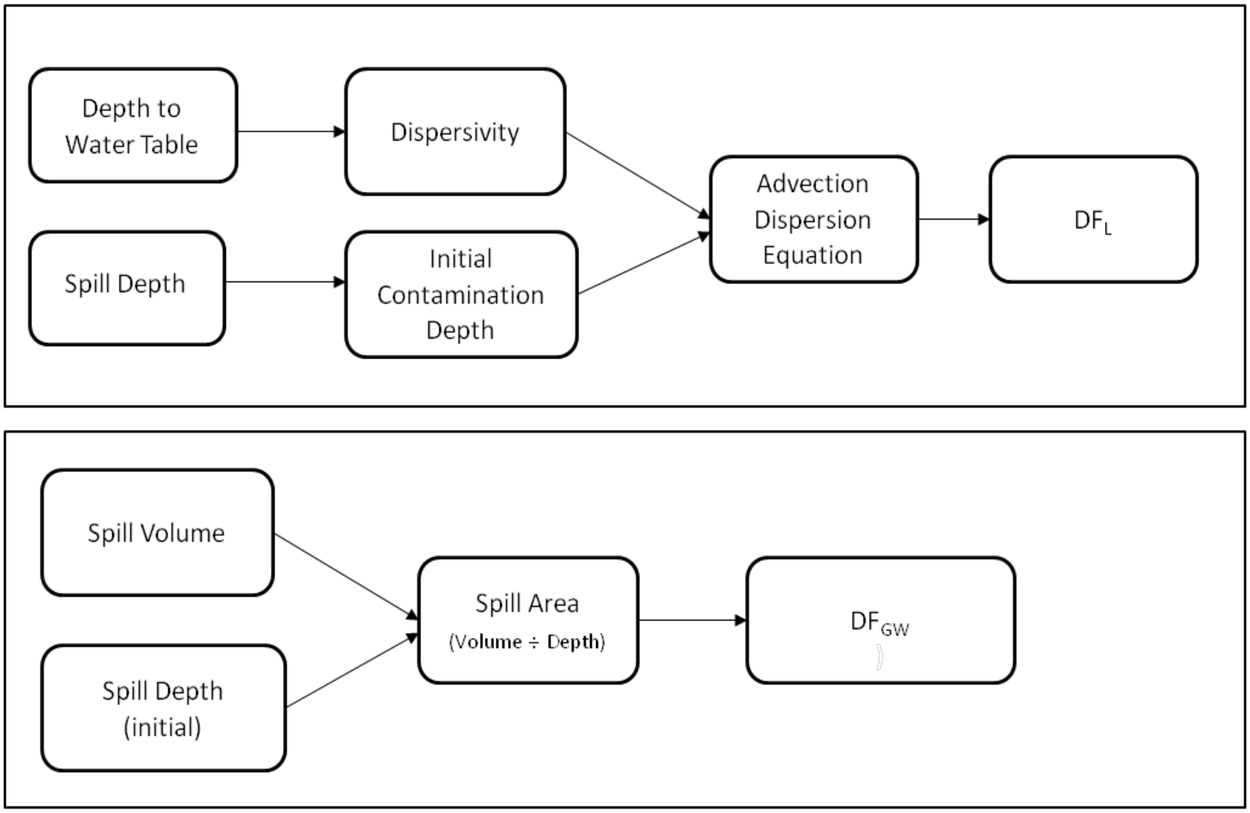

Figure 5.7 Schematic of Groundwater Pathway DF Monte Carlo Sampling

Table 5.5 Summary of Spill to Groundwater DFs

Percentile	Unsaturated Zone (DF_L)	Saturated Zone (DF_{gw})	Overall DF
10%	385	5.8×10^{74}	5.7×10^{76}
25%	204	5.3×10^{45}	5.4×10^{47}
50%	101	1.1×10^{26}	1.1×10^{28}
75%	51	3.0×10^{14}	3.2×10^{16}
90%	28	4.9×10^{7}	5.3×10^{9}
95%	19	17,788	1.9×10^{6}

Notes:

Based on 1 million Monte Carlo samples.

For any given Monte Carlo sample, the overall DF is the product of the respective values of the unsaturated and saturated zone DFs. However, given that independent random variables govern each component DF, the percentiles of the overall DF are not given by the product of the respective unsaturated- and saturated-zone DFs at the same percentiles.

The saturated zone DFs presented above are not directly comparable to the US EPA-reported values (US EPA, 1996), since the US EPA percentiles are associated with a corresponding spill area, whereas the above values correspond to a range of spill areas, which are a function of the potential spill volume.

When interpreting the percentiles associated with any particular DF, the percentile is the cumulative probability that the DF will be equal to, or greater than, the reported value.[48] For example the 50th percentile unsaturated zone DF is 101. This means that the unsaturated zone DF was 101, or greater, in 50% of the Monte Carlo simulations. The 95th percentile DF_L (19) means that the DF was 19 or greater, in 95% of the simulations, and, conversely, the DF_L was less than 19 in 5% of the simulations. The groundwater DF_{GW}, and overall groundwater pathway DF values have a similar interpretation.

5.3.3.4 Groundwater HF Chemical Exposure Concentrations

We applied the overall DF values presented above to the concentrations of constituents in HF fluid and flowback fluid to derive a range of concentration levels for these constituents that could potentially be found in drinking water wells under a wide variety of conditions in the event of a spill using the conservative assumptions we have described. Table 5.6 summarizes the groundwater exposure concentrations for HESI HF constituents used in our risk analysis. Table 5.7 presents exposure concentrations assuming the spill consists of flowback fluid. These concentration estimates were utilized to quantify potential human health risks associated with the ingestion of drinking water containing constituents found in HF fluids or flowback fluids, as discussed in Section 7.

5.3.4 Surface Spill Impacts to Surface Water

Surface spills could also potentially impact surface water resources, which in some cases may serve as drinking water sources. In this section, we use mixing (dilution) estimates to examine the potential impacts to surface water associated with a surface spill of HF fluids or flowback fluid, under the conservative assumption that 100% of the spill discharges to a nearby stream.

If a surface spill occurs and the fluid migrates to a nearby river/stream, it is necessary to estimate the concentration of the HF fluid or flowback fluid constituents in the river/stream in order to assess potential health risks. Analogous to the groundwater dilution assessment, the concentration of HF constituents in surface water is given by the following mass balance mixing equation, which assumes 100% of the constituents in a HF spill are transported to the surface water:

$$C_{sw} = C_{HF} \frac{Q_{HF}}{(Q_{HF}+Q_{sw})} \tag{5.8}$$

where:

C_{sw} = Chemical concentration in surface water (µg/L)
C_{HF} = Chemical concentration in HF fluid or flowback fluid spilled (µg/L)
Q_{HF} = Discharge of HF fluid or flowback fluid to surface water (m^3/day)
Q_{sw} = Flow of surface water in the mixing zone (m^3/day)

The degree of dilution of a constituent is simply given by:

$$C_{sw} = \frac{C_{HF}}{DF_{sw}}$$

where DF_{sw} is the surface water dilution factor:

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[48] As will be discussed later, the DF probabilities (percentiles) are based on the presumption a spill has occurred, and do not account for the probability of a spill occurring.

$$DF_{sw} = \frac{Q_{HF} + Q_{sw}}{Q_{HF}}$$

Thus, the concentration of constituents in surface water (C_{sw}) resulting from a spill can be calculated using a DF that is a function of the spill volume (Q_{HF}) relative to the surface water volumetric flow rate (Q_{sw}). It should be emphasized that this approach is conservative in that it assumes 100% of the HF fluid constituents reach the surface water body, *i.e.*, no mitigation measures are used to contain the spill, none of the fluid spilled is retained in soil before reaching the water body, and none of the constituents in spilled fluid degrade before reaching the water body. This set of conditions is likely to be unrealistic and overstates the amount of spilled fluid (containing HF or flowback fluid constituents) that might reach a surface water body. Moreover, many well pads are likely to be situated in areas that are not proximate to streams/rivers.[49]

As discussed in Section 5.3.2, we developed a distribution of HF fluid or flowback fluid spill volumes in the event a spill occurs. The spill volume is represented by Q_{HF} in Equation 5.8. In order to determine the surface water dilution factor, it is necessary to also determine the volumetric flow rate (Q_{SW}) for the surface water impacted.

5.3.4.1 Representative Surface Water Flow

Given the inherent temporal and regional variability of stream flow, the exact flow conditions that could be present in the event of an HF fluid or flowback fluid spill are unpredictable. However, with the wealth of available long-term stream gauge monitoring data throughout the US, we have developed a distribution of possible stream flows that we used in our analysis. Moreover, as discussed below, our analysis conservatively developed a distribution of <u>low</u> flows, because low flow volumes lead to less dilution, which yields conservative, or health-protective, results in our analysis.

As discussed in Section 3.3, in order to evaluate the degree of possible regional variation in the distribution of low flows, we obtained maps defining regional climate zones (in terms of "aridity" indices) and overlaid these boundaries on the network of USGS gauging stations falling within the tight sedimentary oil/gas formations in the US (see Figure 3.3). The gauging stations within these basins span four climatic regions: arid, semi-arid, temperate, and semi-humid. For each of these four climate regions, we extracted the USGS daily streamflow gauging data using the following criteria:

1. Data were selected from stations with 350 days per year or more of records to ensure a robust data set.
2. The minimum average daily stream flow for an entire year of record had to be greater than zero (*e.g.*, any stations for which the average of the 350+ days of streamflow measurements were zero, were not included in order to avoid ephemeral streams). We included all other streams, including very small ones that might not be large enough to serve as a drinking water source.
3. Stations with a minimum of 5 years of monitoring were selected to ensure a robust data set.

Based on these criteria, we calculated the average daily flow for each year of record at each selected gauging station. From this data set, we then selected the year with <u>lowest</u> average daily flow from all

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[49] Many states have regulations specifying the minimum distance between a well pad and any streams. For example, in Pennsylvania horizontal wells must generally be located at least 300 feet from a stream (Pennsylvania General Assembly, Undated).

years of record at each station. Thus, for each station, this gave a single average daily low-flow value over all years of record. We did this for every gauging station to develop a probability distribution of low-flow values for all gauging stations within each climate region (the data fit lognormal distributions, such that the log10 low flows fit a normal distribution). A summary of the USGS data for each of the four climate regions is given below.

Table 5.8 Summary Statistics for USGS Low Annual Mean Daily Discharge

Climate Zone	Number of Stations	Average Years of Record	Log_{10} Average (cfs)	Log_{10} Standard Deviation (cfs)
Arid (3-7)	199	21.8	1.34	0.89
Semi-arid (2-3)	560	22.7	1.37	0.88
Temperate (1-2)	2,316	26.8	1.89	0.89
Semi-humid (0.33-1)	384	27.9	1.99	0.84
Arid/Semi-arid Combined	759	22.5	1.36	0.88
Temperate/Semi-humid	2,700	27.0	1.90	0.88

Based on a statistical comparison of these low-flow statistics, the data for the arid and semi-arid regions were not statistically different, and the data for the temperate and semi-humid regions are also not statistically different (Figure 5.8). Thus, for the probabilistic analysis we have calculated the possible impacts of HF spills impacting surface waters for two separate climatic regions: arid/semi-arid, and temperate/semi-humid.

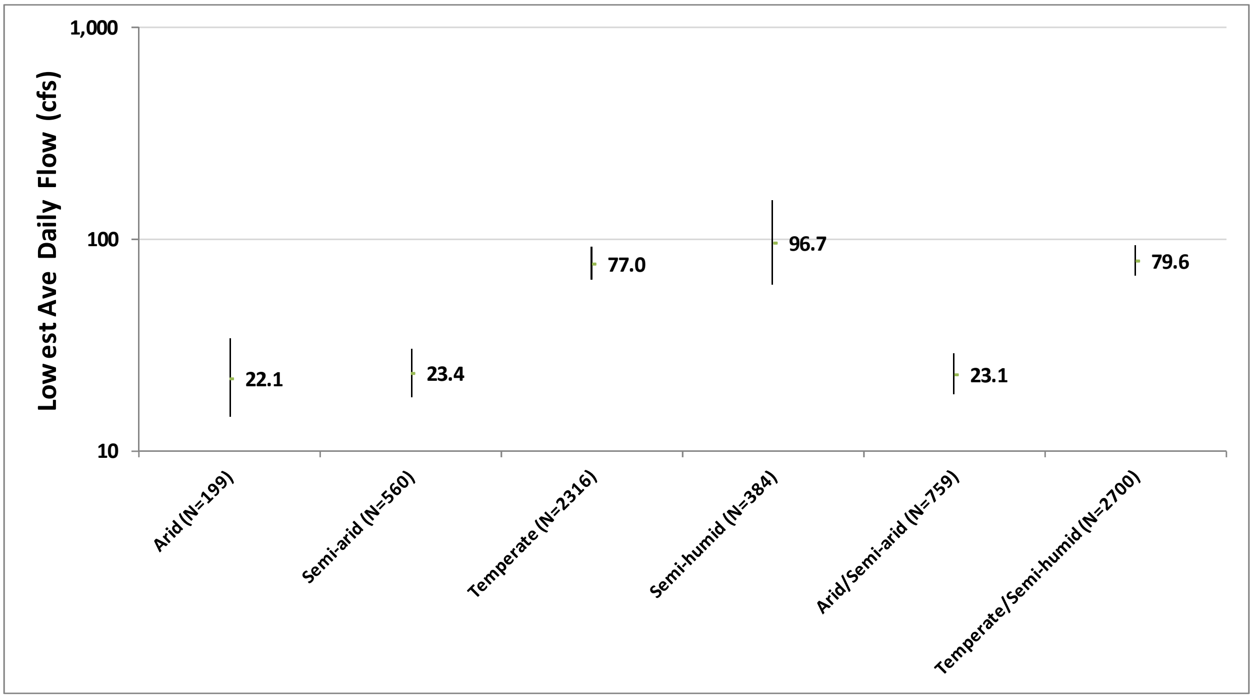

Figure 5.8 Comparison of Low Flow Data by Climate (Aridity) Zones

As noted previously, our surface water exposure analysis also assumed that 100% of the chemicals spilled on the well pad could reach a surface water body *via* rainfall and runoff. This assumption ignores mitigation measures such as possible well setbacks and spill containment practices. The use of low streamflow values, coupled with the assumption that 100% of any spilled HF additives reach the surface drinking water source, are assumptions that yield "high-end" estimates of potential human exposure for the surface water exposure pathway.

A related factor in our surface water exposure analysis was the period over which constituents in potential spills might migrate to and mix into a stream. In selecting the appropriate period for mixing to occur, we considered the likelihood of spill events having direct (immediate/short term) *versus* indirect (longer term) impacts on a nearby stream, and the physical processes that might convey HF fluid or flowback fluid constituents from the location of a surface spill to a nearby surface water body.[50]

Based on available data, spills associated with HF activities that directly impact surface water, which might raise concerns regarding short-term impacts, are rare. For example, based on the information in the PADEP OGM violation database (discussed earlier, see also Section 5.3.2), only about 6 out of every 10,000 wells (0.06%) experienced a spill that had a direct impact on a stream.[51] The rarity of these events is partly due to the fact that well pads are located some distance from nearby streams and there are only a very limited number of unlikely scenarios in which a spill might migrate quickly over such distances to a stream.

Given the low probability of incidents that might lead to short-term impacts, it was more relevant to focus our analysis on potential long-term effects, *i.e.*, for the vast majority of spills that do not reach streams quickly.[52] From a human health perspective, long-term effects (chronic impacts) are generally defined by exposure periods of seven years,[53] or in some instances one-year, or longer.[54] From this perspective, selecting a mixing period that matches the exposure period for potential long term health effects is consistent with risk assessment methodology (*i.e.*, in order to calculate an exposure point concentration in drinking water throughout this time period).

In addition to these exposure period considerations, an appropriate mixing period can also be derived from an assessment of physical processes that could transport HF constituents from an area of spill-impacted soil (well pad) to a stream. These include direct overland runoff (*i.e.*, constituents carried with water and eroding soil particles that runs over the land surface) and slower migration underground (*i.e.*, movement with groundwater that then discharges into a stream). Direct overland runoff and soil erosion are episodic processes (*i.e.*, not "continuous") influenced by the frequency and magnitude of rainfall events. In order for 100% of spilled constituents to migrate to a stream as we have assumed, the surface runoff/erosion process is more likely to occur over timescales on the order of years (rather than days or months). If the migration to surface water is *via* groundwater flow, the timescales could be even longer – in many cases decades or more (Winter *et al.*, 1998). Thus, a time period on the order of years is considered to be a conservatively short transport timescale for all the constituents in a spill area to be transported to a stream.

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[50] For the groundwater pathway, no mixing period was explicitly included both because groundwater travel would likely have timescales of years or decades, and because for the unsaturated zone component we conservatively selected the "peak" plume concentration (which may not occur for decades), rather than specifying a specific time-frame for the analysis.

[51] This is based on 4 of 234 spills (1.7%) in the PADEP OGM database that indicate direct impacts to a stream. When combined with the overall spill frequency (3.3%), this gives 0.06% probability that HF activities could result in an HF spill directly impacting a stream.

[52] We also note that risk-based concentrations for long term exposure are generally lower (more restrictive) than their corresponding benchmarks based on short-term exposures.

[53] US EPA, 2002.

[54] ATSDR "Minimum Risk Levels" (MRLs) define chronic exposures as 365 days or more. http://www.atsdr.cdc.gov/mrls/index.asp.

Based on the foregoing considerations, we selected an averaging period of 1 year as a conservative (*i.e.*, health protective) approach. Our approach and selected mixing period are likely to be very conservative when compared to long-term exposure periods appropriate for long term human health effects (*i.e.*, US EPA Risk Assessment Forum indicates periods of 7 years or more when developing reference doses), and timescales for the operative transport processes to convey HF constituents to a stream.[55]

5.3.4.2 Surface Water DF

Based on the spill volume distribution described earlier, and the foregoing methods for developing a distribution of surface water mixing volumes, we derived a distribution of surface water DFs in the event a surface spill occurs. The Monte Carlo sampling process for developing the surface water DF distribution is shown schematically below (Figure 5.9). Random samples were iteratively drawn from the underlying probability distributions of spill volumes and surface water stream flow and each combination yielded a single value of the calculated DF. Based on repeated samples (1 million total) a probability distribution of DF values was generated. A summary of selected percentiles of this surface water DF distribution is given in Table 5.9.

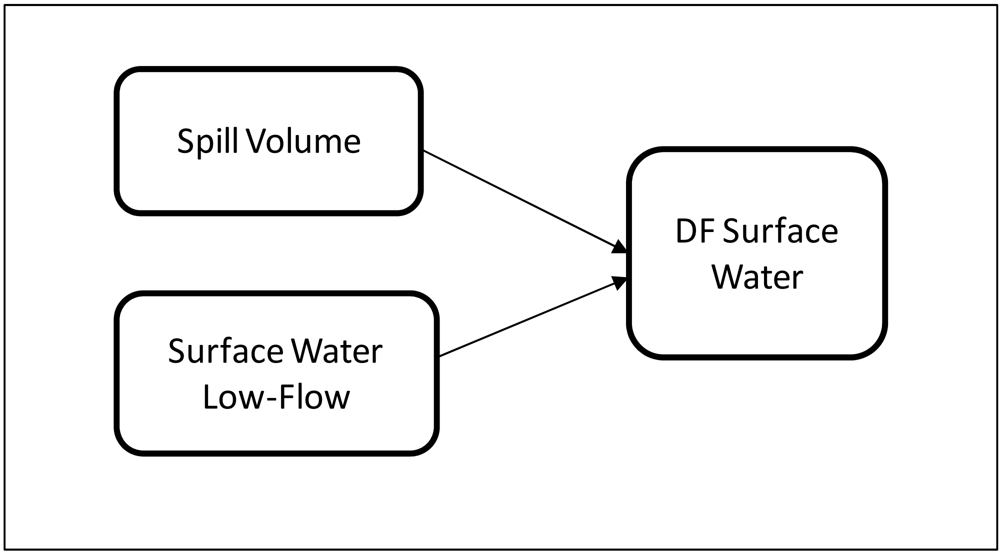

Figure 5.9 Schematic of Surface Water DF Monte Carlo Sampling

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[55] Note also that we have not accounted for the additional dilution that would occur due to direct rainfall, nor have we included any dilution if the transport to surface water is *via* groundwater.

Table 5.9 Summary Percentiles of Surface Water DFs

Percentile	Arid/ Semi-arid	Temperate/ Semi-humid
	DF	DF
10%	1.0×10^{10}	3.6×10^{10}
25%	1.3×10^{9}	4.7×10^{9}
50%	1.4×10^{8}	4.9×10^{8}
75%	1.5×10^{7}	5.1×10^{7}
90%	2.0×10^{6}	6.7×10^{6}
95%	592,480	2.0×10^{6}

Note:
Based on 1 million Monte Carlo samples.

As noted earlier, when interpreting the percentiles associated with any particular DF, the percentile is the cumulative probability that the DF will be equal to, or greater than, the reported value.[56] For example, the 95th percentile DF for arid/semi-arid regions (592,480) means that the DF was 592,480 or greater in 95% of the simulations; conversely, the DF was less than 592,480 in 5% of the simulations.

As with the DFs for the groundwater pathway, we applied this distribution of DFs for the surface water pathway to the concentrations of constituents in HF fluids and flowback fluid, yielding concentrations of those constituents in surface water that could result from a spill under a wide range of conditions, including combinations of large spill volumes mixing in with low stream flow conditions. Tables 5.6 and 5.7 present the modeled concentrations of HF fluid constituents and flowback fluid constituents for the surface water exposure pathway (they also include EPCs for the groundwater pathway). These concentration estimates were utilized to quantify human health risks *via* drinking water, as discussed in Section 7.

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[56] As will be discussed later, the DF probabilities (percentiles) are based on the presumption a spill has occurred, and do not account for the probability of a spill occurring.

Table 5.6 Summary of Exposure Point Concentrations (EPCs) Associated with Minimum and Maximum Chemical Concentrations for HESI HF Sytems

CAS No.	Chemical	Min Wellhead Conc (µg/L)	Max Wellhead Conc (µg/L)	EPC at 50th Percentile DF (µg/L)						EPC at 90th Percentile DF (µg/L)					
				Surface Water (Arid/Semi-Arid)		Surface Water (Temperate/ Semi-Humid)		Groundwater		Surface Water (Arid/Semi-Arid)		Surface Water (Temperate/ Semi-Humid)		Groundwater	
				Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
CBI	Aldehyde	217	3,169,750	2.E-06	2.E-02	4.E-07	6.E-03	2.E-26	3.E-22	1.E-04	2.E+00	3.E-05	5.E-01	4.E-08	6.E-04
68410-62-8	Naphthenic acid ethoxylate	71	2,572,951	5.E-07	2.E-02	1.E-07	5.E-03	6.E-27	2.E-22	4.E-05	1.E+00	1.E-05	4.E-01	1.E-08	5.E-04
71-48-7	Cobalt acetate	22,957	104,400	2.E-04	7.E-04	5.E-05	2.E-04	2.E-24	9.E-24	1.E-02	5.E-02	3.E-03	2.E-02	4.E-06	2.E-05
CBI	Alkyl sulfonate	570,603	2,359,022	4.E-03	2.E-02	1.E-03	5.E-03	5.E-23	2.E-22	3.E-01	1.E+00	9.E-02	4.E-01	1.E-04	4.E-04
631-61-8	Ammonium acetate	6,044	660,754	4.E-05	5.E-03	1.E-05	1.E-03	5.E-25	6.E-23	3.E-03	3.E-01	9.E-04	1.E-01	1.E-06	1.E-04
64742-48-9	Naphtha, hydrotreated heavy	84,930	2,831,831	6.E-04	2.E-02	2.E-04	6.E-03	8.E-24	3.E-22	4.E-02	1.E+00	1.E-02	4.E-01	2.E-05	5.E-04
107-19-7	Propargyl alcohol	247	53,378	2.E-06	4.E-04	5.E-07	1.E-04	2.E-26	5.E-24	1.E-04	3.E-02	4.E-05	8.E-03	5.E-08	1.E-05
CBI	EDTA/Copper chelate	4,315	884,509	3.E-05	6.E-03	9.E-06	2.E-03	4.E-25	8.E-23	2.E-03	4.E-01	6.E-04	1.E-01	8.E-07	2.E-04
61791-26-2	Polyoxylated fatty amine salt	290	1,185,692	2.E-06	8.E-03	6.E-07	2.E-03	3.E-26	1.E-22	1.E-04	6.E-01	4.E-05	2.E-01	5.E-08	2.E-04
7681-82-5	Sodium iodide	1,465	148,211	1.E-05	1.E-03	3.E-06	3.E-04	1.E-25	1.E-23	7.E-04	7.E-02	2.E-04	2.E-02	3.E-07	3.E-05
7727-54-0	Ammonium persulfate	77,317	153,676	6.E-04	1.E-03	2.E-04	3.E-04	7.E-24	1.E-23	4.E-02	8.E-02	1.E-02	2.E-02	1.E-05	3.E-05
111-40-0	Diethylenetriamine	1,017	208,521	7.E-06	1.E-03	2.E-06	4.E-04	9.E-26	2.E-23	5.E-04	1.E-01	2.E-04	3.E-02	2.E-07	4.E-05
111-76-2	Ethylene glycol monobutyl ether	225,238	931,193	2.E-03	7.E-03	5.E-04	2.E-03	2.E-23	8.E-23	1.E-01	5.E-01	3.E-02	1.E-01	4.E-05	2.E-04
81741-28-8	Tributyl tetradecyl phosphonium chloride	12,069	24,367	9.E-05	2.E-04	2.E-05	5.E-05	1.E-24	2.E-24	6.E-03	1.E-02	2.E-03	4.E-03	2.E-06	5.E-06
7758-19-2	Chlorous acid, sodium salt	34,764	480,277	2.E-04	3.E-03	7.E-05	1.E-03	3.E-24	4.E-23	2.E-02	2.E-01	5.E-03	7.E-02	7.E-06	9.E-05
67-56-1	Methanol	205	3,063,037	1.E-06	2.E-02	4.E-07	6.E-03	2.E-26	3.E-22	1.E-04	2.E+00	3.E-05	5.E-01	4.E-08	6.E-04
7775-27-1	Sodium persulfate	746	377,141	5.E-06	3.E-03	2.E-06	8.E-04	7.E-26	3.E-23	4.E-04	2.E-01	1.E-04	6.E-02	1.E-07	7.E-05
590-29-4	Potassium formate	212,404	437,030	2.E-03	3.E-03	4.E-04	9.E-04	2.E-23	4.E-23	1.E-01	2.E-01	3.E-02	7.E-02	4.E-05	8.E-05
12125-02-9	Ammonium chloride	1,219	952,935	9.E-06	7.E-03	2.E-06	2.E-03	1.E-25	9.E-23	6.E-04	5.E-01	2.E-04	1.E-01	2.E-07	2.E-04
111-46-6	Diethylene glycol	75,079	310,398	5.E-04	2.E-03	2.E-04	6.E-04	7.E-24	3.E-23	4.E-02	2.E-01	1.E-02	5.E-02	1.E-05	6.E-05
13709-94-9	Potassium metaborate	47,850	602,200	3.E-04	4.E-03	1.E-04	1.E-03	4.E-24	5.E-23	2.E-02	3.E-01	7.E-03	9.E-02	9.E-06	1.E-04
68551-12-2	Alcohols, C12-16, ethoxylated	412	1,045,385	3.E-06	7.E-03	8.E-07	2.E-03	4.E-26	1.E-22	2.E-04	5.E-01	6.E-05	2.E-01	8.E-08	2.E-04
CBI	Borate salt	266,392	548,110	2.E-03	4.E-03	5.E-04	1.E-03	2.E-23	5.E-23	1.E-01	3.E-01	4.E-02	8.E-02	5.E-05	1.E-04
1319-33-1	Ulexite	385,811	533,203	3.E-03	4.E-03	8.E-04	1.E-03	4.E-23	5.E-23	2.E-01	3.E-01	6.E-02	8.E-02	7.E-05	1.E-04
61791-14-8	Amines, coco alkyl, ethoxylated	68	616,560	5.E-07	4.E-03	1.E-07	1.E-03	6.E-27	6.E-23	3.E-05	3.E-01	1.E-05	9.E-02	1.E-08	1.E-04
64742-94-5	Heavy aromatic petroleum naphtha	66	96,094	5.E-07	7.E-04	1.E-07	2.E-04	6.E-27	9.E-24	3.E-05	5.E-02	1.E-05	1.E-02	1.E-08	2.E-05
64742-47-8	Hydrotreated light petroleum distillate	10,160	238,433	7.E-05	2.E-03	2.E-05	5.E-04	9.E-25	2.E-23	5.E-03	1.E-01	2.E-03	4.E-02	2.E-06	4.E-05
95-63-6	1,2,4 Trimethylbenzene	1	1,811	9.E-09	1.E-05	3.E-09	4.E-06	1.E-28	2.E-25	6.E-07	9.E-04	2.E-07	3.E-04	2.E-10	3.E-07
CBI	Terpenoid	6,015	136,812	4.E-05	1.E-03	1.E-05	3.E-04	5.E-25	1.E-23	3.E-03	7.E-02	9.E-04	2.E-02	1.E-06	3.E-05
CBI	Fatty acid tall oil	91	988,077	6.E-07	7.E-03	2.E-07	2.E-03	8.E-27	9.E-23	5.E-05	5.E-01	1.E-05	1.E-01	2.E-08	2.E-04
7681-52-9	Sodium hypochlorite	27,478	37,653	2.E-04	3.E-04	6.E-05	8.E-05	2.E-24	3.E-24	1.E-02	2.E-02	4.E-03	6.E-03	5.E-06	7.E-06
CBI	Guar gum derivative	778,086	5,267,613	6.E-03	4.E-02	2.E-03	1.E-02	7.E-23	5.E-22	4.E-01	3.E+00	1.E-01	8.E-01	1.E-04	1.E-03
64-17-5	Ethanol	297	729,702	2.E-06	5.E-03	6.E-07	1.E-03	3.E-26	7.E-23	1.E-04	4.E-01	4.E-05	1.E-01	6.E-08	1.E-04
CBI	Fatty acid tall oil amide	1,016	23,843	7.E-06	2.E-04	2.E-06	5.E-05	9.E-26	2.E-24	5.E-04	1.E-02	2.E-04	4.E-03	2.E-07	4.E-06
9000-30-0	Guar gum	85,034	3,490,851	6.E-04	2.E-02	2.E-04	7.E-03	8.E-24	3.E-22	4.E-02	2.E+00	1.E-02	5.E-01	2.E-05	7.E-04
CBI	Olefin	99	21,351	7.E-07	2.E-04	2.E-07	4.E-05	9.E-27	2.E-24	5.E-05	1.E-02	1.E-05	3.E-03	2.E-08	4.E-06
127087-87-0	Nonylphenol ethoxylated	25	36,228	2.E-07	3.E-04	5.E-08	7.E-05	2.E-27	3.E-24	1.E-05	2.E-02	4.E-06	5.E-03	5.E-09	7.E-06
91-20-3	Naphthalene	7	10,778	5.E-08	8.E-05	2.E-08	2.E-05	7.E-28	1.E-24	4.E-06	5.E-03	1.E-06	2.E-03	1.E-09	2.E-06
CBI	Terpenoid	11,104	41,764	8.E-05	3.E-04	2.E-05	9.E-05	1.E-24	4.E-24	6.E-03	2.E-02	2.E-03	6.E-03	2.E-06	8.E-06
108-24-7	Acetic anhydride	4,413	6,455,842	3.E-05	5.E-02	9.E-06	1.E-02	4.E-25	6.E-22	2.E-03	3.E+00	7.E-04	1.E+00	8.E-07	1.E-03
10486-00-7	Sodium perborate tetrahydrate	7,671	120,060	5.E-05	9.E-04	2.E-05	2.E-04	7.E-25	1.E-23	4.E-03	6.E-02	1.E-03	2.E-02	1.E-06	2.E-05
68951-67-7	Alcohols, C14-C15, ethoxylated	618	133,446	4.E-06	1.E-03	1.E-06	3.E-04	6.E-26	1.E-23	3.E-04	7.E-02	9.E-05	2.E-02	1.E-07	3.E-05
64-19-7	Acetic acid	1,758	4,303,895	1.E-05	3.E-02	4.E-06	9.E-03	2.E-25	4.E-22	9.E-04	2.E+00	3.E-04	6.E-01	3.E-07	8.E-04
67-63-0	Isopropanol	176	2,774,519	1.E-06	2.E-02	4.E-07	6.E-03	2.E-26	3.E-22	9.E-05	1.E+00	3.E-05	4.E-01	3.E-08	5.E-04
CBI	Quaternary ammonium compound	76,414	118,653	5.E-04	8.E-04	2.E-04	2.E-04	7.E-24	1.E-23	4.E-02	6.E-02	1.E-02	2.E-02	1.E-05	2.E-05
121888-68-4	Bentonite, benzyl(hydrogenated tallow alkyl) dimethylammonium stearate complex	11,711	74,557	8.E-05	5.E-04	2.E-05	2.E-04	1.E-24	7.E-24	6.E-03	4.E-02	2.E-03	1.E-02	2.E-06	1.E-05
78330-21-9	Ethoxylated branched C13 alcohol	15,710	71,445	1.E-04	5.E-04	3.E-05	1.E-04	1.E-24	6.E-24	8.E-03	4.E-02	2.E-03	1.E-02	3.E-06	1.E-05
52-51-7	2-Bromo-2-nitro-1,3-propanediol	4,914	18,009	4.E-05	1.E-04	1.E-05	4.E-05	4.E-25	2.E-24	2.E-03	9.E-03	7.E-04	3.E-03	9.E-07	3.E-06
CBI	Ethoxylate fatty acid	28,120	168,970	2.E-04	1.E-03	6.E-05	3.E-04	3.E-24	2.E-23	1.E-02	8.E-02	4.E-03	3.E-02	5.E-06	3.E-05
CBI	Ethoxylated fatty acid	27,246	168,970	2.E-04	1.E-03	6.E-05	3.E-04	2.E-24	2.E-23	1.E-02	8.E-02	4.E-03	3.E-02	5.E-06	3.E-05

Table 5.6 Summary of Exposure Point Concentrations (EPCs) Associated with Minimum and Maximum Chemical Concentrations for HESI HF Sytems

CAS No.	Chemical	Min Wellhead Conc (µg/L)	Max Wellhead Conc (µg/L)	EPC at 50th Percentile DF (µg/L)						EPC at 90th Percentile DF (µg/L)					
				Surface Water (Arid/Semi-Arid)		Surface Water (Temperate/ Semi-Humid)		Groundwater		Surface Water (Arid/Semi-Arid)		Surface Water (Temperate/ Semi-Humid)		Groundwater	
				Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
7772-98-7	Sodium thiosulfate	1,763,151	3,620,876	1.E-02	3.E-02	4.E-03	7.E-03	2.E-22	3.E-22	9.E-01	2.E+00	3.E-01	5.E-01	3.E-04	7.E-04
CBI	Surfactant mixture	14,334	19,810	1.E-04	1.E-04	3.E-05	4.E-05	1.E-24	2.E-24	7.E-03	1.E-02	2.E-03	3.E-03	3.E-06	4.E-06
9012-54-8	Hemicellulase enzyme	108	3,005	8.E-07	2.E-05	2.E-07	6.E-06	1.E-26	3.E-25	5.E-05	2.E-03	2.E-05	4.E-04	2.E-08	6.E-07
10043-52-4	Calcium chloride	6,625	24,491	5.E-05	2.E-04	1.E-05	5.E-05	6.E-25	2.E-24	3.E-03	1.E-02	1.E-03	4.E-03	1.E-06	5.E-06
7757-83-7	Sodium sulfite	14,693	30,174	1.E-04	2.E-04	3.E-05	6.E-05	1.E-24	3.E-24	7.E-03	2.E-02	2.E-03	5.E-03	3.E-06	6.E-06
CBI	Ethoxylate fatty acid	17,530	112,693	1.E-04	8.E-04	4.E-05	2.E-04	2.E-24	1.E-23	9.E-03	6.E-02	3.E-03	2.E-02	3.E-06	2.E-05
50-00-0	Formaldehyde	291	11,765	2.E-06	8.E-05	6.E-07	2.E-05	3.E-26	1.E-24	1.E-04	6.E-03	4.E-05	2.E-03	5.E-08	2.E-06
14808-60-7	Crystalline silica, quartz	35	36,258	2.E-07	3.E-04	7.E-08	7.E-05	3.E-27	3.E-24	2.E-05	2.E-02	5.E-06	5.E-03	7.E-09	7.E-06
CBI	Olefin	62	13,345	4.E-07	1.E-04	1.E-07	3.E-05	6.E-27	1.E-24	3.E-05	7.E-03	9.E-06	2.E-03	1.E-08	3.E-06
3468-63-1	C.I. Pigment Orange 5	281	291	2.E-06	2.E-06	6.E-07	6.E-07	3.E-26	3.E-26	1.E-04	1.E-04	4.E-05	4.E-05	5.E-08	5.E-08
7631-86-9	Silica, amorphous -– fumed	12,005	27,013	9.E-05	2.E-04	2.E-05	6.E-05	1.E-24	2.E-24	6.E-03	1.E-02	2.E-03	4.E-03	2.E-06	5.E-06
CBI	Inorganic salt	28,974	107,111	2.E-04	8.E-04	6.E-05	2.E-04	3.E-24	1.E-23	1.E-02	5.E-02	4.E-03	2.E-02	5.E-06	2.E-05
CBI	Proprietary	13,598	18,792	1.E-04	1.E-04	3.E-05	4.E-05	1.E-24	2.E-24	7.E-03	9.E-03	2.E-03	3.E-03	3.E-06	4.E-06
7722-76-1	Ammonium phosphate	586	59,285	4.E-06	4.E-04	1.E-06	1.E-04	5.E-26	5.E-24	3.E-04	3.E-02	9.E-05	9.E-03	1.E-07	1.E-05
CBI	Surfactant mixture	7,818	10,805	6.E-05	8.E-05	2.E-05	2.E-05	7.E-25	1.E-24	4.E-03	5.E-03	1.E-03	2.E-03	1.E-06	2.E-06
CBI	Olefin	4	890	3.E-08	6.E-06	8.E-09	2.E-06	4.E-28	8.E-26	2.E-06	4.E-04	6.E-07	1.E-04	8.E-10	2.E-07
1310-73-2	Sodium hydroxide	5,455	573,737	4.E-05	4.E-03	1.E-05	1.E-03	5.E-25	5.E-23	3.E-03	3.E-01	8.E-04	9.E-02	1.E-06	1.E-04
584-08-7	Potassium carbonate	245,793	1,117,790	2.E-03	8.E-03	5.E-04	2.E-03	2.E-23	1.E-22	1.E-01	6.E-01	4.E-02	2.E-01	5.E-05	2.E-04
68953-58-2	Quaternary ammonium compounds, bis(hydrogenated tallow alkyl) dimethyl,salts with bentonite	2,460	68,627	2.E-05	5.E-04	5.E-06	1.E-04	2.E-25	6.E-24	1.E-03	3.E-02	4.E-04	1.E-02	5.E-07	1.E-05
7647-14-5	Sodium chloride	3,095	1,279,579	2.E-05	9.E-03	6.E-06	3.E-03	3.E-25	1.E-22	2.E-03	6.E-01	5.E-04	2.E-01	6.E-07	2.E-04
71-23-8	Propanol	18,894	38,802	1.E-04	3.E-04	4.E-05	8.E-05	2.E-24	4.E-24	9.E-03	2.E-02	3.E-03	6.E-03	4.E-06	7.E-06
56-81-5	Glycerine	14,884	30,567	1.E-04	2.E-04	3.E-05	6.E-05	1.E-24	3.E-24	7.E-03	2.E-02	2.E-03	5.E-03	3.E-06	6.E-06
7791-18-6	Magnesium chloride hexahydrate	13,489	49,867	1.E-04	4.E-04	3.E-05	1.E-04	1.E-24	5.E-24	7.E-03	2.E-02	2.E-03	7.E-03	3.E-06	9.E-06
CBI	Fatty acid ester	203	4,769	1.E-06	3.E-05	4.E-07	1.E-05	2.E-26	4.E-25	1.E-04	2.E-03	3.E-05	7.E-04	4.E-08	9.E-07
7757-82-6	Sodium sulfate	0	241,392	3.E-09	2.E-03	8.E-10	5.E-04	3.E-29	2.E-23	2.E-07	1.E-01	6.E-08	4.E-02	7.E-11	5.E-05
9004-32-4	Sodium carboxymethyl cellulose	4,373	8,998	3.E-05	6.E-05	9.E-06	2.E-05	4.E-25	8.E-25	2.E-03	4.E-03	7.E-04	1.E-03	8.E-07	2.E-06
112926-00-8	Silica gel	2,606	3,602	2.E-05	3.E-05	5.E-06	7.E-06	2.E-25	3.E-25	1.E-03	2.E-03	4.E-04	5.E-04	5.E-07	7.E-07
CBI	Carbohydrate	969	27,045	7.E-06	2.E-04	2.E-06	6.E-05	9.E-26	2.E-24	5.E-04	1.E-02	1.E-04	4.E-03	2.E-07	5.E-06
CBI	Olefin	4	890	3.E-08	6.E-06	8.E-09	2.E-06	4.E-28	8.E-26	2.E-06	4.E-04	6.E-07	1.E-04	8.E-10	2.E-07
144-55-8	Sodium bicarbonate	48,019	108,054	3.E-04	8.E-04	1.E-04	2.E-04	4.E-24	1.E-23	2.E-02	5.E-02	7.E-03	2.E-02	9.E-06	2.E-05
1310-58-3	Potassium hydroxide	3,748	47,170	3.E-05	3.E-04	8.E-06	1.E-04	3.E-25	4.E-24	2.E-03	2.E-02	6.E-04	7.E-03	7.E-07	9.E-06
2836-32-0	Sodium glycolate	75	155	5.E-07	1.E-06	2.E-07	3.E-07	7.E-27	1.E-26	4.E-05	8.E-05	1.E-05	2.E-05	1.E-08	3.E-08
CBI	Fatty acid ester ethoxylate	135	3,179	1.E-06	2.E-05	3.E-07	6.E-06	1.E-26	3.E-25	7.E-05	2.E-03	2.E-05	5.E-04	3.E-08	6.E-07
12174-11-7	Attapulgite	12,064	24,822	9.E-05	2.E-04	2.E-05	5.E-05	1.E-24	2.E-24	6.E-03	1.E-02	2.E-03	4.E-03	2.E-06	5.E-06
CBI	Quaternary ammonium salt	122	1,193,596	9.E-07	9.E-03	2.E-07	2.E-03	1.E-26	1.E-22	6.E-05	6.E-01	2.E-05	2.E-01	2.E-08	2.E-04
15619-48-4	Chloromethylnaphthalene quinoline quaternary amine	4	1,590,803	3.E-08	1.E-02	8.E-09	3.E-03	4.E-28	1.E-22	2.E-06	8.E-01	6.E-07	2.E-01	8.E-10	3.E-04
94266-47-4	Citrus, extract	88,108	136,812	6.E-04	1.E-03	2.E-04	3.E-04	8.E-24	1.E-23	4.E-02	7.E-02	1.E-02	2.E-02	2.E-05	3.E-05
9043-30-5	Fatty alcohol polyglycol ether surfactant	762	21,265	5.E-06	2.E-04	2.E-06	4.E-05	7.E-26	2.E-24	4.E-04	1.E-02	1.E-04	3.E-03	1.E-07	4.E-06
CBI	Oxylated phenolic resin	49	72,456	4.E-07	5.E-04	1.E-07	1.E-04	4.E-27	7.E-24	2.E-05	4.E-02	7.E-06	1.E-02	9.E-09	1.E-05
CBI	Oxylated phenolic resin	173	253,595	1.E-06	2.E-03	4.E-07	5.E-04	2.E-26	2.E-23	9.E-05	1.E-01	3.E-05	4.E-02	3.E-08	5.E-05
CBI	Organic phosphonate	96,426	3,894,092	7.E-04	3.E-02	2.E-04	8.E-03	9.E-24	4.E-22	5.E-02	2.E+00	1.E-02	6.E-01	2.E-05	7.E-04
CBI	Polyacrylamide copolymer	18,898	443,486	1.E-04	3.E-03	4.E-05	9.E-04	2.E-24	4.E-23	9.E-03	2.E-01	3.E-03	7.E-02	4.E-06	8.E-05
CBI	Cured acrylic resin	7,173	32,622	5.E-05	2.E-04	1.E-05	7.E-05	7.E-25	3.E-24	4.E-03	2.E-02	1.E-03	5.E-03	1.E-06	6.E-06
68527-49-1	Reaction product of acetophenone, formaldehyde, thiourea and oleic acid in dimethyl formamide	523	112,984	4.E-06	8.E-04	1.E-06	2.E-04	5.E-26	1.E-23	3.E-04	6.E-02	8.E-05	2.E-02	1.E-07	2.E-05
101033-44-7	Triethanolamine zirconate	85,768	176,136	6.E-04	1.E-03	2.E-04	4.E-04	8.E-24	2.E-23	4.E-02	9.E-02	1.E-02	3.E-02	2.E-05	3.E-05
68909-34-2	Zirconium, acetate lactate oxo ammonium complexes	188,346	856,536	1.E-03	6.E-03	4.E-04	2.E-03	2.E-23	8.E-23	9.E-02	4.E-01	3.E-02	1.E-01	4.E-05	2.E-04
7647-01-0	Hydrochloric acid	757	160,547,973	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]
Notes:			DF =		1.4E+08		4.9E+08		1.1E+28		2.0E+06		6.7E+06		5.3E+09

[a] Hydrochloric acid will not persist after spill.

DF = Dilution Factor.

Table 5.6 Summary of Exposure Point Concentrations (EPCs) Associated with Minimum and Maximum Chemical Concentrations for HESI HF Sytems

CAS No.	Chemical	Min Wellhead Conc (µg/L)	Max Wellhead Conc (µg/L)	EPC at 95th Percentile DF (µg/L)					
				Surface Water (Arid/Semi-Arid)		Surface Water (Temperate/ Semi-Humid)		Groundwater	
				Min	Max	Min	Max	Min	Max
CBI	Aldehyde	217	3,169,750	4.E-04	5.E+00	1.E-04	2.E+00	1.E-04	2.E+00
68410-62-8	Naphthenic acid ethoxylate	71	2,572,951	1.E-04	4.E+00	4.E-05	1.E+00	4.E-05	1.E+00
71-48-7	Cobalt acetate	22,957	104,400	4.E-02	2.E-01	1.E-02	5.E-02	1.E-02	5.E-02
CBI	Alkyl sulfonate	570,603	2,359,022	1.E+00	4.E+00	3.E-01	1.E+00	3.E-01	1.E+00
631-61-8	Ammonium acetate	6,044	660,754	1.E-02	1.E+00	3.E-03	3.E-01	3.E-03	3.E-01
64742-48-9	Naphtha, hydrotreated heavy	84,930	2,831,831	1.E-01	5.E+00	4.E-02	1.E+00	4.E-02	1.E+00
107-19-7	Propargyl alcohol	247	53,378	4.E-04	9.E-02	1.E-04	3.E-02	1.E-04	3.E-02
CBI	EDTA/Copper chelate	4,315	884,509	7.E-03	1.E+00	2.E-03	4.E-01	2.E-03	5.E-01
61791-26-2	Polyoxylated fatty amine salt	290	1,185,692	5.E-04	2.E+00	1.E-04	6.E-01	2.E-04	6.E-01
7681-82-5	Sodium iodide	1,465	148,211	2.E-03	3.E-01	7.E-04	7.E-02	8.E-04	8.E-02
7727-54-0	Ammonium persulfate	77,317	153,676	1.E-01	3.E-01	4.E-02	8.E-02	4.E-02	8.E-02
111-40-0	Diethylenetriamine	1,017	208,521	2.E-03	4.E-01	5.E-04	1.E-01	5.E-04	1.E-01
111-76-2	Ethylene glycol monobutyl ether	225,238	931,193	4.E-01	2.E+00	1.E-01	5.E-01	1.E-01	5.E-01
81741-28-8	Tributyl tetradecyl phosphonium chloride	12,069	24,367	2.E-02	4.E-02	6.E-03	1.E-02	6.E-03	1.E-02
7758-19-2	Chlorous acid, sodium salt	34,764	480,277	6.E-02	8.E-01	2.E-02	2.E-01	2.E-02	3.E-01
67-56-1	Methanol	205	3,063,037	3.E-04	5.E+00	1.E-04	2.E+00	1.E-04	2.E+00
7775-27-1	Sodium persulfate	746	377,141	1.E-03	6.E-01	4.E-04	2.E-01	4.E-04	2.E-01
590-29-4	Potassium formate	212,404	437,030	4.E-01	7.E-01	1.E-01	2.E-01	1.E-01	2.E-01
12125-02-9	Ammonium chloride	1,219	952,935	2.E-03	2.E+00	6.E-04	5.E-01	6.E-04	5.E-01
111-46-6	Diethylene glycol	75,079	310,398	1.E-01	5.E-01	4.E-02	2.E-01	4.E-02	2.E-01
13709-94-9	Potassium metaborate	47,850	602,200	8.E-02	1.E+00	2.E-02	3.E-01	3.E-02	3.E-01
68551-12-2	Alcohols, C12-16, ethoxylated	412	1,045,385	7.E-04	2.E+00	2.E-04	5.E-01	2.E-04	6.E-01
CBI	Borate salt	266,392	548,110	4.E-01	9.E-01	1.E-01	3.E-01	1.E-01	3.E-01
1319-33-1	Ulexite	385,811	533,203	7.E-01	9.E-01	2.E-01	3.E-01	2.E-01	3.E-01
61791-14-8	Amines, coco alkyl, ethoxylated	68	616,560	1.E-04	1.E+00	3.E-05	3.E-01	4.E-05	3.E-01
64742-94-5	Heavy aromatic petroleum naphtha	66	96,094	1.E-04	2.E-01	3.E-05	5.E-02	3.E-05	5.E-02
64742-47-8	Hydrotreated light petroleum distillate	10,160	238,433	2.E-02	4.E-01	5.E-03	1.E-01	5.E-03	1.E-01
95-63-6	1,2,4 Trimethylbenzene	1	1,811	2.E-06	3.E-03	6.E-07	9.E-04	7.E-07	1.E-03
CBI	Terpenoid	6,015	136,812	1.E-02	2.E-01	3.E-03	7.E-02	3.E-03	7.E-02
CBI	Fatty acid tall oil	91	988,077	2.E-04	2.E+00	5.E-05	5.E-01	5.E-05	5.E-01
7681-52-9	Sodium hypochlorite	27,478	37,653	5.E-02	6.E-02	1.E-02	2.E-02	1.E-02	2.E-02
CBI	Guar gum derivative	778,086	5,267,613	1.E+00	9.E+00	4.E-01	3.E+00	4.E-01	3.E+00
64-17-5	Ethanol	297	729,702	5.E-04	1.E+00	1.E-04	4.E-01	2.E-04	4.E-01
CBI	Fatty acid tall oil amide	1,016	23,843	2.E-03	4.E-02	5.E-04	1.E-02	5.E-04	1.E-02
9000-30-0	Guar gum	85,034	3,490,851	1.E-01	6.E+00	4.E-02	2.E+00	4.E-02	2.E+00
CBI	Olefin	99	21,351	2.E-04	4.E-02	5.E-05	1.E-02	5.E-05	1.E-02
127087-87-0	Nonylphenol ethoxylated	25	36,228	4.E-05	6.E-02	1.E-05	2.E-02	1.E-05	2.E-02
91-20-3	Naphthalene	7	10,778	1.E-05	2.E-02	4.E-06	5.E-03	4.E-06	6.E-03
CBI	Terpenoid	11,104	41,764	2.E-02	7.E-02	6.E-03	2.E-02	6.E-03	2.E-02
108-24-7	Acetic anhydride	4,413	6,455,842	7.E-03	1.E+01	2.E-03	3.E+00	2.E-03	3.E+00
10486-00-7	Sodium perborate tetrahydrate	7,671	120,060	1.E-02	2.E-01	4.E-03	6.E-02	4.E-03	6.E-02
68951-67-7	Alcohols, C14-C15, ethoxylated	618	133,446	1.E-03	2.E-01	3.E-04	7.E-02	3.E-04	7.E-02
64-19-7	Acetic acid	1,758	4,303,895	3.E-03	7.E+00	9.E-04	2.E+00	9.E-04	2.E+00
67-63-0	Isopropanol	176	2,774,519	3.E-04	5.E+00	9.E-05	1.E+00	9.E-05	1.E+00
CBI	Quaternary ammonium compound	76,414	118,653	1.E-01	2.E-01	4.E-02	6.E-02	4.E-02	6.E-02
121888-68-4	Bentonite, benzyl(hydrogenated tallow alkyl) dimethylammonium stearate complex	11,711	74,557	2.E-02	1.E-01	6.E-03	4.E-02	6.E-03	4.E-02
78330-21-9	Ethoxylated branched C13 alcohol	15,710	71,445	3.E-02	1.E-01	8.E-03	4.E-02	8.E-03	4.E-02
52-51-7	2-Bromo-2-nitro-1,3-propanediol	4,914	18,009	8.E-03	3.E-02	2.E-03	9.E-03	3.E-03	9.E-03
CBI	Ethoxylate fatty acid	28,120	168,970	5.E-02	3.E-01	1.E-02	9.E-02	1.E-02	9.E-02
CBI	Ethoxylated fatty acid	27,246	168,970	5.E-02	3.E-01	1.E-02	9.E-02	1.E-02	9.E-02

Table 5.6 Summary of Exposure Point Concentrations (EPCs) Associated with Minimum and Maximum Chemical Concentrations for HESI HF Sytems

CAS No.	Chemical	Min Wellhead Conc (µg/L)	Max Wellhead Conc (µg/L)	EPC at 95th Percentile DF (µg/L)					
				Surface Water (Arid/Semi-Arid)		Surface Water (Temperate/ Semi-Humid)		Groundwater	
				Min	Max	Min	Max	Min	Max
7772-98-7	Sodium thiosulfate	1,763,151	3,620,876	3.E+00	6.E+00	9.E-01	2.E+00	9.E-01	2.E+00
CBI	Surfactant mixture	14,334	19,810	2.E-02	3.E-02	7.E-03	1.E-02	8.E-03	1.E-02
9012-54-8	Hemicellulase enzyme	108	3,005	2.E-04	5.E-03	5.E-05	2.E-03	6.E-05	2.E-03
10043-52-4	Calcium chloride	6,625	24,491	1.E-02	4.E-02	3.E-03	1.E-02	3.E-03	1.E-02
7757-83-7	Sodium sulfite	14,693	30,174	2.E-02	5.E-02	7.E-03	2.E-02	8.E-03	2.E-02
CBI	Ethoxylate fatty acid	17,530	112,693	3.E-02	2.E-01	9.E-03	6.E-02	9.E-03	6.E-02
50-00-0	Formaldehyde	291	11,765	5.E-04	2.E-02	1.E-04	6.E-03	2.E-04	6.E-03
14808-60-7	Crystalline silica, quartz	35	36,258	6.E-05	6.E-02	2.E-05	2.E-02	2.E-05	2.E-02
CBI	Olefin	62	13,345	1.E-04	2.E-02	3.E-05	7.E-03	3.E-05	7.E-03
3468-63-1	C.I. Pigment Orange 5	281	291	5.E-04	5.E-04	1.E-04	1.E-04	1.E-04	2.E-04
7631-86-9	Silica, amorphous -– fumed	12,005	27,013	2.E-02	5.E-02	6.E-03	1.E-02	6.E-03	1.E-02
CBI	Inorganic salt	28,974	107,111	5.E-02	2.E-01	1.E-02	5.E-02	2.E-02	6.E-02
CBI	Proprietary	13,598	18,792	2.E-02	3.E-02	7.E-03	9.E-03	7.E-03	1.E-02
7722-76-1	Ammonium phosphate	586	59,285	1.E-03	1.E-01	3.E-04	3.E-02	3.E-04	3.E-02
CBI	Surfactant mixture	7,818	10,805	1.E-02	2.E-02	4.E-03	5.E-03	4.E-03	6.E-03
CBI	Olefin	4	890	7.E-06	2.E-03	2.E-06	4.E-04	2.E-06	5.E-04
1310-73-2	Sodium hydroxide	5,455	573,737	9.E-03	1.E+00	3.E-03	3.E-01	3.E-03	3.E-01
584-08-7	Potassium carbonate	245,793	1,117,790	4.E-01	2.E+00	1.E-01	6.E-01	1.E-01	6.E-01
68953-58-2	Quaternary ammonium compounds, bis(hydrogenated tallow alkyl) dimethyl,salts with bentonite	2,460	68,627	4.E-03	1.E-01	1.E-03	3.E-02	1.E-03	4.E-02
7647-14-5	Sodium chloride	3,095	1,279,579	5.E-03	2.E+00	2.E-03	6.E-01	2.E-03	7.E-01
71-23-8	Propanol	18,894	38,802	3.E-02	7.E-02	1.E-02	2.E-02	1.E-02	2.E-02
56-81-5	Glycerine	14,884	30,567	3.E-02	5.E-02	8.E-03	2.E-02	8.E-03	2.E-02
7791-18-6	Magnesium chloride hexahydrate	13,489	49,867	2.E-02	8.E-02	7.E-03	3.E-02	7.E-03	3.E-02
CBI	Fatty acid ester	203	4,769	3.E-04	8.E-03	1.E-04	2.E-03	1.E-04	3.E-03
7757-82-6	Sodium sulfate	0	241,392	6.E-07	4.E-01	2.E-07	1.E-01	2.E-07	1.E-01
9004-32-4	Sodium carboxymethyl cellulose	4,373	8,998	7.E-03	2.E-02	2.E-03	5.E-03	2.E-03	5.E-03
112926-00-8	Silica gel	2,606	3,602	4.E-03	6.E-03	1.E-03	2.E-03	1.E-03	2.E-03
CBI	Carbohydrate	969	27,045	2.E-03	5.E-02	5.E-04	1.E-02	5.E-04	1.E-02
CBI	Olefin	4	890	7.E-06	2.E-03	2.E-06	4.E-04	2.E-06	5.E-04
144-55-8	Sodium bicarbonate	48,019	108,054	8.E-02	2.E-01	2.E-02	5.E-02	3.E-02	6.E-02
1310-58-3	Potassium hydroxide	3,748	47,170	6.E-03	8.E-02	2.E-03	2.E-02	2.E-03	2.E-02
2836-32-0	Sodium glycolate	75	155	1.E-04	3.E-04	4.E-05	8.E-05	4.E-05	8.E-05
CBI	Fatty acid ester ethoxylate	135	3,179	2.E-04	5.E-03	7.E-05	2.E-03	7.E-05	2.E-03
12174-11-7	Attapulgite	12,064	24,822	2.E-02	4.E-02	6.E-03	1.E-02	6.E-03	1.E-02
CBI	Quaternary ammonium salt	122	1,193,596	2.E-04	2.E+00	6.E-05	6.E-01	6.E-05	6.E-01
15619-48-4	Chloromethylnaphthalene quinoline quaternary amine	4	1,590,803	7.E-06	3.E+00	2.E-06	8.E-01	2.E-06	8.E-01
94266-47-4	Citrus, extract	88,108	136,812	1.E-01	2.E-01	4.E-02	7.E-02	5.E-02	7.E-02
9043-30-5	Fatty alcohol polyglycol ether surfactant	762	21,265	1.E-03	4.E-02	4.E-04	1.E-02	4.E-04	1.E-02
CBI	Oxylated phenolic resin	49	72,456	8.E-05	1.E-01	2.E-05	4.E-02	3.E-05	4.E-02
CBI	Oxylated phenolic resin	173	253,595	3.E-04	4.E-01	9.E-05	1.E-01	9.E-05	1.E-01
CBI	Organic phosphonate	96,426	3,894,092	2.E-01	7.E+00	5.E-02	2.E+00	5.E-02	2.E+00
CBI	Polyacrylamide copolymer	18,898	443,486	3.E-02	7.E-01	1.E-02	2.E-01	1.E-02	2.E-01
CBI	Cured acrylic resin	7,173	32,622	1.E-02	6.E-02	4.E-03	2.E-02	4.E-03	2.E-02
68527-49-1	Reaction product of acetophenone, formaldehyde, thiourea and oleic acid in dimethyl formamide	523	112,984	9.E-04	2.E-01	3.E-04	6.E-02	3.E-04	6.E-02
101033-44-7	Triethanolamine zirconate	85,768	176,136	1.E-01	3.E-01	4.E-02	9.E-02	5.E-02	9.E-02
68909-34-2	Zirconium, acetate lactate oxo ammonium complexes	188,346	856,536	3.E-01	1.E+00	1.E-01	4.E-01	1.E-01	5.E-01
7647-01-0	Hydrochloric acid	757	160,547,973	[a]	[a]	[a]	[a]	[a]	[a]
Notes:			DF =		592,480		1,982,300		1.9E+06

[a] Hydrochloric acid will not persist after spill.

DF = Dilution Factor.

Table 5.7 Summary of Flowback Fluid Constituent Exposure Point Concentrations (EPCs) Used in Risk Analysis

CAS	Parameter	Highest Median (µg/L)	EPC at 50th Percentile DF (µg/L)			EPC at 90th Percentile DF (µg/L)			EPC at 95th Percentile DF (µg/L)		
			Surface Water		Groundwater	Surface Water		Groundwater	Surface Water		Groundwater
			Arid/ Semi-Arid	Temperate/ Semi-Humid		Arid/ Semi-Arid	Temperate/ Semi-Humid		Arid/ Semi-Arid	Temperate/ Semi-Humid	
7429-90-5	Aluminum-DISS	227	2.E-06	5.E-07	2.E-26	1.E-04	3.E-05	4.E-08	4.E-04	1.E-04	1.E-04
7440-36-0	Antimony-DISS	5	4.E-08	1.E-08	5.E-28	3.E-06	7.E-07	9.E-10	8.E-06	3.E-06	3.E-06
7440-38-2	Arsenic-DISS	13	9.E-08	3.E-08	1.E-27	7.E-06	2.E-06	2.E-09	2.E-05	7.E-06	7.E-06
7440-39-3	Barium-DISS	496,000	4.E-03	1.E-03	5.E-23	2.E-01	7.E-02	9.E-05	8.E-01	3.E-01	3.E-01
7440-42-8	Boron-DISS	12,400	9.E-05	3.E-05	1.E-24	6.E-03	2.E-03	2.E-06	2.E-02	6.E-03	7.E-03
24959-67-9	Bromide	607,000	4.E-03	1.E-03	6.E-23	3.E-01	9.E-02	1.E-04	1.E+00	3.E-01	3.E-01
7440-43-9	Cadmium-DISS	3	2.E-08	6.E-09	3.E-28	2.E-06	4.E-07	6.E-10	5.E-06	2.E-06	2.E-06
7440-47-3	Chromium	82	6.E-07	2.E-07	7.E-27	4.E-05	1.E-05	2.E-08	1.E-04	4.E-05	4.E-05
7440-47-3	Chromium (VI)	5	4.E-08	1.E-08	5.E-28	3.E-06	7.E-07	9.E-10	8.E-06	3.E-06	3.E-06
7440-47-3	Chromium (VI)-diss	539	4.E-06	1.E-06	5.E-26	3.E-04	8.E-05	1.E-07	9.E-04	3.E-04	3.E-04
7440-47-3	Chromium III	25	2.E-07	5.E-08	2.E-27	1.E-05	4.E-06	5.E-09	4.E-05	1.E-05	1.E-05
7440-47-3	Chromium-DISS	7	5.E-08	1.E-08	6.E-28	4.E-06	1.E-06	1.E-09	1.E-05	4.E-06	4.E-06
7440-48-4	Cobalt-DISS	250	2.E-06	5.E-07	2.E-26	1.E-04	4.E-05	5.E-08	4.E-04	1.E-04	1.E-04
7440-50-8	Copper-DISS	13	9.E-08	3.E-08	1.E-27	6.E-06	2.E-06	2.E-09	2.E-05	6.E-06	7.E-06
57-12-5	Cyanide, Total	5	4.E-08	1.E-08	5.E-28	3.E-06	7.E-07	9.E-10	8.E-06	3.E-06	3.E-06
57-12-5	Cyanide, Total	5	4.E-08	1.E-08	5.E-28	3.E-06	7.E-07	9.E-10	8.E-06	3.E-06	3.E-06
7439-92-1	Lead-DISS	13	9.E-08	3.E-08	1.E-27	7.E-06	2.E-06	2.E-09	2.E-05	7.E-06	7.E-06
7439-93-2	Lithium-DISS	61,350	4.E-04	1.E-04	6.E-24	3.E-02	9.E-03	1.E-05	1.E-01	3.E-02	3.E-02
7439-96-5	Manganese-DISS	2,975	2.E-05	6.E-06	3.E-25	1.E-03	4.E-04	6.E-07	5.E-03	2.E-03	2.E-03
7439-97-6	Mercury-DISS	0	7.E-10	2.E-10	9.E-30	5.E-08	1.E-08	2.E-11	2.E-07	5.E-08	5.E-08
7439-98-7	Molybdenum-DISS	84	6.E-07	2.E-07	8.E-27	4.E-05	1.E-05	2.E-08	1.E-04	4.E-05	4.E-05
7440-02-0	Nickel-DISS	20	1.E-07	4.E-08	2.E-27	1.E-05	3.E-06	4.E-09	3.E-05	1.E-05	1.E-05
7782-49-2	Selenium-DISS	3	2.E-08	6.E-09	3.E-28	2.E-06	4.E-07	6.E-10	5.E-06	2.E-06	2.E-06
7440-22-4	Silver-DISS	3	2.E-08	6.E-09	3.E-28	2.E-06	4.E-07	6.E-10	5.E-06	2.E-06	2.E-06
7440-24-6	Strontium-DISS	1,300,000	9.E-03	3.E-03	1.E-22	7.E-01	2.E-01	2.E-04	2.E+00	7.E-01	7.E-01
14808-79-8	Sulfate	500,000	4.E-03	1.E-03	5.E-23	3.E-01	7.E-02	9.E-05	8.E-01	3.E-01	3.E-01
7440-28-0	Thallium-DISS	5	4.E-08	1.E-08	5.E-28	3.E-06	7.E-07	9.E-10	8.E-06	3.E-06	3.E-06
7440-31-5	Tin-DISS	500	4.E-06	1.E-06	5.E-26	3.E-04	7.E-05	9.E-08	8.E-04	3.E-04	3.E-04
7440-32-6	Titanium-DISS	250	2.E-06	5.E-07	2.E-26	1.E-04	4.E-05	5.E-08	4.E-04	1.E-04	1.E-04
7440-66-6	Zinc-DISS	147	1.E-06	3.E-07	1.E-26	7.E-05	2.E-05	3.E-08	2.E-04	7.E-05	8.E-05
105-67-9	2,4-Dimethylphenol	5	4.E-08	1.E-08	5.E-28	3.E-06	7.E-07	9.E-10	8.E-06	3.E-06	3.E-06
91-57-6	2-Methylnaphthalene	3	2.E-08	5.E-09	2.E-28	1.E-06	4.E-07	5.E-10	4.E-06	1.E-06	1.E-06
95-48-7	2-Methylphenol	5	4.E-08	1.E-08	5.E-28	3.E-06	7.E-07	9.E-10	8.E-06	3.E-06	3.E-06
108-39-4/10	3/4-methylphenol	5	4.E-08	1.E-08	5.E-28	3.E-06	7.E-07	9.E-10	8.E-06	3.E-06	3.E-06
83-32-9	Acenaphthene	1	7.E-09	2.E-09	9.E-29	5.E-07	1.E-07	2.E-10	2.E-06	5.E-07	5.E-07
98-86-2	Acetophenone	5	4.E-08	1.E-08	5.E-28	3.E-06	7.E-07	9.E-10	8.E-06	3.E-06	3.E-06
100-51-6	Benzyl alcohol	5	4.E-08	1.E-08	5.E-28	3.E-06	7.E-07	9.E-10	8.E-06	3.E-06	3.E-06
117-81-7	Bis(2-ethylhexyl)phthalate	5	4.E-08	1.E-08	5.E-28	3.E-06	7.E-07	9.E-10	8.E-06	3.E-06	3.E-06
218-01-9	Chrysene	1	7.E-09	2.E-09	9.E-29	5.E-07	1.E-07	2.E-10	2.E-06	5.E-07	5.E-07
84-66-2	Diethyl phthalate	5	4.E-08	1.E-08	5.E-28	3.E-06	7.E-07	9.E-10	8.E-06	3.E-06	3.E-06
84-74-2	Di-n-butyl phthalate	5	4.E-08	1.E-08	5.E-28	3.E-06	7.E-07	9.E-10	8.E-06	3.E-06	3.E-06
117-84-0	Di-n-octyl phthalate	5	4.E-08	1.E-08	5.E-28	3.E-06	7.E-07	9.E-10	8.E-06	3.E-06	3.E-06
206-44-0	Fluoranthene	1	7.E-09	2.E-09	9.E-29	5.E-07	1.E-07	2.E-10	2.E-06	5.E-07	5.E-07
86-73-7	Fluorene	1	7.E-09	2.E-09	9.E-29	5.E-07	1.E-07	2.E-10	2.E-06	5.E-07	5.E-07
85-01-8	Phenanthrene	1	7.E-09	2.E-09	9.E-29	5.E-07	1.E-07	2.E-10	2.E-06	5.E-07	5.E-07
108-95-2	Phenol	1	7.E-09	2.E-09	9.E-29	5.E-07	1.E-07	2.E-10	2.E-06	5.E-07	5.E-07
64743-03-9	Phenols	18	1.E-07	4.E-08	2.E-27	9.E-06	3.E-06	3.E-09	3.E-05	9.E-06	9.E-06
129-00-0	Pyrene	1	7.E-09	2.E-09	9.E-29	5.E-07	1.E-07	2.E-10	2.E-06	5.E-07	5.E-07
110-86-1	Pyridine	14	1.E-07	3.E-08	1.E-27	7.E-06	2.E-06	3.E-09	2.E-05	7.E-06	7.E-06
87-61-6	1,2,3-Trichlorobenzene	3	2.E-08	5.E-09	2.E-28	1.E-06	4.E-07	5.E-10	4.E-06	1.E-06	1.E-06

Table 5.7 Summary of Flowback Fluid Constituent Exposure Point Concentrations (EPCs) Used in Risk Analysis

CAS	Parameter	Highest Median (µg/L)	EPC at 50th Percentile DF (µg/L)			EPC at 90th Percentile DF (µg/L)			EPC at 95th Percentile DF (µg/L)		
			Surface Water		Groundwater	Surface Water		Groundwater	Surface Water		Groundwater
			Arid/ Semi-Arid	Temperate/ Semi-Humid		Arid/ Semi-Arid	Temperate/ Semi-Humid		Arid/ Semi-Arid	Temperate/ Semi-Humid	
95-63-6	1,2,4 trimethylbenzene	5	4.E-08	1.E-08	5.E-28	3.E-06	7.E-07	9.E-10	8.E-06	3.E-06	3.E-06
108-67-8	1,3,5-Trimethylbenzene	5	4.E-08	1.E-08	5.E-28	3.E-06	7.E-07	9.E-10	8.E-06	3.E-06	3.E-06
107-06-2	1,2-Dichloroethane	5	4.E-08	1.E-08	5.E-28	3.E-06	7.E-07	9.E-10	8.E-06	3.E-06	3.E-06
78-93-3	2-Butanone	3	2.E-08	5.E-09	2.E-28	1.E-06	4.E-07	5.E-10	4.E-06	1.E-06	1.E-06
99-87-6	4-Isopropyltoluene	5	4.E-08	1.E-08	5.E-28	3.E-06	7.E-07	9.E-10	8.E-06	3.E-06	3.E-06
67-64-1	Acetone	37	3.E-07	8.E-08	3.E-27	2.E-05	6.E-06	7.E-09	6.E-05	2.E-05	2.E-05
71-43-2	Benzene	480	3.E-06	1.E-06	4.E-26	2.E-04	7.E-05	9.E-08	8.E-04	2.E-04	3.E-04
75-15-0	Carbon Disulfide	3	2.E-08	6.E-09	3.E-28	2.E-06	4.E-07	6.E-10	5.E-06	2.E-06	2.E-06
100-41-4	Ethyl Benzene	54	4.E-07	1.E-07	5.E-27	3.E-05	8.E-06	1.E-08	9.E-05	3.E-05	3.E-05
98-82-8	Isopropylbenzene (cumene)	3	2.E-08	6.E-09	3.E-28	2.E-06	4.E-07	6.E-10	5.E-06	2.E-06	2.E-06
75-09-2	Methylene Chloride	3	2.E-08	6.E-09	3.E-28	2.E-06	4.E-07	6.E-10	5.E-06	2.E-06	2.E-06
91-20-3	Naphthalene	3	2.E-08	6.E-09	3.E-28	2.E-06	4.E-07	6.E-10	5.E-06	2.E-06	2.E-06
103-65-1	n-Propylbenzene	5	4.E-08	1.E-08	5.E-28	3.E-06	7.E-07	9.E-10	8.E-06	3.E-06	3.E-06
108-88-3	Toluene	833	6.E-06	2.E-06	8.E-26	4.E-04	1.E-04	2.E-07	1.E-03	4.E-04	4.E-04
1330-20-7	xylenes	444	3.E-06	9.E-07	4.E-26	2.E-04	7.E-05	8.E-08	7.E-04	2.E-04	2.E-04
95-47-6	o-Xylene	5	4.E-08	1.E-08	5.E-28	3.E-06	7.E-07	9.E-10	8.E-06	3.E-06	3.E-06
64-19-7	Acetic acid	116,300	8.E-04	2.E-04	1.E-23	6.E-02	2.E-02	2.E-05	2.E-01	6.E-02	6.E-02
64-17-5	Ethanol	5,000	4.E-05	1.E-05	5.E-25	3.E-03	7.E-04	9.E-07	8.E-03	3.E-03	3.E-03
107-21-1	Ethylene glycol	25,000	2.E-04	5.E-05	2.E-24	1.E-02	4.E-03	5.E-06	4.E-02	1.E-02	1.E-02
67-63-0	Isopropanol	5,000	4.E-05	1.E-05	5.E-25	3.E-03	7.E-04	9.E-07	8.E-03	3.E-03	3.E-03
67-56-1	Methanol	5,000	4.E-05	1.E-05	5.E-25	3.E-03	7.E-04	9.E-07	8.E-03	3.E-03	3.E-03
71-36-3	n-Butanol	5,000	4.E-05	1.E-05	5.E-25	3.E-03	7.E-04	9.E-07	8.E-03	3.E-03	3.E-03
79-09-4	Propionic Acid	28,600	2.E-04	6.E-05	3.E-24	1.E-02	4.E-03	5.E-06	5.E-02	1.E-02	2.E-02
64-18-6	Formic acid	1,200	9.E-06	2.E-06	1.E-25	6.E-04	2.E-04	2.E-07	2.E-03	6.E-04	6.E-04
NORM		**pCi/L**									
	RA 228	504	4.E-06	1.E-06	5.E-26	3.E-04	8.E-05	1.E-07	8.E-04	3.E-04	3.E-04
	RA 226	611	4.E-06	1.E-06	6.E-26	3.E-04	9.E-05	1.E-07	1.E-03	3.E-04	3.E-04
	Uranium 238	0.061	4.E-10	1.E-10	6.E-30	3.E-08	9.E-09	1.E-11	1.E-07	3.E-08	3.E-08
	Uranium 235	0	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00
	PB 214	174	1.E-06	4.E-07	2.E-26	9.E-05	3.E-05	3.E-08	3.E-04	9.E-05	9.E-05
	PB 212	60	4.E-07	1.E-07	5.E-27	3.E-05	9.E-06	1.E-08	1.E-04	3.E-05	3.E-05
	Gross alpha [a]	6,845	5.E-05	1.E-05	6.E-25	3.E-03	1.E-03	1.E-06	1.E-02	3.E-03	4.E-03
	Gross beta [a]	1,170	8.E-06	2.E-06	1.E-25	6.E-04	2.E-04	2.E-07	2.E-03	6.E-04	6.E-04
Notes:		DF =	1.4E+08	4.9E+08	1.1E+28	2.0E+06	6.7E+06	5.3E+09	592,480	1,982,300	1.9E+06

"-DISS" suffix indicates dissolved results.

"Highest Median" = highest median from multiple data sets (see Appendix A).

DF = Dilution Factor.

[a] Rowan *et al.* (2011) reports that gross alpha and gross beta are likely dominated by RA-226 and RA-228 sources.

6 Human Health Chemical Hazard Analysis

Once we had determined concentrations of constituents of HF fluids and flowback fluid that might be found in drinking water in the event of a spill, the next step in the analysis was to determine whether these concentration levels might pose a human health risk. In order to do this, following established US EPA risk assessment guidelines and methods (US EPA, 1996), we determined "risk-based concentrations" (RBCs) in drinking water for the various constituents of the HESI HF fluid systems and the flowback fluid from HF operations. RBCs represent the chemical concentration in drinking water that would not be expected to pose human health risks. Individuals exposed to concentrations of a chemical below its RBC would not be expected to experience adverse health effects. This section summarizes the methods we used to determine the RBCs we used as health-protective benchmarks in this risk analysis. More detailed information is presented in Appendix D.

6.1 Overview

As reflected in the HESI HF fluid systems, a wide variety of additives and their associated chemical constituents could be used in HF operations in oil and gas plays in tight formations across the country. In Section 6.2, we provide information noting the common uses of many of the HF constituents we considered in our analysis. While that information is not intended for developing chemical RBCs, it does provide perspective on the ordinary occurrences and household uses of some of the HF constituents. We describe the hierarchy we used to determine the chemical-specific RBCs in Section 6.3. As we describe, we preferentially adopted established health-protective drinking water concentrations such as drinking water maximum contaminant levels (MCLs), US EPA tap water Regional Screening Levels (RSLs), and Agency-established toxicity criteria/factors whenever available to determine RBCs. For chemicals lacking this information, we describe the methods used to derive an RBC from published toxicity studies, or to identify toxicity information from chemical surrogates. For the small number of chemicals without quantitative toxicity information, we provide qualitative information on human hazard potential when quantitative risks could not be evaluated.

6.2 Common Uses and Occurrence of HF Constituents

A number of HF constituents are relatively benign compounds used as food additives, are present in a wide variety of household/personal care products, and/or occur naturally in the environment:

- Food Grade Compounds. Many of the HF compounds have been determined by the US Food and Drug Administration (US FDA) to be "Generally Recognized as Safe" or GRAS. This means that when present in food at appropriate concentrations, these compounds do not constitute a health risk. Examples of GRAS compounds used as HF constituents include hydrochloric acid, citric acid, hydrogen peroxide, acetic acid, calcium chloride, ammonium chloride, and sucrose (US FDA, 2006a, 2009a,b). Similarly, US FDA has approved additional food additives appropriate for use under certain conditions (*e.g.*, up to a concentration threshold in certain food products). Examples of these compounds present in HF fluids include: ammonium persulfate, propylene glycol, and formaldehyde (US FDA, 2009c).
- Inert Compounds. US EPA's Office of Pesticide Programs (OPP) has published a list of chemicals considered "minimal risk" inert ingredients found in pesticide products that do not

require tolerance limits when used in accordance with good agricultural and manufacturing practices.[57] Some of the HF chemicals falling into this inert category include: glycerine, sodium benzoate, sodium acetate, and sodium sulfate (US EPA, 2009c).

- Common Household/Personal Care Products: A number of HF constituents are present in household/personal care products. Ethylene glycol, methanol, monoethanolamine, hydrochloric acid, propylene glycol, and lactose are examples of HF constituents found in common household cleaning products. Examples of HF constituents in personal care products include: formaldehyde (hand soap, body wash), cellulose (mascara), citric acid (shampoo, body wash, hand soap, conditioner), and lactose (face scrub, retinol treatment). In addition, 2-ethyl hexanol, ethyl alcohol, triethylene glycol, and propane-1,2-diol (or propylene glycol) are HF constituents that are approved for use in fragrances found in food or personal care products (NLM, 2009; US EPA, 2007).
- Polymers: Several of the HF constituents are polymers – large molecules made up of repeating chemical structural units. Because of their large size polymers have a low potential to cause adverse effects, especially *via* oral and dermal routes. US EPA (2001) stated "polymers with molecular weights greater than 400 generally are not absorbed through the intact skin and substances with molecular weights greater than 1,000 generally are not absorbed through the gastrointestinal (GI) tract. Chemicals not absorbed through the skin or GI tract generally are incapable of eliciting a toxic response. Therefore, there is no reasonable expectation of risk due to cumulative exposure."
- Naturally Occurring Compounds: A number of HF constituents are naturally occurring compounds, *i.e.*, most individuals are exposed to these substances on a daily basis without any adverse effects. Examples of HF compounds naturally found in the environment include: sodium chloride, carbon dioxide, ammonium chloride, fatty acids, guar gum, and sodium carbonate (US EPA, 2009a; JRank Science & Philosophy, Undated; Ingersoll *et al*., 2009; Rhodes, 2008; JECFA, 2006; Daisy *et al*., 2002; Feldman, 2005). Acrylamide (found in some HF constituent polymers) forms naturally during the cooking of certain foods (US FDA, 2006b).

6.3 Hierarchy for Determining RBCs

We used a tiered approach to identify or develop health-protective RBCs for the HF and flowback fluid constituents. Use of tiered hierarchies for defining constituent hazard/toxicity is a standard risk assessment practice (US EPA, 2003, 2012a). This sequential methodology is described below and depicted in Figure 6.1:

- We preferentially used promulgated chemical-specific drinking water Maximum Contaminant Levels (MCLs) as RBCs where available (US EPA, 2009b), as the MCLs represent federally-established acceptable drinking water standards for contaminants that may be found in public water supplies.
- For chemicals lacking an MCL, we used risk-based "tap water" Regional Screening Levels (RSLs) published by the US EPA (2012a) as the RBC, where they were available. RSLs are based on the chronic risks associated with drinking water consumption, and are US EPA-recommended benchmarks for use in screening-level risk assessments (US EPA, 2012d).
- If neither MCLs nor RSLs were available, we used quantitative oral toxicity factors published by US regulatory agencies to calculate health-protective RBCs (US EPA, 1993). The RBCs

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[57] In some cases, some restrictions are specified.

calculated in this manner were based on exposure assumptions consistent with US EPA's RSL methodology (US EPA, 2012a). The specific hierarchy of Agency sources from which the published toxicity factors were obtained is described in Appendix D.

- For compounds that did not have an MCL, RSL, or an established oral toxicity factor, we obtained primary repeated dose oral toxicity data (*i.e.*, a study duration of at least 28 days) for the compound or its surrogate, and derived a chronic Reference Dose (RfD) *de novo* (which we then used to calculate an RBC). The chronic toxicity data in these studies included No Observed Adverse Effect Levels (NOAELs) and/or Lowest Observed Adverse Effect Levels (LOAELs); to be health-protective, we selected the lowest reported NOAEL or LOAEL, if multiple studies were available. We derived an RfD following US EPA methods defined in the Integrated Risk Information System (IRIS), using the NOAEL/LOAEL in conjunction with the appropriate safety factors recommended by US EPA guidance (US EPA, 2002).

More detailed information on the specific sources and methods used to establish the chemical RBCs is presented in Appendix D. Table D.2 contains all the chemical RBCs used in this risk analysis.

6.4 HF Constituents with No RBCs

For HF components that did not have quantitative chronic oral toxicity information, we were unable to derive an RBC. For these 12 components, we performed a qualitative assessment and cross-referenced the component against government regulatory lists indicating if the chemical was Generally Recognized as Safe (US FDA), a minimal risk inert pesticide ingredient (US EPA), or met the requirements for determination of a "low risk" polymers (US EPA). Of these 12 compounds, four (4) are classified as inert/low hazard constituents. More detailed information on the specific sources and methods used to qualitatively evaluate these chemicals is presented in Appendix D. The "RBC Basis Notes" column in Table D.2 contains the results of this qualitative assessment.

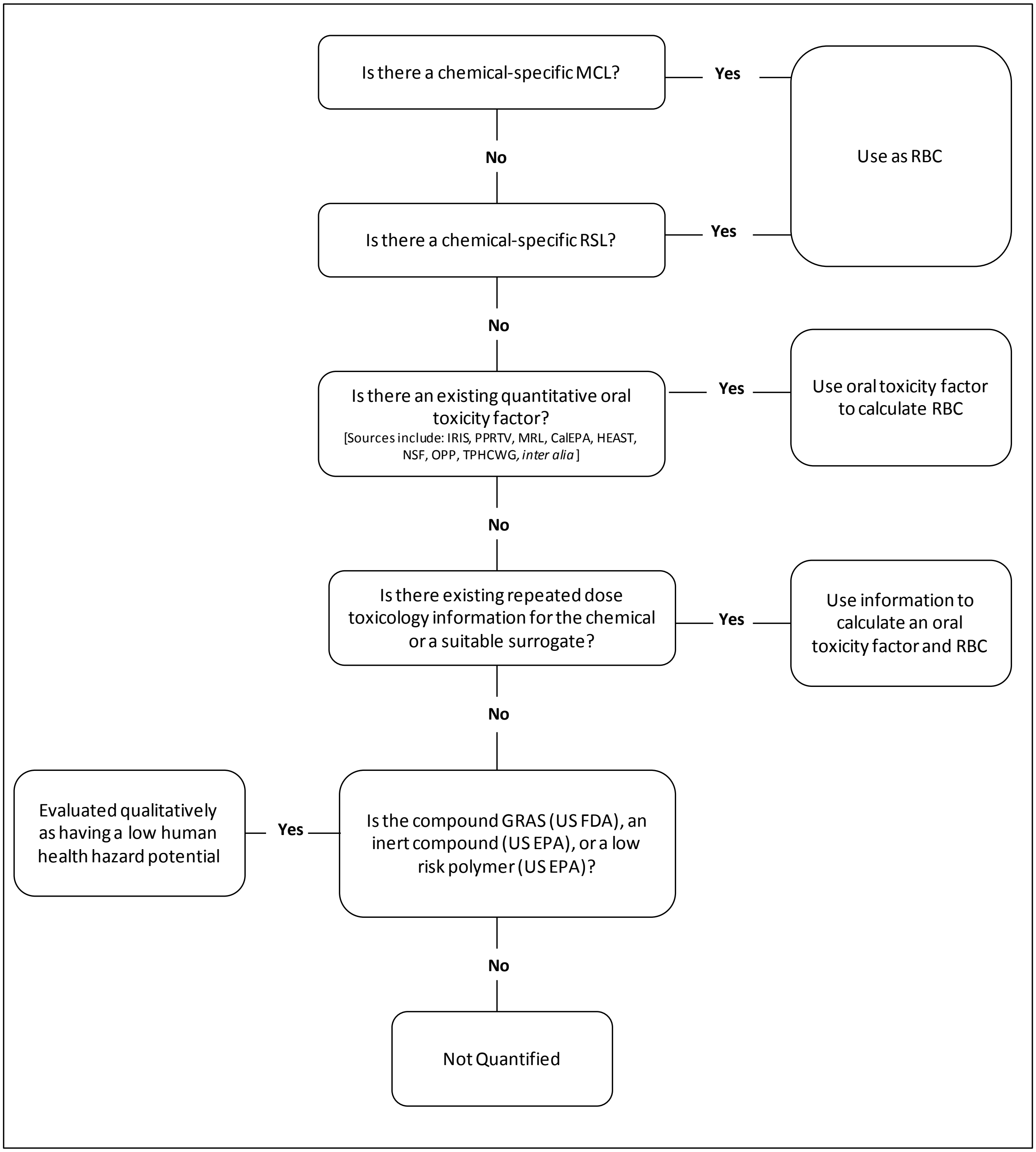

Figure 6.1 Toxicological Information Hierarchy in the Human Health Risk Evaluation

7 Risk Characterization

This section discusses the approach used and the results of the human health risk analysis for potential drinking water exposures associated with the use of HF fluids in tight formations across the country. As noted in Section 5, our analysis showed that given the extremely low probability that HF fluids would escape from a properly constructed well and the implausibility of HF fluids migrating upward from a target formation to reach a drinking water aquifer, we did not quantify those risks.

We did quantify the potential risks associated with accidental spills of HF constituents. In the risk characterization step for these spills, the chemical risk based concentrations (RBCs) we developed as health-protective benchmarks (as discussed in Section 6), were compared to the predicted exposure concentrations of the HF constituents in groundwater and surface water (Section 5), to assess the potential for human health risks.

The human health risk characterization for our analysis is presented as an HQ,[58] or hazard quotient, relating the estimated HF chemical concentration in drinking water (based on dilution for each respective pathway as described in Section 5), to the concentration below which adverse health effects are not expected, *i.e.*, the chemical's RBC:

$$HQ = \frac{C_{HF}/_{DF}}{RBC}$$

The numerator of this equation gives the concentration in the drinking water (where the DF is the dilution factor for the particular exposure pathway). Calculated HQ values less than 1 (*i.e.*, the exposure concentration in drinking water is less than the compound's health-based RBC) indicate no adverse health effects are anticipated.

Our probabilistic approach produced a distribution of DF values, and thus it also produces a corresponding distribution of HQ values (the RBCs are a single value for each chemical). In order to provide a conservative, health protective, indication of the results of our analysis, we have summarized the results for not only the central tendency (50th percentile DF values) but also several upper percentiles in the output (HQ) distribution (*e.g.*, 90th and 95th percentile DF values). As noted earlier, each of these percentiles represents the cumulative probability that a DF is greater than or equal to the associated DF value (*e.g.*, the 95th percentile DF means that the DF was greater than or equal to the particular DF in 95% of the Monte Carlo simulations, and less than the particular value of the DF in 5% of the simulations).

When considering the results from this probabilistic analysis, it is important to understand what the results reported for any particular DF percentile represent. The DF percentiles are based on the presumption that a spill has occurred (that is, they are a function of spill volume and other environmental variables). However, as discussed earlier, the likelihood of spills occurring during HF activities, based on the experience in Pennsylvania, is 3.3%.[59] Using this spill frequency, there is a 96.7% likelihood

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[58] Note, the HQ value in our analysis is an indicator of whether the computed exposure concentration exceeds the health-based RBC, regardless of the constituent's toxicity end point or mode of action.

[59] The way we have conducted this part of the analysis may result in an undercounting of the number of "unconventional" wells drilled to which the number of spills at "unconventional" well sites should be compared, leading to a potential overestimation of the rate of spills at these well sites.

(probability) that there would be no release of HF constituents at all during typical HF operations, and thus 96.7% of the HQs would be zero (no exposure).

In order to determine the overall likelihood, or probability, of any particular HQ outcome for a given well, the spill probability, and cumulative probability of any particular DF must be combined using the following expression:

Overall HQ Probability = (100% - Spill Frequency) + (Spill Frequency × DF Percentile/100)

For example, the HQ for isopropanol for the surface water pathway in an arid or semi-arid climate where there is typical (50th percentile) dilution is 1×10^{-7} (0.0000001). This means that *if* a spill occurs in an arid climate, there is a 50% chance that the HQ associated with the surface water pathway will be less than 1×10^{-7}. Using a 3.3% spill rate, there is an overall likelihood of 98.4% that a given well in an arid or semi-arid region will experience a maximum HQ of 1×10^{-7} or less for isopropanol. Similarly, the HQ for isopropanol for the 95th percentile DF for surface water in an arid or semi-arid region is 3×10^{-5} (0.00003). Using the same 3.3% spill rate, this means there is a 99.8% probability that the same well in an arid or semi-arid region would experience a maximum HQ of 3×10^{-5} for the surface water pathway.

7.1 HESI HF Constituents

As summarized in Table 7.1, for both the surface water and groundwater exposure pathways, the calculated HQ values for all constituents in the typical HESI HF fluids are less than one (1.0) at the 50th, 90th, and 95th percentile DF values (98.4%, 99.7%, and 99.8% overall probability). As summarized earlier (Section 5), we examined the range of HF constituent concentrations for the HESI HF systems. This is because several of the different HF systems may contain some of the same chemicals, but at different concentrations. As a conservative approach, we used the maximum chemical concentrations across all HESI HF systems in calculating the HQs.

We also summed the individual chemical HQs to calculate an overall Hazard Index ("HI") for each of the typical HESI HF fluid systems. This approach is a common risk assessment practice in order to provide insight on the potential health impacts associated with exposure to multiple chemicals. However, an HI must be interpreted with caution because different chemicals very often have different toxicity endpoints (*e.g.*, chemicals can affect different internal organs, some effects may be neurological while others affect growth, *etc.*). When chemicals do not exhibit similar health effects, summing their HQs to determine a Hazard Index for their combined impacts is not necessarily meaningful. Nevertheless, by convention we have summed the chemical HQs for each of the HF fluid systems as a conservative (*i.e.*, health-protective) approach. The Hazard Indices for surface spills of individual HF stages are summarized in Table 7.2 for both the surface water and groundwater exposure pathways. As shown in these tables, the Hazard Indices are less than 1.0, at the 50th, 90th and 95th percentile DF values (98.4%, 99.7%, and 99.8% overall probability).

These individual HQs, and overall HF fluid system HI results provide a high degree of confidence that there would be little likelihood of potential human health concerns associated with the potential for surface spills of HF fluid or flowback fluid.

As noted, we did not quantify human health risks associated with migration of HF constituents from tight oil and gas formations to overlying potable aquifers. As discussed in Section 5, the DFs for this hypothetical migration pathway are much greater than the DFs utilized in the surface spill scenarios for which we have quantified the possible human health risks. Any potential risks associated with migration of HF constituents from tight oil and gas formations would be many times lower than those we have quantified.

These results indicate that the potential human health risks posed by constituents present in typical HESI HF fluid systems *via* drinking water exposures are insignificant, as defined by Agency-based guidelines. These risks can be viewed as insignificant because even using a number of conservative assumptions that collectively yield conservative – possibly unrealistically conservative – results, the calculated HQs were generally orders of magnitude less than 1, and the Hazard Indices were also less than 1.

7.2 Flowback Fluid Constituents

Hazard Quotients were quantified for the surface spill scenario using the flowback fluid data reported in Section 2. The calculated HQ values for all flowback fluid constituents for the surface water and groundwater pathways (Table 7.3) are below 1 at the 50th, 90th and 95th percentile DF values (98.4%, 99.7%, and 99.8% overall probability). Similar to the case for HF systems, we also computed a Hazard Index (HI) by summing the HQs for all the individual flowback fluid constituents, and the HI for flowback fluid is also less than 1 (Table 7.3).

These results indicate that the potential human health risks posed by constituents measured in HF flowback fluid *via* drinking water exposures are insignificant, as defined by Agency-based guidelines.

Table 7.1 Summary of Chemical Hazard Quotients (HQs) Associated with Maximum Chemical Concentrations for HESI HF Sytems

CAS No.	Chemical	RBC (µg/L)	HQ at 50th Percentile DF			HQ at 90th Percentile DF			HQ at 95th Percentile DF		
			Surface Water		Groundwater	Surface Water		Groundwater	Surface Water		Groundwater
			Arid/ Semi-Arid	Temperate/ Semi-Humid		Arid/ Semi-Arid	Temperate/ Semi-Humid		Arid/ Semi-Arid	Temperate/ Semi-Humid	
		Max HQ:	**0.0002**	**0.00005**	**2.E-24**	**0.01**	**0.003**	**4.E-06**	**0.04**	**0.01**	**1.E-02**
CBI	Aldehyde	1250	2.E-05	5.E-06	2.E-25	1.E-03	4.E-04	5.E-07	4.E-03	1.E-03	1.E-03
68410-62-8	Naphthenic acid ethoxylate	500	4.E-05	1.E-05	5.E-25	3.E-03	8.E-04	1.E-06	9.E-03	3.E-03	3.E-03
71-48-7	Cobalt acetate	4.7	2.E-04	5.E-05	2.E-24	1.E-02	3.E-03	4.E-06	4.E-02	1.E-02	1.E-02
CBI	Alkyl sulfonate	5000	3.E-06	1.E-06	4.E-26	2.E-04	7.E-05	9.E-08	8.E-04	2.E-04	2.E-04
631-61-8	Ammonium acetate	300	2.E-05	4.E-06	2.E-25	1.E-03	3.E-04	4.E-07	4.E-03	1.E-03	1.E-03
64742-48-9	Naphtha, hydrotreated heavy	1,500	1.E-05	4.E-06	2.E-25	9.E-04	3.E-04	4.E-07	3.E-03	1.E-03	1.E-03
107-19-7	Propargyl alcohol	31	1.E-05	4.E-06	2.E-25	9.E-04	3.E-04	3.E-07	3.E-03	9.E-04	9.E-04
CBI	EDTA/Copper chelate	630	1.E-05	3.E-06	1.E-25	7.E-04	2.E-04	3.E-07	2.E-03	7.E-04	7.E-04
61791-26-2	Polyoxylated fatty amine salt	1,080	8.E-06	2.E-06	1.E-25	5.E-04	2.E-04	2.E-07	2.E-03	6.E-04	6.E-04
7681-82-5	Sodium iodide	160	7.E-06	2.E-06	8.E-26	5.E-04	1.E-04	2.E-07	2.E-03	5.E-04	5.E-04
7727-54-0	Ammonium persulfate	205	5.E-06	2.E-06	7.E-26	4.E-04	1.E-04	1.E-07	1.E-03	4.E-04	4.E-04
111-40-0	Diethylenetriamine	350	4.E-06	1.E-06	5.E-26	3.E-04	9.E-05	1.E-07	1.E-03	3.E-04	3.E-04
111-76-2	Ethylene glycol monobutyl ether	1,600	4.E-06	1.E-06	5.E-26	3.E-04	9.E-05	1.E-07	1.E-03	3.E-04	3.E-04
81741-28-8	Tributyl tetradecyl phosphonium chloride	43	4.E-06	1.E-06	5.E-26	3.E-04	8.E-05	1.E-07	1.E-03	3.E-04	3.E-04
7758-19-2	Chlorous acid, sodium salt	1,000	3.E-06	1.E-06	4.E-26	2.E-04	7.E-05	9.E-08	8.E-04	2.E-04	3.E-04
67-56-1	Methanol	7,800	3.E-06	8.E-07	4.E-26	2.E-04	6.E-05	7.E-08	7.E-04	2.E-04	2.E-04
7775-27-1	Sodium persulfate	455	6.E-06	2.E-06	8.E-26	4.E-04	1.E-04	2.E-07	1.E-03	4.E-04	4.E-04
590-29-4	Potassium formate	64,600	5.E-08	1.E-08	6.E-28	3.E-06	1.E-06	1.E-09	1.E-05	3.E-06	4.E-06
12125-02-9	Ammonium chloride	3,420	2.E-06	6.E-07	3.E-26	1.E-04	4.E-05	5.E-08	5.E-04	1.E-04	1.E-04
111-46-6	Diethylene glycol	1,500	1.E-06	4.E-07	2.E-26	1.E-04	3.E-05	4.E-08	3.E-04	1.E-04	1.E-04
13709-94-9	Potassium metaborate	3,100	1.E-06	4.E-07	2.E-26	1.E-04	3.E-05	4.E-08	3.E-04	1.E-04	1.E-04
68551-12-2	Alcohols, C12-16, ethoxylated	5,625	1.E-06	4.E-07	2.E-26	9.E-05	3.E-05	4.E-08	3.E-04	9.E-05	1.E-04
CBI	Borate salt	3,100	1.E-06	4.E-07	2.E-26	9.E-05	3.E-05	3.E-08	3.E-04	9.E-05	9.E-05
1319-33-1	Ulexite	3,100	1.E-06	4.E-07	2.E-26	9.E-05	3.E-05	3.E-08	3.E-04	9.E-05	9.E-05
61791-14-8	Amines, coco alkyl, ethoxylated	3,750	1.E-06	3.E-07	1.E-26	8.E-05	2.E-05	3.E-08	3.E-04	8.E-05	9.E-05
64742-94-5	Heavy aromatic petroleum naphtha	600	1.E-06	3.E-07	1.E-26	8.E-05	2.E-05	3.E-08	3.E-04	8.E-05	8.E-05
64742-47-8	Hydrotreated light petroleum distillate	1,500	1.E-06	3.E-07	1.E-26	8.E-05	2.E-05	3.E-08	3.E-04	8.E-05	8.E-05
95-63-6	1,2,4 Trimethylbenzene	15	9.E-07	2.E-07	1.E-26	6.E-05	2.E-05	2.E-08	2.E-04	6.E-05	6.E-05
CBI	Terpenoid	12,500	8.E-08	2.E-08	1.E-27	5.E-06	2.E-06	2.E-09	2.E-05	6.E-06	6.E-06
CBI	Fatty acid tall oil	125,000	6.E-08	2.E-08	7.E-28	4.E-06	1.E-06	1.E-09	1.E-05	4.E-06	4.E-06
7681-52-9	Sodium hypochlorite	475	6.E-07	2.E-07	7.E-27	4.E-05	1.E-05	1.E-08	1.E-04	4.E-05	4.E-05
CBI	Guar gum derivative	81,413	5.E-07	1.E-07	6.E-27	3.E-05	1.E-05	1.E-08	1.E-04	3.E-05	3.E-05
64-17-5	Ethanol	12,000	4.E-07	1.E-07	6.E-27	3.E-05	9.E-06	1.E-08	1.E-04	3.E-05	3.E-05
CBI	Fatty acid tall oil amide	500	3.E-07	1.E-07	4.E-27	2.E-05	7.E-06	9.E-09	8.E-05	2.E-05	3.E-05
9000-30-0	Guar gum	81,413	3.E-07	9.E-08	4.E-27	2.E-05	6.E-06	8.E-09	7.E-05	2.E-05	2.E-05
CBI	Olefin	500	3.E-07	9.E-08	4.E-27	2.E-05	6.E-06	8.E-09	7.E-05	2.E-05	2.E-05
127087-87-0	Nonylphenol ethoxylated	10,000	3.E-08	7.E-09	3.E-28	2.E-06	5.E-07	7.E-10	6.E-06	2.E-06	2.E-06
91-20-3	Naphthalene	310	2.E-07	7.E-08	3.E-27	2.E-05	5.E-06	7.E-09	6.E-05	2.E-05	2.E-05
CBI	Terpenoid	12,500	2.E-08	7.E-09	3.E-28	2.E-06	5.E-07	6.E-10	6.E-06	2.E-06	2.E-06
108-24-7	Acetic anhydride	214,200	2.E-07	6.E-08	3.E-27	2.E-05	4.E-06	6.E-09	5.E-05	2.E-05	2.E-05
10486-00-7	Sodium perborate tetrahydrate	5,000	2.E-07	5.E-08	2.E-27	1.E-05	4.E-06	5.E-09	4.E-05	1.E-05	1.E-05
68951-67-7	Alcohols, C14-C15, ethoxylated	5,625	2.E-07	5.E-08	2.E-27	1.E-05	4.E-06	4.E-09	4.E-05	1.E-05	1.E-05
64-19-7	Acetic acid	214,200	1.E-07	4.E-08	2.E-27	1.E-05	3.E-06	4.E-09	3.E-05	1.E-05	1.E-05
67-63-0	Isopropanol	150,000	1.E-07	4.E-08	2.E-27	9.E-06	3.E-06	3.E-09	3.E-05	9.E-06	1.E-05
CBI	Quaternary ammonium compound	6,600	1.E-07	4.E-08	2.E-27	9.E-06	3.E-06	3.E-09	3.E-05	9.E-06	9.E-06
121888-68-4	Bentonite, benzyl(hydrogenated tallow alkyl) dimethylammonium stearate complex	5,000	1.E-07	3.E-08	1.E-27	7.E-06	2.E-06	3.E-09	3.E-05	8.E-06	8.E-06
78330-21-9	Ethoxylated branched C13 alcohol	5,625	9.E-08	3.E-08	1.E-27	6.E-06	2.E-06	2.E-09	2.E-05	6.E-06	7.E-06
52-51-7	2-Bromo-2-nitro-1,3-propanediol	1,500	9.E-08	2.E-08	1.E-27	6.E-06	2.E-06	2.E-09	2.E-05	6.E-06	6.E-06
CBI	Ethoxylate fatty acid	15,000	8.E-08	2.E-08	1.E-27	6.E-06	2.E-06	2.E-09	2.E-05	6.E-06	6.E-06
CBI	Ethoxylated fatty acid	15,000	8.E-08	2.E-08	1.E-27	6.E-06	2.E-06	2.E-09	2.E-05	6.E-06	6.E-06
7772-98-7	Sodium thiosulfate	500,000	5.E-08	1.E-08	7.E-28	4.E-06	1.E-06	1.E-09	1.E-05	4.E-06	4.E-06
CBI	Surfactant mixture	3,900	4.E-08	1.E-08	5.E-28	3.E-06	8.E-07	1.E-09	9.E-06	3.E-06	3.E-06
9012-54-8	Hemicellulase enzyme	600	4.E-08	1.E-08	5.E-28	3.E-06	7.E-07	9.E-10	8.E-06	3.E-06	3.E-06
10043-52-4	Calcium chloride	50,000	3.E-09	1.E-09	4.E-29	2.E-07	7.E-08	9.E-11	8.E-07	2.E-07	3.E-07
7757-83-7	Sodium sulfite	7,200	3.E-08	9.E-09	4.E-28	2.E-06	6.E-07	8.E-10	7.E-06	2.E-06	2.E-06

Table 7.1 Summary of Chemical Hazard Quotients (HQs) Associated with Maximum Chemical Concentrations for HESI HF Sytems

CAS No.	Chemical	RBC (µg/L)	HQ at 50th Percentile DF			HQ at 90th Percentile DF			HQ at 95th Percentile DF		
			Surface Water		Groundwater	Surface Water		Groundwater	Surface Water		Groundwater
			Arid/ Semi-Arid	Temperate/ Semi-Humid		Arid/ Semi-Arid	Temperate/ Semi-Humid		Arid/ Semi-Arid	Temperate/ Semi-Humid	
		Max HQ:	**0.0002**	**0.00005**	**2.E-24**	**0.01**	**0.003**	**4.E-06**	**0.04**	**0.01**	**1.E-02**
CBI	Ethoxylate fatty acid	28,625	3.E-08	8.E-09	4.E-28	2.E-06	6.E-07	7.E-10	7.E-06	2.E-06	2.E-06
50-00-0	Formaldehyde	3,100	3.E-08	8.E-09	3.E-28	2.E-06	6.E-07	7.E-10	6.E-06	2.E-06	2.E-06
14808-60-7	Crystalline silica, quartz	37,500	7.E-09	2.E-09	9.E-29	5.E-07	1.E-07	2.E-10	2.E-06	5.E-07	5.E-07
CBI	Olefin	5,000	2.E-08	5.E-09	2.E-28	1.E-06	4.E-07	5.E-10	5.E-06	1.E-06	1.E-06
3468-63-1	C.I. Pigment Orange 5	125	2.E-08	5.E-09	2.E-28	1.E-06	3.E-07	4.E-10	4.E-06	1.E-06	1.E-06
7631-86-9	Silica, amorphous -– fumed	37,500	5.E-09	1.E-09	7.E-29	4.E-07	1.E-07	1.E-10	1.E-06	4.E-07	4.E-07
CBI	Inorganic salt	50,000	2.E-08	4.E-09	2.E-28	1.E-06	3.E-07	4.E-10	4.E-06	1.E-06	1.E-06
CBI	Proprietary	9,000	1.E-08	4.E-09	2.E-28	1.E-06	3.E-07	4.E-10	4.E-06	1.E-06	1.E-06
7722-76-1	Ammonium phosphate	30,000	1.E-08	4.E-09	2.E-28	1.E-06	3.E-07	4.E-10	3.E-06	1.E-06	1.E-06
CBI	Surfactant mixture	5,625	1.E-08	4.E-09	2.E-28	1.E-06	3.E-07	4.E-10	3.E-06	1.E-06	1.E-06
CBI	Olefin	500	1.E-08	4.E-09	2.E-28	9.E-07	3.E-07	3.E-10	3.E-06	9.E-07	9.E-07
1310-73-2	Sodium hydroxide	492,857	8.E-09	2.E-09	1.E-28	6.E-07	2.E-07	2.E-10	2.E-06	6.E-07	6.E-07
584-08-7	Potassium carbonate	1,005,000	8.E-09	2.E-09	1.E-28	6.E-07	2.E-07	2.E-10	2.E-06	6.E-07	6.E-07
68953-58-2	Quaternary ammonium compounds, bis(hydrogenated tallow alkyl) dimethyl,salts with bentonite	62,500	8.E-09	2.E-09	1.E-28	5.E-07	2.E-07	2.E-10	2.E-06	6.E-07	6.E-07
7647-14-5	Sodium chloride	1,243,500	7.E-09	2.E-09	9.E-29	5.E-07	2.E-07	2.E-10	2.E-06	5.E-07	5.E-07
71-23-8	Propanol	43,575	6.E-09	2.E-09	8.E-29	4.E-07	1.E-07	2.E-10	2.E-06	4.E-07	5.E-07
56-81-5	Glycerine	400,000	5.E-10	2.E-10	7.E-30	4.E-08	1.E-08	1.E-11	1.E-07	4.E-08	4.E-08
7791-18-6	Magnesium chloride hexahydrate	75,000	5.E-09	1.E-09	6.E-29	3.E-07	1.E-07	1.E-10	1.E-06	3.E-07	3.E-07
CBI	Fatty acid ester	9,000	4.E-09	1.E-09	5.E-29	3.E-07	8.E-08	1.E-10	9.E-07	3.E-07	3.E-07
7757-82-6	Sodium sulfate	500,000	3.E-09	1.E-09	4.E-29	2.E-07	7.E-08	9.E-11	8.E-07	2.E-07	3.E-07
9004-32-4	Sodium carboxymethyl cellulose	585,000	1.E-10	3.E-11	1.E-30	8.E-09	2.E-09	3.E-12	3.E-08	8.E-09	8.E-09
112926-00-8	Silica gel	37,500	7.E-10	2.E-10	9.E-30	5.E-08	1.E-08	2.E-11	2.E-07	5.E-08	5.E-08
CBI	Carbohydrate	105,000	2.E-09	5.E-10	2.E-29	1.E-07	4.E-08	5.E-11	4.E-07	1.E-07	1.E-07
CBI	Olefin	5,000	1.E-09	4.E-10	2.E-29	9.E-08	3.E-08	3.E-11	3.E-07	9.E-08	9.E-08
144-55-8	Sodium bicarbonate	856,500	9.E-10	3.E-10	1.E-29	6.E-08	2.E-08	2.E-11	2.E-07	6.E-08	7.E-08
1310-58-3	Potassium hydroxide	1,005,000	3.E-10	1.E-10	4.E-30	2.E-08	7.E-09	9.E-12	8.E-08	2.E-08	2.E-08
2836-32-0	Sodium glycolate	3,750	3.E-10	8.E-11	4.E-30	2.E-08	6.E-09	8.E-12	7.E-08	2.E-08	2.E-08
CBI	Fatty acid ester ethoxylate	5,000	5.E-09	1.E-09	6.E-29	3.E-07	9.E-08	1.E-10	1.E-06	3.E-07	3.E-07
12174-11-7	Attapulgite	1,920,000	9.E-11	3.E-11	1.E-30	6.E-09	2.E-09	2.E-12	2.E-08	7.E-09	7.E-09
94266-47-4	Citrus, extract	[a]									
CBI	Cured acrylic resin	[a]									
9043-30-5	Fatty alcohol polyglycol ether surfactant	[a]									
CBI	Oxylated phenolic resin	[a]									
15619-48-4	Chloromethylnaphthalene quinoline quaternary amine	[b]									
CBI	Organic phosphonate	[b]									
CBI	Oxylated phenolic resin	[b]									
CBI	Polyacrylamide copolymer	[b]									
CBI	Quaternary ammonium salt	[b]									
68527-49-1	Reaction product of acetophenone, formaldehyde, thiourea and oleic acid in dimethyl formamide	[b]									
101033-44-7	Triethanolamine zirconate	[b]									
68909-34-2	Zirconium, acetate lactate oxo ammonium complexes	[b]									
7647-01-0	Hydrochloric acid	7	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]
Notes:		DF =	1.4E+08	4.9E+08	1.1E+28	2.0E+06	6.7E+06	5.3E+09	592,480	1,982,300	1,900,000

CBI = Confidential Business Information; DF = Dilution Factor.

[a] Inert compounds or low hazard polymers. See Appendix D.

[b] No quantitative toxicity data.

[c] Hydrochloric acid will not persist after spill.

Table 7.2 Summary of Hazard Indices for HESI HF Fluid Systems

Formulation	Phase	HF Volume (gal)	Hazard Index at 50th Percentile DF			Hazard Index at 90th Percentile DF			Hazard Index at 95th Percentile DF		
			Surface Water		Groundwater	Surface Water		Groundwater	Surface Water		Groundwater
			Arid/ Semi-Arid	Temperate/ Semi-Humid		Arid/ Semi-Arid	Temperate/ Semi-Humid		Arid/ Semi-Arid	Temperate/ Semi-Humid	
		Max Hazard Index:	**0.0002**	**0.0001**	**3.E-24**	**0.01**	**0.004**	**5.E-06**	**0.05**	**0.01**	**1.E-02**
Foam frac 01	TW	5,340	6.E-06	2.E-06	7.E-26	4.E-04	1.E-04	2.E-07	1.E-03	4.E-04	4.E-04
Foam frac 01	XLF	22,082	2.E-04	6.E-05	3.E-24	1.E-02	4.E-03	5.E-06	5.E-02	1.E-02	1.E-02
Foam frac 01	TW + XLF	27,422	2.E-04	5.E-05	2.E-24	1.E-02	3.E-03	4.E-06	4.E-02	1.E-02	1.E-02
Foam frac 01	TW + XLF+Pre03	32,422	1.E-04	4.E-05	2.E-24	1.E-02	3.E-03	4.E-06	3.E-02	1.E-02	1.E-02
Foam frac 01	TW + XLF+Pre01	61,422	8.E-05	2.E-05	1.E-24	6.E-03	2.E-03	2.E-06	2.E-02	6.E-03	6.E-03
Foam frac 01	TW + XLF+Pre02	100,422	1.E-04	3.E-05	1.E-24	7.E-03	2.E-03	3.E-06	2.E-02	7.E-03	7.E-03
Gel frac 01	XLF	1,915,000	6.E-06	2.E-06	7.E-26	4.E-04	1.E-04	2.E-07	1.E-03	4.E-04	4.E-04
Gel frac 01	XLF	1,915,000	6.E-06	2.E-06	7.E-26	4.E-04	1.E-04	2.E-07	1.E-03	4.E-04	4.E-04
Gel frac 01	XLF+Pre03	1,920,000	6.E-06	2.E-06	7.E-26	4.E-04	1.E-04	2.E-07	1.E-03	4.E-04	4.E-04
Gel frac 01	XLF+Pre01	1,949,000	6.E-06	2.E-06	8.E-26	4.E-04	1.E-04	2.E-07	1.E-03	4.E-04	4.E-04
Gel frac 01	XLF+Pre02	1,988,000	8.E-06	2.E-06	1.E-25	6.E-04	2.E-04	2.E-07	2.E-03	6.E-04	6.E-04
Hybrid frac 01	LF	170,000	2.E-05	5.E-06	2.E-25	1.E-03	4.E-04	5.E-07	4.E-03	1.E-03	1.E-03
Hybrid frac 01	WF	4,500,000	4.E-06	1.E-06	5.E-26	2.E-04	7.E-05	9.E-08	8.E-04	2.E-04	3.E-04
Hybrid frac 01	LF + WF	4,670,000	4.E-06	1.E-06	5.E-26	3.E-04	9.E-05	1.E-07	1.E-03	3.E-04	3.E-04
Hybrid frac 01	LF + WF+Pre03	4,675,000	4.E-06	1.E-06	5.E-26	3.E-04	9.E-05	1.E-07	1.E-03	3.E-04	3.E-04
Hybrid frac 01	LF + WF+Pre01	4,704,000	4.E-06	1.E-06	5.E-26	3.E-04	9.E-05	1.E-07	1.E-03	3.E-04	3.E-04
Hybrid frac 01	LF + WF+Pre02	4,743,000	5.E-06	1.E-06	7.E-26	4.E-04	1.E-04	1.E-07	1.E-03	4.E-04	4.E-04
Hybrid frac 02	TW	816,750	7.E-06	2.E-06	9.E-26	5.E-04	1.E-04	2.E-07	2.E-03	5.E-04	5.E-04
Hybrid frac 02	XLF	2,329,000	1.E-05	4.E-06	2.E-25	9.E-04	3.E-04	3.E-07	3.E-03	9.E-04	9.E-04
Hybrid frac 02	TW + XLF	3,145,750	1.E-05	3.E-06	1.E-25	8.E-04	2.E-04	3.E-07	3.E-03	8.E-04	8.E-04
Hybrid frac 02	TW + XLF+Pre03	3,150,750	1.E-05	3.E-06	1.E-25	8.E-04	2.E-04	3.E-07	3.E-03	8.E-04	8.E-04
Hybrid frac 02	TW + XLF+Pre01	3,179,750	1.E-05	3.E-06	1.E-25	8.E-04	2.E-04	3.E-07	3.E-03	8.E-04	8.E-04
Hybrid frac 02	TW + XLF+Pre02	3,218,750	1.E-05	4.E-06	2.E-25	9.E-04	3.E-04	3.E-07	3.E-03	9.E-04	9.E-04
Hybrid frac 03	LF	29,203	9.E-06	3.E-06	1.E-25	6.E-04	2.E-04	2.E-07	2.E-03	6.E-04	6.E-04
Hybrid frac 03	XLF	97,000	5.E-06	1.E-06	6.E-26	3.E-04	1.E-04	1.E-07	1.E-03	3.E-04	3.E-04
Hybrid frac 03	LF+XLF	126,203	6.E-06	2.E-06	7.E-26	4.E-04	1.E-04	1.E-07	1.E-03	4.E-04	4.E-04
Hybrid frac 03	LF+XLF+Pre03	131,203	6.E-06	2.E-06	8.E-26	4.E-04	1.E-04	2.E-07	1.E-03	4.E-04	4.E-04
Hybrid frac 03	LF+XLF+Pre01	160,203	8.E-06	2.E-06	1.E-25	5.E-04	2.E-04	2.E-07	2.E-03	5.E-04	6.E-04
Hybrid frac 03	LF+XLF+Pre02	199,203	3.E-05	9.E-06	4.E-25	2.E-03	7.E-04	8.E-07	8.E-03	2.E-03	2.E-03
Hybrid frac 04	TW	393,700	3.E-06	9.E-07	4.E-26	2.E-04	7.E-05	8.E-08	7.E-04	2.E-04	2.E-04
Hybrid frac 04	Flush	461,993	3.E-06	7.E-07	3.E-26	2.E-04	5.E-05	7.E-08	6.E-04	2.E-04	2.E-04
Hybrid frac 04	XLF	2,154,500	2.E-05	7.E-06	3.E-25	2.E-03	5.E-04	6.E-07	6.E-03	2.E-03	2.E-03
Hybrid frac 04	TW+XLF+Flush	3,010,193	2.E-05	5.E-06	2.E-25	1.E-03	4.E-04	5.E-07	4.E-03	1.E-03	1.E-03
Hybrid frac 04	TW+XLF+Flush+Pre03	3,015,193	2.E-05	5.E-06	2.E-25	1.E-03	4.E-04	5.E-07	4.E-03	1.E-03	1.E-03
Hybrid frac 04	TW+XLF+Flush+Pre01	3,044,193	2.E-05	5.E-06	2.E-25	1.E-03	4.E-04	5.E-07	4.E-03	1.E-03	1.E-03
Hybrid frac 04	TW+XLF+Flush+Pre02	3,083,193	2.E-05	6.E-06	3.E-25	1.E-03	4.E-04	5.E-07	5.E-03	1.E-03	1.E-03

Table 7.2 Summary of Hazard Indices for HESI HF Fluid Systems

Formulation	Phase	HF Volume (gal)	Hazard Index at 50th Percentile DF			Hazard Index at 90th Percentile DF			Hazard Index at 95th Percentile DF		
			Surface Water			Surface Water			Surface Water		
			Arid/ Semi-Arid	Temperate/ Semi-Humid	Groundwater	Arid/ Semi-Arid	Temperate/ Semi-Humid	Groundwater	Arid/ Semi-Arid	Temperate/ Semi-Humid	Groundwater
		Max Hazard Index:	**0.0002**	**0.0001**	**3.E-24**	**0.01**	**0.004**	**5.E-06**	**0.05**	**0.01**	**1.E-02**
Hybrid frac 05	TW	849,000	4.E-06	1.E-06	5.E-26	3.E-04	8.E-05	1.E-07	9.E-04	3.E-04	3.E-04
Hybrid frac 05	XLF	1,247,100	2.E-05	5.E-06	2.E-25	1.E-03	4.E-04	5.E-07	4.E-03	1.E-03	1.E-03
Hybrid frac 05	TW+XLF	2,096,100	1.E-05	4.E-06	2.E-25	9.E-04	3.E-04	3.E-07	3.E-03	9.E-04	9.E-04
Hybrid frac 05	TW+XLF+Pre03	2,101,100	1.E-05	4.E-06	2.E-25	9.E-04	3.E-04	3.E-07	3.E-03	9.E-04	9.E-04
Hybrid frac 05	TW+XLF+Pre01	2,130,100	1.E-05	4.E-06	2.E-25	9.E-04	3.E-04	3.E-07	3.E-03	9.E-04	9.E-04
Hybrid frac 05	TW+XLF+Pre02	2,169,100	1.E-05	4.E-06	2.E-25	1.E-03	3.E-04	4.E-07	3.E-03	1.E-03	1.E-03
Hybrid frac 06	TW	7,000	2.E-05	6.E-06	3.E-25	1.E-03	4.E-04	5.E-07	5.E-03	1.E-03	1.E-03
Hybrid frac 06	LF	175,680	2.E-05	5.E-06	2.E-25	1.E-03	3.E-04	4.E-07	4.E-03	1.E-03	1.E-03
Hybrid frac 06	XLF	1,179,324	2.E-05	5.E-06	2.E-25	1.E-03	4.E-04	5.E-07	4.E-03	1.E-03	1.E-03
Hybrid frac 06	LF+XLF+TW	1,362,004	2.E-05	5.E-06	2.E-25	1.E-03	4.E-04	5.E-07	4.E-03	1.E-03	1.E-03
Hybrid frac 06	LF+XLF+TW+Pre03	1,367,004	2.E-05	5.E-06	2.E-25	1.E-03	4.E-04	5.E-07	4.E-03	1.E-03	1.E-03
Hybrid frac 06	LF+XLF+TW+Pre01	1,396,004	2.E-05	5.E-06	2.E-25	1.E-03	4.E-04	5.E-07	4.E-03	1.E-03	1.E-03
Hybrid frac 06	LF+XLF+TW+Pre02	1,435,004	2.E-05	6.E-06	3.E-25	1.E-03	4.E-04	5.E-07	5.E-03	1.E-03	1.E-03
Water frac 01	WF	4,500,000	4.E-06	1.E-06	5.E-26	2.E-04	7.E-05	9.E-08	8.E-04	2.E-04	3.E-04
Water frac 01	WF	4,500,000	4.E-06	1.E-06	5.E-26	2.E-04	7.E-05	9.E-08	8.E-04	2.E-04	3.E-04
Water frac 01	WF+Pre03	4,505,000	4.E-06	1.E-06	5.E-26	2.E-04	7.E-05	9.E-08	8.E-04	2.E-04	3.E-04
Water frac 01	WF+Pre01	4,534,000	4.E-06	1.E-06	5.E-26	3.E-04	8.E-05	1.E-07	9.E-04	3.E-04	3.E-04
Water frac 01	WF+Pre02	4,573,000	5.E-06	1.E-06	6.E-26	3.E-04	1.E-04	1.E-07	1.E-03	3.E-04	3.E-04
Water frac 02	WF	4,500,000	4.E-06	1.E-06	5.E-26	3.E-04	8.E-05	1.E-07	9.E-04	3.E-04	3.E-04
Water frac 02	WF	4,500,000	4.E-06	1.E-06	5.E-26	3.E-04	8.E-05	1.E-07	9.E-04	3.E-04	3.E-04
Water frac 02	WF+Pre03	4,505,000	4.E-06	1.E-06	5.E-26	3.E-04	8.E-05	1.E-07	9.E-04	3.E-04	3.E-04
Water frac 02	WF+Pre01	4,534,000	4.E-06	1.E-06	5.E-26	3.E-04	8.E-05	1.E-07	9.E-04	3.E-04	3.E-04
Water frac 02	WF+Pre02	4,573,000	5.E-06	1.E-06	6.E-26	3.E-04	1.E-04	1.E-07	1.E-03	3.E-04	4.E-04
Water frac 03	WF	7,310,000	3.E-06	8.E-07	3.E-26	2.E-04	6.E-05	7.E-08	6.E-04	2.E-04	2.E-04
Water frac 03	WF	7,310,000	3.E-06	8.E-07	3.E-26	2.E-04	6.E-05	7.E-08	6.E-04	2.E-04	2.E-04
Water frac 03	WF+Pre03	7,315,000	3.E-06	8.E-07	3.E-26	2.E-04	6.E-05	7.E-08	6.E-04	2.E-04	2.E-04
Water frac 03	WF+Pre01	7,344,000	3.E-06	8.E-07	3.E-26	2.E-04	6.E-05	7.E-08	6.E-04	2.E-04	2.E-04
Water frac 03	WF+Pre02	7,383,000	3.E-06	1.E-06	4.E-26	2.E-04	7.E-05	9.E-08	8.E-04	2.E-04	3.E-04
Water frac 04	Flush	204,600	6.E-07	2.E-07	7.E-27	4.E-05	1.E-05	2.E-08	1.E-04	4.E-05	4.E-05
Water frac 04	LF	502,200	3.E-06	8.E-07	3.E-26	2.E-04	6.E-05	7.E-08	6.E-04	2.E-04	2.E-04
Water frac 04	LF+Flush	706,800	2.E-06	6.E-07	3.E-26	1.E-04	4.E-05	6.E-08	5.E-04	1.E-04	2.E-04
Water frac 04	LF+Flush+Pre03	711,800	2.E-06	6.E-07	3.E-26	2.E-04	5.E-05	6.E-08	5.E-04	2.E-04	2.E-04
Water frac 04	LF+Flush+Pre01	740,800	3.E-06	8.E-07	3.E-26	2.E-04	6.E-05	7.E-08	6.E-04	2.E-04	2.E-04
Water frac 04	LF+Flush+Pre02	779,800	9.E-06	3.E-06	1.E-25	6.E-04	2.E-04	2.E-07	2.E-03	6.E-04	7.E-04
Notes:		DF =	1.4E+08	4.9E+08	1.1E+28	2.0E+06	6.7E+06	5.3E+09	592,480	2.0E+06	1.9E+06

DF = Dilution Factor; LF = Linear Fluid; TW = Treated Water; XLF = Cross-linked Fluid.

Pre01, Pre02, Pre03: Pre-fracturing acid treatments.

Table 7.3 Summary of Chemical Hazard Quotients (HQs) Associated with Highest Median Flowback Fluid Chemical Concentrations

CAS	Parameter	Highest Median Concentration (µg/L)	RBC (µg/L)	HQ at 50th Percentile DF			HQ at 90th Percentile DF			HQ at 95th Percentile DF		
				Surface Water		Groundwater	Surface Water		Groundwater	Surface Water		Groundwater
				Arid/ Semi-Arid	Temperate/ Semi-Humid		Arid/ Semi-Arid	Temperate/ Semi-Humid		Arid/ Semi-Arid	Temperate/ Semi-Humid	
			Max Chem. HQ:	0.00001	0.000004	2.E-25	0.001	0.0003	4E-07	0.003	0.001	0.00104
7429-90-5	Aluminum-DISS	227	16,000	1.E-10	3.E-11	1.E-30	7.E-09	2.E-09	3.E-12	2.E-08	7.E-09	7.E-09
7440-36-0	Antimony-DISS	5	6	6.E-09	2.E-09	8.E-29	4.E-07	1.E-07	2.E-10	1.E-06	4.E-07	4.E-07
7440-38-2	Arsenic-DISS	13	10	9.E-09	3.E-09	1.E-28	7.E-07	2.E-07	2.E-10	2.E-06	7.E-07	7.E-07
7440-39-3	Barium-DISS	496,000	2,000	2.E-06	5.E-07	2.E-26	1.E-04	4.E-05	5.E-08	4.E-04	1.E-04	1.E-04
7440-42-8	Boron-DISS	12,400	3,100	3.E-08	8.E-09	4.E-28	2.E-06	6.E-07	8.E-10	7.E-06	2.E-06	2.E-06
24959-67-9	Bromide	607,000	2,000	2.E-06	6.E-07	3.E-26	2.E-04	5.E-05	6.E-08	5.E-04	2.E-04	2.E-04
7440-43-9	Cadmium-DISS	3	5	4.E-09	1.E-09	5.E-29	3.E-07	9.E-08	1.E-10	1.E-06	3.E-07	3.E-07
7440-47-3	Chromium	82	100	6.E-09	2.E-09	7.E-29	4.E-07	1.E-07	2.E-10	1.E-06	4.E-07	4.E-07
7440-47-3	Chromium (VI)	5	100	4.E-10	1.E-10	5.E-30	3.E-08	7.E-09	9.E-12	8.E-08	3.E-08	3.E-08
7440-47-3	Chromium (VI)-diss	539	100	4.E-08	1.E-08	5.E-28	3.E-06	8.E-07	1.E-09	9.E-06	3.E-06	3.E-06
7440-47-3	Chromium III	25	100	2.E-09	5.E-10	2.E-29	1.E-07	4.E-08	5.E-11	4.E-07	1.E-07	1.E-07
7440-47-3	Chromium-DISS	7	100	5.E-10	1.E-10	6.E-30	4.E-08	1.E-08	1.E-11	1.E-07	4.E-08	4.E-08
7440-48-4	Cobalt-DISS	250	4.7	4.E-07	1.E-07	5.E-27	3.E-05	8.E-06	1.E-08	9.E-05	3.E-05	3.E-05
7440-50-8	Copper-DISS	13	1,300	7.E-11	2.E-11	9.E-31	5.E-09	1.E-09	2.E-12	2.E-08	5.E-09	5.E-09
57-12-5	Cyanide, Total	5	9.4	4.E-09	1.E-09	5.E-29	3.E-07	8.E-08	1.E-10	9.E-07	3.E-07	3.E-07
57-12-5	Cyanide, Total	5	9.4	4.E-09	1.E-09	5.E-29	3.E-07	8.E-08	1.E-10	9.E-07	3.E-07	3.E-07
7439-92-1	Lead-DISS	13	15	6.E-09	2.E-09	8.E-29	4.E-07	1.E-07	2.E-10	1.E-06	4.E-07	5.E-07
7439-93-2	Lithium-DISS	61,350	31	1.E-05	4.E-06	2.E-25	1.E-03	3.E-04	4.E-07	3.E-03	1.E-03	1.E-03
7439-96-5	Manganese-DISS	2,975	380	6.E-08	2.E-08	7.E-28	4.E-06	1.E-06	1.E-09	1.E-05	4.E-06	4.E-06
7439-97-6	Mercury-DISS	0	2	4.E-10	1.E-10	5.E-30	3.E-08	7.E-09	9.E-12	8.E-08	3.E-08	3.E-08
7439-98-7	Molybdenum-DISS	84	78	8.E-09	2.E-09	1.E-28	5.E-07	2.E-07	2.E-10	2.E-06	5.E-07	6.E-07
7440-02-0	Nickel-DISS	20	310	5.E-10	1.E-10	6.E-30	3.E-08	1.E-08	1.E-11	1.E-07	3.E-08	3.E-08
7782-49-2	Selenium-DISS	3	78	3.E-10	8.E-11	3.E-30	2.E-08	6.E-09	7.E-12	6.E-08	2.E-08	2.E-08
7440-22-4	Silver-DISS	3	78	3.E-10	8.E-11	3.E-30	2.E-08	6.E-09	7.E-12	6.E-08	2.E-08	2.E-08
7440-24-6	Strontium-DISS	1,300,000	9,400	1.E-06	3.E-07	1.E-26	7.E-05	2.E-05	3.E-08	2.E-04	7.E-05	7.E-05
14808-79-8	Sulfate	500,000	500,000	7.E-09	2.E-09	9.E-29	5.E-07	1.E-07	2.E-10	2.E-06	5.E-07	5.E-07
7440-28-0	Thallium-DISS	5	0.16	2.E-07	6.E-08	3.E-27	2.E-05	5.E-06	6.E-09	5.E-05	2.E-05	2.E-05
7440-31-5	Tin-DISS	500	9,400	4.E-10	1.E-10	5.E-30	3.E-08	8.E-09	1.E-11	9.E-08	3.E-08	3.E-08
7440-32-6	Titanium-DISS	250	45,000	4.E-11	1.E-11	5.E-31	3.E-09	8.E-10	1.E-12	9.E-09	3.E-09	3.E-09
7440-66-6	Zinc-DISS	147	4,700	2.E-10	6.E-11	3.E-30	2.E-08	5.E-09	6.E-12	5.E-08	2.E-08	2.E-08
105-67-9	2,4-Dimethylphenol	5	310	1.E-10	3.E-11	1.E-30	8.E-09	2.E-09	3.E-12	3.E-08	8.E-09	8.E-09
91-57-6	2-Methylnaphthalene	3	63	3.E-10	9.E-11	4.E-30	2.E-08	6.E-09	8.E-12	7.E-08	2.E-08	2.E-08
95-48-7	2-Methylphenol	5	780	5.E-11	1.E-11	6.E-31	3.E-09	1.E-09	1.E-12	1.E-08	3.E-09	3.E-09
108-39-4/10	3/4-methylphenol (RBC based on 3-methylphenol)	5	780	5.E-11	1.E-11	6.E-31	3.E-09	1.E-09	1.E-12	1.E-08	3.E-09	3.E-09
83-32-9	Acenaphthene	1	940	8.E-12	2.E-12	1.E-31	5.E-10	2.E-10	2.E-13	2.E-09	5.E-10	6.E-10
98-86-2	Acetophenone	5	1,600	2.E-11	6.E-12	3.E-31	2.E-09	5.E-10	6.E-13	5.E-09	2.E-09	2.E-09
100-51-6	Benzyl alcohol	5	1,600	2.E-11	6.E-12	3.E-31	2.E-09	5.E-10	6.E-13	5.E-09	2.E-09	2.E-09
117-81-7	Bis(2-ethylhexyl)phthalate	5	4.8	7.E-09	2.E-09	9.E-29	5.E-07	2.E-07	2.E-10	2.E-06	5.E-07	5.E-07
218-01-9	Chrysene	1	2.9	2.E-09	7.E-10	3.E-29	2.E-07	5.E-08	7.E-11	6.E-07	2.E-07	2.E-07
84-66-2	Diethyl phthalate	5	13,000	3.E-12	8.E-13	3.E-32	2.E-10	6.E-11	7.E-14	6.E-10	2.E-10	2.E-10
84-74-2	Di-n-butyl phthalate	5	1,600	2.E-11	6.E-12	3.E-31	2.E-09	5.E-10	6.E-13	5.E-09	2.E-09	2.E-09
117-84-0	Di-n-octyl phthalate	5	190	2.E-10	5.E-11	2.E-30	1.E-08	4.E-09	5.E-12	4.E-08	1.E-08	1.E-08
206-44-0	Fluoranthene	1	630	1.E-11	3.E-12	1.E-31	8.E-10	2.E-10	3.E-13	3.E-09	8.E-10	8.E-10
86-73-7	Fluorene	1	630	1.E-11	3.E-12	1.E-31	8.E-10	2.E-10	3.E-13	3.E-09	8.E-10	8.E-10
85-01-8	Phenanthrene	1	600	1.E-11	3.E-12	2.E-31	8.E-10	2.E-10	3.E-13	3.E-09	8.E-10	9.E-10
108-95-2	Phenol	1	4,700	2.E-12	4.E-13	2.E-32	1.E-10	3.E-11	4.E-14	4.E-10	1.E-10	1.E-10
64743-03-9	Phenols	18	4,700	3.E-11	8.E-12	3.E-31	2.E-09	6.E-10	7.E-13	6.E-09	2.E-09	2.E-09
129-00-0	Pyrene	1	470	2.E-11	4.E-12	2.E-31	1.E-09	3.E-10	4.E-13	4.E-09	1.E-09	1.E-09
110-86-1	Pyridine	14	16	6.E-09	2.E-09	8.E-29	4.E-07	1.E-07	2.E-10	1.E-06	4.E-07	5.E-07
87-61-6	1,2,3-Trichlorobenzene	3	13	1.E-09	4.E-10	2.E-29	1.E-07	3.E-08	4.E-11	3.E-07	1.E-07	1.E-07
95-63-6	1,2,4 trimethylbenzene	5	15	2.E-09	7.E-10	3.E-29	2.E-07	5.E-08	6.E-11	6.E-07	2.E-07	2.E-07

Table 7.3 Summary of Chemical Hazard Quotients (HQs) Associated with Highest Median Flowback Fluid Chemical Concentrations

CAS	Parameter	Highest Median Concentration (µg/L)	RBC (µg/L)	HQ at 50th Percentile DF			HQ at 90th Percentile DF			HQ at 95th Percentile DF		
				Surface Water		Groundwater	Surface Water		Groundwater	Surface Water		Groundwater
				Arid/ Semi-Arid	Temperate/ Semi-Humid		Arid/ Semi-Arid	Temperate/ Semi-Humid		Arid/ Semi-Arid	Temperate/ Semi-Humid	
			Max Chem. HQ:	**0.00001**	**0.000004**	**2.E-25**	**0.001**	**0.0003**	**4E-07**	**0.003**	**0.001**	**0.00104**
108-67-8	1,3,5-Trimethylbenzene	5	160	2.E-10	6.E-11	3.E-30	2.E-08	5.E-09	6.E-12	5.E-08	2.E-08	2.E-08
107-06-2	1,2-Dichloroethane	5	16,000	2.E-12	6.E-13	3.E-32	2.E-10	5.E-11	6.E-14	5.E-10	2.E-10	2.E-10
78-93-3	2-Butanone	3	9,400	2.E-12	5.E-13	2.E-32	1.E-10	4.E-11	5.E-14	4.E-10	1.E-10	1.E-10
99-87-6	4-Isopropyltoluene	5	2,310	2.E-11	4.E-12	2.E-31	1.E-09	3.E-10	4.E-13	4.E-09	1.E-09	1.E-09
67-64-1	Acetone	37	14,000	2.E-11	5.E-12	2.E-31	1.E-09	4.E-10	5.E-13	4.E-09	1.E-09	1.E-09
71-43-2	Benzene	480	5	7.E-07	2.E-07	9.E-27	5.E-05	1.E-05	2.E-08	2.E-04	5.E-05	5.E-05
75-15-0	Carbon Disulfide	3	1,600	1.E-11	4.E-12	2.E-31	9.E-10	3.E-10	4.E-13	3.E-09	9.E-10	1.E-09
100-41-4	Ethyl Benzene	54	700	6.E-10	2.E-10	7.E-30	4.E-08	1.E-08	1.E-11	1.E-07	4.E-08	4.E-08
98-82-8	Isopropylbenzene (cumene)	3	1,600	1.E-11	4.E-12	2.E-31	9.E-10	3.E-10	4.E-13	3.E-09	9.E-10	1.E-09
75-09-2	Methylene Chloride	3	5	4.E-09	1.E-09	5.E-29	3.E-07	9.E-08	1.E-10	1.E-06	3.E-07	3.E-07
91-20-3	Naphthalene	3	310	7.E-11	2.E-11	9.E-31	5.E-09	1.E-09	2.E-12	2.E-08	5.E-09	5.E-09
103-65-1	n-Propylbenzene	5	530	7.E-11	2.E-11	9.E-31	5.E-09	1.E-09	2.E-12	2.E-08	5.E-09	5.E-09
108-88-3	Toluene	833	1,000	6.E-09	2.E-09	8.E-29	4.E-07	1.E-07	2.E-10	1.E-06	4.E-07	4.E-07
1330-20-7	xylenes	444	10,000	3.E-10	9.E-11	4.E-30	2.E-08	7.E-09	8.E-12	7.E-08	2.E-08	2.E-08
95-47-6	o-Xylene	5	10,000	4.E-12	1.E-12	5.E-32	3.E-10	7.E-11	9.E-14	8.E-10	3.E-10	3.E-10
64-19-7	Acetic acid	116,300	214,200	4.E-09	1.E-09	5.E-29	3.E-07	8.E-08	1.E-10	9.E-07	3.E-07	3.E-07
64-17-5	ethanol	5,000	12,000	3.E-09	9.E-10	4.E-29	2.E-07	6.E-08	8.E-11	7.E-07	2.E-07	2.E-07
107-21-1	ethylene glycol	25,000	31,000	6.E-09	2.E-09	7.E-29	4.E-07	1.E-07	2.E-10	1.E-06	4.E-07	4.E-07
67-63-0	Isopropanol	5,000	150,000	2.E-10	7.E-11	3.E-30	2.E-08	5.E-09	6.E-12	6.E-08	2.E-08	2.E-08
67-56-1	Methanol	5,000	7,800	5.E-09	1.E-09	6.E-29	3.E-07	1.E-07	1.E-10	1.E-06	3.E-07	3.E-07
71-36-3	n-Butanol	5,000	1,600	2.E-08	6.E-09	3.E-28	2.E-06	5.E-07	6.E-10	5.E-06	2.E-06	2.E-06
79-09-4	Propionic Acid	28,600	2,585	8.E-08	2.E-08	1.E-27	6.E-06	2.E-06	2.E-09	2.E-05	6.E-06	6.E-06
64-18-6	Formic acid	1,200	14,000	6.E-10	2.E-10	8.E-30	4.E-08	1.E-08	2.E-11	1.E-07	4.E-08	5.E-08
NORM		**pCi/L**	**RBC (pCi/L)**									
			Max NORM HQ:	**3.E-06**	**9.E-07**	**4.E-26**	**2.E-04**	**7.E-05**	**9.E-08**	**8.E-04**	**2.E-04**	**2.E-04**
	RA 228	504	5	7.E-07	2.E-07	9.E-27	5.E-05	2.E-05	2.E-08	2.E-04	5.E-05	5.E-05
	RA 226	611	5	9.E-07	2.E-07	1.E-26	6.E-05	2.E-05	2.E-08	2.E-04	6.E-05	6.E-05
	Uranium 238	0.061	0.607	7.E-10	2.E-10	9.E-30	5.E-08	1.E-08	2.E-11	2.E-07	5.E-08	5.E-08
	Uranium 235	0	0.737	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00
	PB 214	174	154	8.E-09	2.E-09	1.E-28	6.E-07	2.E-07	2.E-10	2.E-06	6.E-07	6.E-07
	PB 212	60	2.12	2.E-07	6.E-08	3.E-27	1.E-05	4.E-06	5.E-09	5.E-05	1.E-05	1.E-05
	Gross alpha	6,845	15	3.E-06	9.E-07	4.E-26	2.E-04	7.E-05	9.E-08	8.E-04	2.E-04	2.E-04
	Gross beta	1,170	[a]									
			Sum HQs =	3.E-05	7.E-06	3.E-25	2.E-03	5.E-04	7.E-07	6.E-03	2.E-03	2.E-03
Notes:			DF=	1.4E+08	4.9E+08	1.1E+28	2.0E+06	6.7E+06	5.3E+09	592,480	1,982,300	1.9E+06

Highest median concentration (see Appendix A.)

[a] Gross beta RBC 4 mrem/yr for all sources. Rowan *et al.* (2011) reported that RA-228 is likely dominant source of beta emissions. Using RBC of 5 pCi/L for gross beta, would give all HQs far below 1.

8 Conclusions

This study, which elaborates on a related analysis focused on the Marcellus Shale formation in New York (Gradient, 2012), addresses health risk concerns associated with the use of HF fluids in tight formations across the country and their potential impacts on drinking water. Our analysis encompasses both the intended use of these fluids as well as the potential human health impacts of unintended spills of fluids containing HF constituents.

As we have noted, oil and gas production wells are carefully constructed to isolate the fluids in the well from drinking water aquifers through which the well passes (zonal isolation) and there is very little likelihood that HF fluids would escape from a properly constructed well. Moreover, our earlier analysis of the Marcellus Shale formation in New York (Gradient, 2012), and our further analysis in this report, confirms that migration of HF fluid constituents from deeply buried tight formations up through overlying bedrock to a surface aquifer is an implausible chemical migration pathway. Tight oil and gas formations are set in very restrictive environments that inherently limit fluid migration due to the presence of multiple layers of low permeability rock, fluid density stratification and other factors. During the hydraulic fracturing phase, elevated HF pressures are applied for a short duration (a matter of hours/days). This period of elevated pressure is far too short to mobilize HF constituents upward through thousands of feet of bedrock – much of it of very low permeability – to potable aquifers. In addition, given the significant thickness of bedrock (typically thousands of feet) overlying target formations and the natural mechanisms that inhibit fracture propagation, the fracturing pressures are not expected to result in interconnected fractures to overlying potable aquifers. Moreover, our analysis, supported by fracture monitoring data, indicates that natural faults have been insignificant for enhancing upward fluid migration beyond the fracture network and there is no expectation that HF could initiate the types of large fault movements that might create a pathway for fluid migration to shallow potable groundwater. Finally, after the initial fracturing phase, development of the gas well – which includes recovery of flowback fluid – will cause any fluid (and HF constituents) within the well capture zone to flow preferentially toward the gas well rather than upward through the formation. Any fluids beyond the capture zone of the gas well will remain hydraulically isolated at depth due to the same mechanisms that have trapped saline water and hydrocarbons for hundreds of millions of years.

Even if groundwater migration from tight formations to a potable aquifer were hypothetically assumed, in comparison to the surface spill scenarios, dilution for upward migration from the target formation is expected to be significantly greater (if upward migration occurs at all). Considering that this DF is based on extreme assumptions (*e.g.*, assumed upward flow and high-end gradient) and does not account for dilution resulting from mixing of HF constituents with bedrock porewater, the DF is expected to be orders of magnitude higher than this computed value. Such large dilution under this implausible scenario would reduce HF fluid constituent concentrations in the overlying aquifer to concentrations well below health-based standards/benchmarks. Given the overall implausibility and high DF, this exposure pathway does not pose a threat to drinking water resources.

In our evaluation of potential impacts of unintended surface spills of HF fluid and flowback fluid, we adopted conservative (health protective) approaches in our analysis that more likely than not over predict the possible impacts of such spills should they occur (*e.g.*, 100% of the spill was assumed for this study to impact an underlying groundwater resource and 100% was also assumed to impact a nearby surface water resource). Using established methods and models, together with a probabilistic framework that covered a wide range of conditions, we estimated dilution factors for each exposure pathway to assess the possible concentrations of HF and flowback fluid constituents in drinking water that might result from hypothetical spills. We adopted Agency-established risk assessment methods to assess the potential human health risks associated with HF and flowback fluid constituents impacting potential ground water and surface water resources used for drinking water.

The results of our analysis indicate that potential human health risks associated with exposure to constituents in HESI HF fluids and flowback fluids *via* drinking water (and other household uses of water) as a result of spills are expected to be insignificant as defined by Agency-based risk management guidelines. Notwithstanding the numerous conservative assumptions (highlighted below) used in our analysis that, when taken together, would greatly overestimate risk, the concentration levels of constituents that we estimated could hypothetically be present in drinking water sources for purposes of this analysis were all less than their RBCs, *i.e.*, the concentration levels below which adverse health effects would not be expected to occur, at overall probability levels of greater than 99%. Moreover, even when the HF fluid systems or the flowback fluid is considered as a whole, the cumulative risk associated with these fluids is still insignificant (*i.e.*, the Hazard Indices for these fluids are less than 1.0 at overall probability levels of greater than 99%). Based on the range of spill scenarios evaluated and conservative analysis we employed, should such spills occur, associated exposure and human health risks are expected to be insignificant due to environmental dilution mechanisms which are expected to reduce concentrations in potable aquifers and surface waters to levels well below health-based drinking water concentrations. We note also that our analysis does not account for any spill mitigation measures, such as spill containment or spill recovery activities.

Conservative Assumptions

No containment or mitigation measures were included

100% of spill assumed to impact both surface water and groundwater

Distribution of low-end stream flow used for surface water dilution

All streams assumed to be direct sources of drinking water

Selected groundwater dilution factors based on US EPA's methodology which assume continuous and infinite sources (whereas HF spills are more appropriately characterized as short term, singular events)

Adsorption and degradation of chemicals was ignored

Based on the foregoing analysis, we conclude that when used in their intended manner in tight oil and gas formations, *i.e.*, pumped into a subsurface formation to induce fractures in the target formation, HF fluids are not expected to pose adverse risk to human health because it is highly unlikely that the fluids will escape from the well and it is implausible that the fluids would migrate from the target formation through overlying bedrock to reach shallow aquifers. Even in the event of surface spills, inherent environmental dilution mechanisms would, with a high degree of confidence (based on our probabilistic analysis covering wide-ranging conditions), reduce concentrations of HF chemicals in either groundwater or surface water below levels of human health concern (RBCs), such that adverse human health impacts are not expected to be significant. Our conclusions are based on examining a broad spectrum of conditions spanning HF operations in tight oil and gas formations across the country. By extension, these conclusions would apply more broadly where similar environmental conditions (including geologic formations) are found in other parts of the world.

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Appendix A

Flowback Fluid Chemical Data

Table A.1a Flowback Fluid Data Used in Risk Evaluation

		NYSDEC SGEIS (2011)					PA DEP (Palmerton)					Hayes (GTI) Report (FB days 1-90)					All Other data							Data from Datasets with Det>2 and Freq>5%			
CAS	Parameter	N	Det	Freq	Median (ug/L)	Max (ug/L)	N	Det	Freq	Median (ug/L)	Max (ug/L)	N	Det	Freq	Median (ug/L)	Max (ug/L)	N	Det	Freq	Median (ug/L)	Max (ug/L)	Source	Note	Highest Medians (ug/L)	Median Source	Max of Maxes (ug/L)	Max Source
	Inorganics																										
7439-90-5	Aluminum-DISS	22	1	5%	1,370	1,370	16	2	13%	200	490	67	56	84%	227	983								227	Hayes (GTI) 2009	983	Hayes (GTI) 2009
7440-36-0	Antimony-DISS											67	27	40%	5	45								5	Hayes (GTI) 2009	45	Hayes (GTI) 2009
7440-38-2	Arsenic-DISS						16	1	6%	75	150	67	36	54%	13	151								13	Hayes (GTI) 2009	151	Hayes (GTI) 2009
7440-39-3	Barium-DISS	22	22	100%	212,000	19,200,000	16	16	100%	327,000	6,660,000	67	67	100%	496,000	13,600,000								496,000	Hayes (GTI) 2009	19,200,000	NY SGEIS 2011
7440-42-8	Boron-DISS											67	67	100%	12,400	155,000								12,400	Hayes (GTI) 2009	155,000	Hayes (GTI) 2009
24959-67-9	Bromide	15	15	100%	607,000	3,070,000	15	15	100%	232	887	65	64	98%	487,000	1,990,000	NA			NA	10,600,000	Alley *et al.* 2011	Shale Gas	607,000	NY SGEIS 2011	10,600,000	Alley *et al.* 2011
7440-43-9	Cadmium-DISS	22	2	9%	26,000	35,000	15	0	0%			67	23	34%	3	12								3	Hayes (GTI) 2009	12	Hayes (GTI) 2009
7440-47-3	Chromium	43	9	21%	82	760,000	16	2	13%	50	98	67	53	79%	18	567	NA			NA	1,000	Alley *et al.* 2011	Oil wells	82	NY SGEIS 2011	760,000	NY SGEIS 2011
7440-47-3	Chromium (VI)											67	12	18%	5	550								5	NY SGEIS 2011	550	NY SGEIS 2011
7440-47-3	Chromium (VI)-diss	19	10	53%	539	7,810						67	8	12%	5	13,200								539	NY SGEIS 2011	13,200	Hayes (GTI) 2009
7440-47-3	Chromium III											67	27	40%	25	209								25	Hayes (GTI) 2009	209	Hayes (GTI) 2009
7440-47-3	Chromium-DISS	22	2	9%	75	92	16	0	0%			67	37	55%	7	76								7	Hayes (GTI) 2009	76	Hayes (GTI) 2009
7440-48-4	Cobalt-DISS	19	1	5%	489	489						67	5	7%	250	250								250	Hayes (GTI) 2009	250	Hayes (GTI) 2009
7440-50-8	Copper-DISS						16	6	38%	10	440	67	18	27%	13	387								13	Hayes (GTI) 2009	440	PA DEP
57-12-5	Cyanide, Total	7	2	29%	13	19						67	25	37%	5	177								5	Hayes (GTI) 2009	177	Hayes (GTI) 2009
7439-92-1	Lead-DISS						16	4	25%	13	443	67	12	18%	2	647								13	PA DEP	647	Hayes (GTI) 2009
7439-93-2	Lithium-DISS	4	4	100%	61,350	144,000	16	16	100%	42,200	163,000	67	66	99%	49,300	323,000								61,350	NY SGEIS 2011	323,000	Hayes (GTI) 2009
7439-96-5	Manganese-DISS	22	12	55%	2,975	18,000	16	16	100%	2,215	8,980	67	67	100%	2,680	21,200								2,975	NY SGEIS 2011	21,200	Hayes (GTI) 2009
7439-97-6	Mercury-DISS											67	16	24%	0.10	0.27								0.10	Hayes (GTI) 2009	0.27	Hayes (GTI) 2009
7439-98-7	Molybdenum-DISS											67	38	57%	84	200								84	Hayes (GTI) 2009	200	Hayes (GTI) 2009
7440-02-0	Nickel-DISS	22	2	9%	72	113	16	0	0%			67	27	40%	20	93								20	Hayes (GTI) 2009	93	Hayes (GTI) 2009
7782-49-2	Selenium-DISS	22	1	5%	1,060	1,060	2	1	50%	126	181	67	3	4%	3	65								3	Hayes (GTI) 2009	65	Hayes (GTI) 2009
7440-22-4	Silver-DISS	22	2	9%	825	109						67	5	7%	3	12								3	Hayes (GTI) 2009	12	Hayes (GTI) 2009
7440-24-6	Strontium-DISS	22	21	95%	629,000	7,290,000	11	11	100%	527,000	4,640,000	67	67	100%	1,300,000	8,460,000								1,300,000	Hayes (GTI) 2009	8,460,000	Hayes (GTI) 2009
14808-79-8	Sulfate	193	169	88%	1,000	1,270,000	16	9	56%	5,000	394,000	67	49	73%	31,800	348,000	33,189			500,000	15,000,000	Benko and Drewes 2008		500,000	Benko and Drewes 2008	15,000,000	Benko and Drewes 2008
7440-28-0	Thallium-DISS						2	0	0%			67	18	27%	5	196								5	Hayes (GTI) 2009	196	Hayes (GTI) 2009
7440-31-5	Tin-DISS											67	9	13%	500	500								500	Hayes (GTI) 2009	500	Hayes (GTI) 2009
7440-32-6	Titanium-DISS											67	33	49%	250	264								250	Hayes (GTI) 2009	264	Hayes (GTI) 2009
7440-66-6	Zinc-DISS	22	1	5%	70	70	16	9	56%	41	950	67	66	99%	147	182,000								147	Hayes (GTI) 2009	182,000	Hayes (GTI) 2009
	SVOCs																										
105-67-9	2,4-Dimethylphenol						12	0	0%			67	8	12%	5	25								5	Hayes (GTI) 2009	25	Hayes (GTI) 2009
91-57-6	2-Methylnaphthalene						11	4	36%	3	1,120	67	13	19%	1	120								3	PA DEP	1,120	PA DEP
95-48-7	2-Methylphenol						12	1	8%	10	13	67	16	24%	5	15								5	Hayes (GTI) 2009	15	Hayes (GTI) 2009
108-39-4/106-44-5	3/4-methylphenol						12	0	0%			67	27	40%	5	16	NA			123	541	Benko and Drewes 2008	p-cresol only	5	Hayes (GTI) 2009	541	Benko and Drewes 2008
83-32-9	Acenaphthene						12	0	0%			67	4	6%	1	1								1	Hayes (GTI) 2009	1	Hayes (GTI) 2009
98-86-2	Acetophenone						12	0	0%			67	22	33%	5	22								5	Hayes (GTI) 2009	22	Hayes (GTI) 2009
100-51-6	Benzyl alcohol											67	6	9%	5	750								5	Hayes (GTI) 2009	750	Hayes (GTI) 2009
117-81-7	Bis(2-ethylhexyl)phthalate	20	2	10%	16	22	12	1	8%	5	11	67	32	48%	5	870								5	Hayes (GTI) 2009	870	Hayes (GTI) 2009
218-01-9	Chrysene						12	0	0%			67	4	6%	1	1								1	Hayes (GTI) 2009	1	Hayes (GTI) 2009
84-66-2	Diethyl phthalate											67	17	25%	5	35								5	Hayes (GTI) 2009	35	Hayes (GTI) 2009
84-74-2	Di-n-butyl phthalate											67	20	30%	5	130								5	Hayes (GTI) 2009	130	Hayes (GTI) 2009
117-84-0	Di-n-octyl phthalate											67	5	7%	5	15								5	Hayes (GTI) 2009	15	Hayes (GTI) 2009
206-44-0	Fluoranthene						12	0	0%			67	4	6%	1	6								1	Hayes (GTI) 2009	6	Hayes (GTI) 2009
86-73-7	Fluorene						12	0	0%			67	9	13%	1	8								1	Hayes (GTI) 2009	8	Hayes (GTI) 2009
85-01-8	Phenanthrene						12	0	0%			67	15	22%	1	29								1	Hayes (GTI) 2009	29	Hayes (GTI) 2009
108-95-2	Phenol	20	1	5%	459	459	12	1	8%	10	105	67	14	21%	1	21	NA			NA	23,000	Benko and Drewes 2008		1	Hayes (GTI) 2009	23,000	Benko and Drewes 2008
64743-03-9	Phenols	20	1	5%	459	459	9	3	33%	50	239	67	55	82%	18	310								18	Hayes (GTI) 2009	310	Hayes (GTI) 2009
129-00-0	Pyrene						12	0	0%			67	9	13%	1	24								1	Hayes (GTI) 2009	24	Hayes (GTI) 2009
110-86-1	Pyridine						12	1	8%	5	404	67	43	64%	14	2,600								14	Hayes (GTI) 2009	2,600	Hayes (GTI) 2009
	VOCs																										
87-61-6	1,2,3-Trichlorobenzene						19	0	0%			67	4	6%	3	170								3	Hayes (GTI) 2009	170	Hayes (GTI) 2009
95-63-6	1,2,4 trimethylbenzene						19	9	47%	5	1,200	67	40	60%	3	4,000								5	PA DEP	4,000	Hayes (GTI) 2009
108-67-8	1,3,5-Trimethylbenzene						19	9	47%	5	264	67	28	42%	3	1,900								5	PA DEP	1,900	Hayes (GTI) 2009
107-06-2	1,2-Dichloroethane						19	3	16%	5	52	67	0	0%	3	3								5	PA DEP	52	PA DEP
78-93-3	2-Butanone											67	4	6%	3	17	NA			NA	370	Benko and Drewes 2008		3	Hayes (GTI) 2009	370	Benko and Drewes 2008
99-87-6	4-Isopropyltoluene						19	3	16%	5	150	67	4	6%	3	54								5	PA DEP	150	PA DEP
67-64-1	Acetone	3	1	33%	681	681	19	10	53%	37	10,000	67	48	72%	16	5,800								37	PA DEP	10,000	PA DEP
71-43-2	Benzene	35	14	40%	480	1,950	19	4	21%	5	616	67	30	45%	3	2,000	NA			10,000	27,000	Benko and Drewes 2008		480	NY SGEIS 2011	27,000	Benko and Drewes 2008
75-15-0	Carbon Disulfide						19	2	11%	5	122	67	5	7%	3	7,300								3	Hayes (GTI) 2009	7,300	Hayes (GTI) 2009
100-41-4	Ethyl Benzene	38	14	37%	54	164	19	2	11%	5	49	67	19	28%	3	650	NA			1,800	19,000	Benko and Drewes 2008		54	NY SGEIS 2011	19,000	Benko and Drewes 2008

CAS	Parameter	NYSDEC SGEIS (2011)					PA DEP (Palmerton)					Hayes (GTI) Report (FB days 1-90)					All Other data							Data from Datasets with Det>2 and Freq>5%			
		N	Det	Freq	Median (ug/L)	Max (ug/L)	N	Det	Freq	Median (ug/L)	Max (ug/L)	N	Det	Freq	Median (ug/L)	Max (ug/L)	N	Det	Freq	Median (ug/L)	Max (ug/L)	Source	Note	Highest Medians (ug/L)	Median Source	Max of Maxes (ug/L)	Max Source
98-82-8	Isopropylbenzene (cumene)						19	2	11%	5	6	67	5	7%	3	160								3	Hayes (GTI) 2009	160	Hayes (GTI) 2009
75-09-2	Methylene Chloride						19	2	11%	5	10	67	4	6%	3	6	NA			179	1,710	Benko and Drewes 2008		3	Hayes (GTI) 2009	6	Hayes (GTI) 2009
91-20-3	Naphthalene	23	1	4%	11	11	19	8	42%	5	1,300	67	17	25%	3	1,400	NA			119	556	Benko and Drewes 2008		3	Hayes (GTI) 2009	1,400	Hayes (GTI) 2009
103-65-1	n-Propylbenzene						19	4	21%	5	40	67	1	1%	3	90								5	PA DEP	40	PA DEP
108-88-3	Toluene	38	15	39%	833	3,190	19	3	16%	5	1,060	67	34	51%	3	6,200	NA			9,700	37,000	Benko and Drewes 2008		833	NY SGEIS 2011	37,000	Benko and Drewes 2008
1330-20-7	xylenes	38	15	39%	444	2,670	19	7	37%	10	1,060	67	34	51%	8	6,500	NA			137	611	Benko and Drewes 2008	m-xylene only	444	NY SGEIS 2011	6,500	Hayes (GTI) 2009
95-47-6	o-Xylene						19	7	37%	5	221													5	PA DEP	221	PA DEP
	Alcohols and acids																										
64-19-7	Acetic acid											50	15	30%	5,000	450,000	27	25	93%	116,300	843,500	Connolly *et al.* 1990	Alberta Basin	116,300	Connolly *et al.* 1990	843,500	Connolly *et al.* 1990
64-17-5	ethanol											54	4	7%	5,000	230,000								5,000	Hayes (GTI) 2009	230,000	Hayes (GTI) 2009
107-21-1	ethylene glycol						16	9	56%	10	130	54	5	9%	25,000	290,000								25,000	Hayes (GTI) 2009	290,000	Hayes (GTI) 2009
67-63-0	Isopropanol											54	17	31%	5,000	280,000								5,000	Hayes (GTI) 2009	280,000	Hayes (GTI) 2009
67-56-1	Methanol											53	22	42%	5,000	4,500,000								5,000	Hayes (GTI) 2009	4,500,000	Hayes (GTI) 2009
71-36-3	n-Butanol											54	4	7%	5,000	47,000								5,000	Hayes (GTI) 2009	47,000	Hayes (GTI) 2009
79-09-4	Propionic Acid											49	0	0%	5,000	5,000	27	26	96%	28,600	74,000	Connolly *et al.* 1990	Alberta Basin	28,600	Connolly *et al.* 1990	74,000	Connolly *et al.* 1990
64-18-6	Formic acid																27	22	81%	1,200	9,100	Connolly *et al.* 1990	Alberta Basin	1,200	Connolly *et al.* 1990	9,100	Connolly *et al.* 1990
	NORM									pCi/L	pCi/L	New York Times			pCi/L	pCi/L				pCi/L	pCi/L			pCi/L		pCi/L	
	RA 228	3	3			18	14	12	86%	57	1,360	44	41		58	2,589	**128**			**504**	**2,589**	USGS 2011		504	USGS 2011	2,589	USGS 2011
	RA 226	3	3			33	14	14	100%	611	9,280	45	45		355	16,920	**139**			**599**	**16,920**	USGS 2011		611	PA DEP	16,920	USGS 2011
	Uranium 238						14	2	14%	0	497	24	12		0.06	497								0.06	NY Times article	497	NY Times 2/26/2011
	Uranium 235						14	1	7%	0	20	22	6		0.00	20								-	NY Times article	20	NY Times 2/26/2011
	PB 214						14	10	71%	174	2,200													174	PA DEP	2,200	PA DEP
	PB 212						14	14	100%	60	1,430													60	PA DEP	1,430	PA DEP
	Gross alpha											183	183		2,512	40,880	**32**			**6,845**	**123,000**	USGS 2011		6,845	USGS 2011	123,000	USGS 2011
	Gross beta																**31**			**1,170**	**11,595**	USGS 2011		1,170	USGS 2011	11,595	USGS 2011

Note:
"DISS" indicates dissolved result (inorganics)

Table A.1b Additional Flowback Fluid Data Considered

		NYSDEC SGEIS (2011)					PADEP (Palmerton)					Hayes (GTI) Report (FB days 1-90)					All Other Data						
CAS	Parameter	N	Det	Freq	Median (µg/L)	Max (µg/L)	N	Det	Freq	Median (µg/L)	Max (µg/L)	N	Det	Freq	Median (µg/L)	Max (µg/L)	N	Det	Freq	Median (µg/L)	Max (µg/L)	Source	Note
	Inorganics																						
7664-41-7	Aqueous ammonia	48	45	94%	44,800	382,000																	
7440-41-7	Beryllium-DISS						16	0	0%			67	3	4%	2	7							
16887-00-6	CHLORIDE	193	193	100%	56,900,000	228,000,000	15	15	100%	34,156,000	83,505,000	65	65	100%	49,000,000	196,000,000	33,189			29,000,000	250,000,000	Benko and Drewes, 2008	
7440-70-2	Calcium-DISS	3	3	100%	22,300,000	31,500,000	16	16	100%	1,855,000	21,000,000	67	67	100%	7,570,000	41,000,000							
7440-70-2	Calcium	187	186	99%	4,241,000	123,000,000	16	16	100%	2,180,000	22,000,000	67	67	100%	7,300,000	33,000,000	33,189			1,500,000	74,000,000	Benko and Drewes, 2008	
16984-48-8	Fluoride	4	2	50%	392,615	780,000						67	12	18%	500	32,900						ND	
7440-09-7	Potassium-DISS	3	3	100%	327,000	7,080,000	16	16	100%	87,000	536,000	67	67	100%	304,000	4,080,000							
7440-09-7	Potassium	33	17	52%	125,000	7,810,000	16	16	100%	136,500	617,000	67	67	100%	301,000	3,950,000	NA			NA	5,490,000	Alley *et al.* , 2011	Shale gas
7439-89-6	Iron-DISS	34	26	76%	63,250	196,000	16	16	100%	36,650	194,000	67	67	100%	34,400	220,000							
7439-89-6	Iron	193	168	87%	29,200	810,000	16	16	100%	32,450	222,000	67	67	100%	53,100	574,000	NA			NA	2,838,000	Alley *et al* ., 2011	Shale gas
7439-95-4	Magnesium-DISS	3	3	100%	2,170,000	3,160,000	16	16	100%	173,500	1,460,000	67	67	100%	632,000	2,550,000							
7439-95-4	Magnesium	193	180	93%	177,000	3,190,000	16	16	100%	172,500	1,540,000	67	67	100%	613,000	2,020,000				NA	25,340,000	Alley *et al* ., 2011	Shale gas
7440-23-5	Sodium-DISS	3	3	100%	54,800,000	77,400,000	16	16	100%	10,800,000	50,500,000	67	67	100%	26,400,000	117,000,000							
7440-23-5	Sodium	42	41	98%	23,500,000	96,700,000	16	16	100%	11,650,000	50,200,000	67	67	100%	21,300,000	95,500,000	33,190			9,400,000	150,000,000	Benko and Drewes, 2008	
14265-45-3	Sulfite	3	3	100%	64,000	64,000						54	51	94%	11,600	73,600							
7723-14-0	Phosphorus	3	3	100%	1,850	4,460						67	47	70%	90	21,800							
7439-90-5	Aluminum	43	12	28%	70	1,200	16	3	19%	200	11,100	67	62	93%	507	47,200	NA			NA	5,290,000	Alley *et al.* , 2011	Shale gas
7440-36-0	Antimony	34	1	3%	260	260						67	33	49%	5	49							
7440-38-2	Arsenic	43	7	16%	90	123	16	2	13%	75	150	67	42	63%	25	135	NA			NA	11,000	Alley *et al* ., 2011	Nat. gas
7440-39-3	Barium	48	47	98%	1,450,000	15,700,000	16	16	100%	1,018,000	7,090,000	67	67	100%	516,000	13,900,000	NA			NA	4,370,000	Alley *et al* ., 2011	Shale gas
7440-41-7	Beryllium	43	1	2%	422,000	422,000	16	1	6%	1	1	67	2	3%	2	3							
7440-42-8	Boron	23	9	39%	2,060	26,800						67	67	100%	12,200	145,000	NA			NA	58,000	Alley *et al* ., 2011	Nat. gas
7440-43-9	Cadmium	43	6	14%	25	1,200	16	0	0%			67	28	42%	3	12	NA			NA	1,210	Alley *et al* ., 2011	Nat. gas
7440-48-4	Cobalt	30	6	20%	398	620						67	5	7%	250	250							
7440-50-8	Copper	43	8	19%	25	157	16	7	44%	10	1,670	67	36	54%	23	4,150	NA			NA	15,000	Alley *et al.* , 2011	Shale gas
57-12-5	Amenable cyanide											67	2	3%	5	140							
7439-92-1	Lead	43	6	14%	35	27,400	16	5	31%	30	1,092	67	36	54%	4	970							
7439-93-2	Lithium	13	13	100%	90,400	297,000	16	16	100%	43,600	174,000	67	66	99%	51,800	323,000	NA			NA	611,000	Alley *et al* ., 2011	Shale gas
7439-96-5	Manganese	43	29	67%	1,890	97,600	16	16	100%	1,950	9,090	67	67	100%	2,810	18,600	NA			NA	96,500	Alley *et al* ., 2011	Shale gas
7439-97-6	Mercury											67	14	21%	0	0							
7439-98-7	Molybdenum	34	12	35%	440	1,080						67	48	72%	44	372							
7440-02-0	Nickel	43	15	35%	30	137	16	1	6%	50	95	67	33	49%	20	769	NA			NA	9,500	Alley *et al* ., 2011	Oil
7782-49-2	Selenium	34	1	3%	58	58	2	1	50%	126	181	67	7	10%	3	96							
7440-22-4	Silver	43	3	7%	204	6,300						67	6	9%	3	9							
7440-24-6	Strontium	36	36	100%	1,115,000	5,841,000	12	12	100%	701,200	4,890,000	67	67	100%	1,240,000	8,020,000	NA			NA	1,310,000	Alley *et al.* , 2011	Shale gas
7440-28-0	Thallium	34	2	6%	180	260	2	0	0%			67	11	16%	5	168							
7440-31-5	Tin											67	8	12%	500	500							
7440-32-6	Titanium	25	1	4%	60	60						67	36	54%	247	313							
7440-66-6	Zinc	43	18	42%	36	8,570,000	16	7	44%	10	1,100	67	65	97%	198	247,000	NA			NA	20,000	Alley *et al.* , 2011	Shale gas
	SVOCs																						
208-96-8	Acenaphthylene						12	0	0%			67	2	3%	1	1							
62-53-3	Aniline						12	0	0%			67	3	4%	5	5							
56-55-3	Benzo(a)anthracene						12	0	0%			67	3	4%	5	5							
50-32-8	Benzo(a)pyrene						12	0	0%			67	3	4%	3	7							
205-99-2	Benzo(b)fluoranthene						12	0	0%			67	2	3%	1	10							
191-24-2	Benzo(ghi)perylene						12	0	0%			67	3	4%	1	7							
207-08-9	Benzo(k)fluoranthene											67	2	3%	1	6							
53-70-3	Dibenz(a,h)anthracene						12	0	0%			67	3	4%	1	11							
132-64-9	Dibenzofuran						12	0	0%			67	2	3%	5	9							
122-39-4	Diphenylamine						12	0	0%			67	2	3%	1	3							
118-74-1	Hexachlorobenzene						12	0	0%			67	2	3%	0	1							

		NYSDEC SGEIS (2011)					PADEP (Palmerton)					Hayes (GTI) Report (FB days 1-90)					All Other Data						
CAS	**Parameter**	**N**	**Det**	**Freq**	**Median (µg/L)**	**Max (µg/L)**	**N**	**Det**	**Freq**	**Median (µg/L)**	**Max (µg/L)**	**N**	**Det**	**Freq**	**Median (µg/L)**	**Max (µg/L)**	**N**	**Det**	**Freq**	**Median (µg/L)**	**Max (µg/L)**	**Source**	**Note**
193-39-5	Indeno(1,2,3-cd)pyrene											67	3	4%	1	10							
86-30-6	N-Nitrosodiphenylamine											67	2	3%	1	3							
	VOCs																						
120-82-1	1,2,4-Trichlorobenzene						19	0	0%			67	2	3%	3	66							
123-91-1	1,4 Dioxane						12	1	8%	5	14,700	67	0	0%	500	500							
75-25-2	Bromoform	26	2	8%	37	39	19	0	0%			67	1	1%	3	6							
124-48-1	Chlorodibromomethane	26	2	8%	4	4	19	0	0%			67	0	0%	3	3							
67-66-3	Chloroform						19	2	11%	5	12	67	2	3%	3	28							
75-27-4	Dichlorobromomethane	29	1	3%	2	2	19	0	0%			67	0	0%	3	3							
74-83-9	Methyl Bromide	26	1	4%	2	2						67	1	1%	3	230							
74-87-3	Methyl Chloride	26	1	4%	16	16	19	0	0%			67	3	4%	3	150							
104-51-8	n-Butylbenzene						19	2	11%	5	1,040	67	1	1%	3	3							
135-98-8	sec-Butylbenzene						19	1	5%	5	130	67	1	1%	3	68							
127-18-4	Tetrachloroethylene	26	1	4%	5	5	19	0	0%			67	1	1%	3	9							
	Alcohols and acids																						
75-65-0	t-Butyl alcohol						19	2	11%	50	305												
107-92-6	Butyric Acid											49	1	2%	5,000	18,000	27	12	44%	0	17,100	Connolly *et al.*, 1990	Alberta Basin
71-23-8	n-Propanol											54	1	2%	5,000	10,000							
57-55-6	Propylene glycol						16	6	38%	1	160	54	7	13%	25,000	300,000							
	NORM																						
	Cesium-137	16	2		10	11																	

Note:
Data were not included in risk analysis due to too few detections, or in case of inorganics, we used reported dissolved concentrations (and did not include common nutrients).

References – Table A.1a and Table A.1b

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Appendix B

Hypothetical Upward Migration Dilution Factor Derivation

Table

B.1 Overview

As discussed in Section 5.1, it is not physically plausible for fractures and faults to create hydraulic connections between fractured oil and gas formations and overlying potable aquifers. Migration through the pore spaces of intact bedrock is similarly implausible. Despite these physical realities, we considered an implausible hypothetical upward migration scenario. We considered scenarios of potential upward flow governed by Darcy's law, which defines the rate of upward flow per unit area (q) as:

$$q = k \frac{\rho g}{\mu} \frac{dh}{dz} \tag{B.1}$$

where:

k = permeability
dh/dz = the upward head gradient
ρ = the density of water
μ = viscosity of water
g = acceleration due to gravity

In this appendix, physically plausible ranges of dh/dz and k are defined and used in standard dilution calculations (similar to other pathways) to estimate the range of hypothetical DF values for this implausible scenario.

B.2 Hypothetical Upward Head Gradient

When upward flow occurs, there are two fundamental controls on the upward head gradient (dh/dz). The first is an upper limit imposed by the mechanical properties of rock (*i.e.*, if dh/dz is high enough it will fracture the rock and relieve built-up pressure). The second is a lower limit needed to overcome density stratification due to the tendency for dense brine to form a stable fluid layer at depth, with less dense fresh water floating on top.

The upper limit to dh/dz is controlled by the maximum pore pressure that can be sustained without fracturing the rock. Rocks can be hydraulically fractured (either naturally or by humans) when pore pressure exceeds the least compressive stress, σ_{min}, which holds fractures closed. The principal direction of σ_{min} varies with depth; it is typically vertical in shallow bedrock and horizontal at depth. The vertical stress is the weight of overburden per unit area, meaning that a pore pressure that exceeds this value would physically push the overburden upward and create a fracture in the horizontal plane. When σ_{min} is horizontal (common at depth), fractures propagate vertically. In either case, the upper bound for σ_{min} is approximately the overburden stress (see Engelder, 1993, for a full discussion of this topic), and therefore, the maximum fluid pressure that can be sustained without fracturing the rock is also approximately equal to the overburden stress. The magnitude of dh/dz under this limiting condition is:

$$\frac{dh_{\max}}{dz} = -\frac{\rho_r - \rho_w}{\rho_w} \tag{B.2}$$

where:

ρ_r = the bulk density of overburden
ρ_w = the density of water (negative values of dh/dz indicate upward flow)

With ρ_r at approximately 2,300 kg m^{-3} and ρ_w at approximately 1,230 kg m^{-3} for brine (assuming a salinity of 350,000 ppm at a temperature of 100 ºC and 20 MPa pressure) (Batzle and Wang, 1992), Equation B.2 indicates that the maximum upward head gradient is limited to about 1.

The lower limit to dh/dz is controlled by density gradients. Unlike shallow groundwater, which is typically fresh water, groundwater in the deep portions of sedimentary basins is typically brine. Salinities in these deep basin waters can range up to 400,000 ppm (Bassett and Bentley, 1982; Hanor, 1983), with densities up to 27 percent greater than fresh water (for a salinity of 400,000 ppm and the same temperature and pressure as before). A common feature of all brines is that they are denser than fresh groundwater, although the chemical composition of brine varies within and between basins (Benko and Drewes, 2008). The stacking of fluids by density results in a stable configuration, which requires additional energy to break and to push a denser fluid upward. Such density gradients are taken into account in basin-scale models of fluid flow by applying a correction factor to dh/dz in the fluid flow equations (Bethke, 1989; Garven, 1995). This correction factor is defined here as the brine density gradient (dh_b / dz):

$$\frac{dh_b}{dz} = \frac{\rho_b - \rho_w}{\rho_w} \qquad \text{(B.3)}$$

For brine with a density of 1,230 kg m^{-3}, Equation B.3 predicts a gradient of 0.23, assuming fresh water has a density of 1,000 kg/m^3. Local density gradients will be much smaller, however, this estimate provides the head gradient needed to move a parcel of brine upward into an overlying freshwater aquifer. If density gradients are ignored, fluid flow models may incorrectly predict that flow is upward in areas where flow is actually downward (Senger and Fogg, 1987).

B.3 Permeability

Permeability and upward head gradients are inherently related. The mechanism for driving potential upward flow from tight oil and gas formations would most likely be related to elevated pressures generated by sediment deposition or oil and gas formation that occurred in the geologic past. In order to properly constrain the range of potential permeability values for the range of head gradients described in Section B.1, we must evaluate the conditions that would allow for elevated pressures to persist at depth over geologic time.

The tight oil and gas formations targeted for hydraulic fracturing (HF) are predominantly in basins where burial and rapid gas generation are no longer occurring. Consequently, in most cases where elevated pressure is present, it was likely generated in the past. Therefore, the question that must be answered is what permeabilities would allow elevated pressure to persist over the time since sediment deposition and rapid gas generation have ceased to be important. These timescales are generally on the order of tens to hundreds of millions of years for basins in the US (Law and Spencer, 1998).

In order for elevated pore pressure to persist over such long timescales, the permeability of overburden rocks must be sufficiently low to prevent pressure from diffusing across them. The magnitude of this permeability can be estimated from simple scaling relationships. For example, Deming (1994) provided a solution to the one-dimensional groundwater flow equation that can be used to estimate permeability:

$$k = z^2 \alpha \mu / 4t \qquad \text{(B.4)}$$

where:

z = overburden thickness
α = compressibility of bedrock
t = timescale for diffusion of pressure
μ = viscosity of water

For timescales of 10 million to 100 million years, overburden thicknesses of 1,000 to 5,000 m (depth range of most black shales), $\alpha = 10^{-9}$ Pa^{-1} (a typical value for shale; Deming, 1994), and $\mu = 0.0005$ Pa-s, the permeability that would allow elevated pressure at these depths would be between 10^{-23} m^2 and 10^{-20} m^2. Note that this range of permeabilities is at the extreme low end of values reported in most standard groundwater hydrology texts (*e.g.*, Freeze and Cherry, 1979), but is consistent with the low permeability shales that are commonly found at depth (*e.g.*, Kwon *et al.*, 2001, and references therein; Corbet and Bethke, 1992; Neuzil, 1986).

Using Equation B.4, we calculated a plausible range of permeability values for conditions of upward flow (*i.e.*, elevated pressure); however, we also needed to define the maximum possible permeability. Similar approaches to Equation B.4 have been used by others to evaluate the permeability that would be required to prevent pressure build up (*i.e.*, prevent upward flow) over geologic time (Townend and Zoback, 2000; Zoback, 2007). These results give the upper bound permeability as approximately 10^{-18} to 10^{-17} m^2. Thus, the range of permeability over which upward flow might occur is constrained to about 10^{-23} to 10^{-17} m^2.

B.4 DF Calculation

Using an approach analogous to the one utilized by US EPA (1996) for developing Soil Screening Levels (SSLs), we calculated the diluted concentration of HF constituents under an unrealistic hypothetical scenario of upward migration:

$$C_{gw} = C_{OG}\left(\frac{Q_{up}}{Q_{up} + Q_{gw}}\right)$$

whether:

C_{gw} is the chemical concentration in an overlying groundwater mixing zone,
C_{OG} is the chemical concentration in the target formation,
Q_{up} is the flow rate of upward migrating fluid, and
Q_{gw} is the flow rate of groundwater in the overlying groundwater mixing zone.

The degree of dilution of a constituent is simply given by:

$$C_{gw} = \frac{C_{OG}}{DF_{aq}}$$

where DF_{aq} is the dilution attenuation factor for upward seepage into an overlying aquifer, shown as:

$$DF_{aq} = \frac{Q_{up} + Q_{gw}}{Q_{up}}$$

The flow rate of upward migrating fluid (Q_{up}) can be estimated as:[1]

$$Q_{up} = K_{up} A_{up} \frac{dh}{dz}$$

where:

K_{up} = effective hydraulic conductivity for upward flow ($K_{up} = k\rho g/\mu$)
dh/dz = upward head gradient
A_{up} = the area of upward HF fluid seepage at the base of the overlying aquifer

For the area of upward HF fluid seepage (A_{up}), we multiplied the length of a horizontal gas well (L_w) by the width of the HF fluid plume if it were to impact an overlying aquifer. The lateral groundwater flow rate in the overlying aquifer, Q_{gw}, was calculated as:

$$Q_{gw} = K_{gw} A_{gw} \frac{dh}{dx}$$

where:

Q_{gw} = groundwater flow rate through the overlying aquifer
K_{gw} = hydraulic conductivity of the overlying aquifer
A_{gw} = cross sectional area of the overlying aquifer
dh/dx = horizontal hydraulic gradient in the overlying aquifer

The cross-sectional area of the overlying aquifer, A_{gw}, was estimated as the plume width multiplied by the aquifer thickness (D). Because the plume width is used to calculate both Q_{gw} and Q_M, it cancels out of the DF calculation and does not need to be specified. The values of variables used in the DF calculations are shown in Table B.1.

Using the above approach for the assessment of hypothetical upward migration the 5th percentile was 9.8×10^6, *i.e.*, 95% of DFs were higher than this one.

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[1] As we have discussed, during oil and gas extraction, the head gradient will be toward the well within the continuous fracture network, not upward to an overlying aquifer.

Table B.1 Variables Used in Hypothetical DF Calculations

Variable	Distribution Type	Parameters	Units	Source/Notes
K_{up}	lognormal	mean = -13; std. dev. = 1	$\log_{10}$ m/s	Based on permeability limits discussed in Section B.3
L_w	lognormal	mean = 3.3; std. dev. = 0.4	$\log_{10}$ ft	Professional judgment
dh/dz	uniform	min = 0.2; max = 1	unitless	Based on limits discussed in Section B.2
K_{gw}	lognormal	mean = -2.629; std. dev. = 1.606	$\log_{10}$ cm/s	US EPA (1996)
D	lognormal	mean = 1.575; std. dev. = 0.515	$\log_{10}$ ft	US EPA (1996)
dh/dx	lognormal	mean = -2.222; std. dev. = 0.77	$\log_{10}$ (unitless)	US EPA (1996)

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Appendix C

Spill to Groundwater Dilution Factor Derivation

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C.1 Unsaturated Zone Advection Dispersion Equation

The transport equation for one-dimensional chemical transport considering the effects of advection, dispersion, retardation and biodegradation can be written in the form of the following partial differential equation (Javendel *et al.*, 1984):

$$D_e \frac{\partial^2 C}{\partial x^2} - \nu_e \frac{\partial C}{\partial x} - \lambda C = \frac{\partial C}{\partial t} \qquad \text{(C.1)}$$

where:

$$D_e = \frac{D}{R} \qquad \text{(C.2)}$$

$$\nu_e = \frac{\nu}{R} \qquad \text{(C.3)}$$

$$v = \frac{I}{\theta}$$

C = aqueous phase contaminant concentration (mg/L)
x = distance along flow path (cm)
t = time (yr)
ν = water infiltration velocity (cm/yr)
ν_e = effective chemical transport velocity in the x direction (cm/yr)
I = net infiltration rate (cm/yr)
θ = soil water content (cm^3-water/cm^3-soil)
D = hydrodynamic dispersion coefficient (cm^2/yr)
D_e = effective dispersion coefficient (cm^2/yr)
R = chemical retardation factor (unitless)
λ = chemical decay constant (yr^{-1})

The retardation coefficient (R) is an indicator of contaminant mobility relative to water mobility and is expressed as:

$$R = \left(1 + \frac{K_d \rho}{\phi} \right) \qquad \text{(C.4)}$$

where:

K_d = soil-water partition coefficient (mL/g)
ρ = soil bulk density (g/cm^3)
ϕ = soil porosity (cm^3/cm^3)

The soil-water partition coefficient (K_d) relates the chemical concentration in soil to the concentration in pore water. For organic compounds, partition coefficient (K_d) is related to the fraction of organic carbon content (f_{oc}) of soils.

$$K_d = f_{oc} K_{oc} \tag{C.5}$$

Values for K_{oc} are available for certain organic chemicals in the literature; f_{oc} is a field measured value. Values of K_{oc} can also be estimated using the partition coefficient between water and octanol (K_{ow}), which is readily available for a number of organic compounds.

Note that while the ADE accounts for chemical adsorption (which reduces chemical migration and increases dilution) no chemical adsorption was modeled in our leaching analysis, such that chemical "retardation" was not considered (*i.e.*, R = 1 in all calculations).

Dispersion caused by hydrodynamic flow variations within porous media is commonly modeled as a function of flow velocity within the porous medium (Freeze and Cherry, 1979):

$$D = \alpha \cdot v \tag{C.6}$$

where:

α = longitudinal dispersivity in the direction of flow (m)
v = average pore water velocity in the direction of flow (m/yr)

We use the following analytical solution to the ADE, which assumes no chemical degradation and an initial thickness of contaminated soil (x_o) with concentration C_o (Enfield *et al.*, 1982):

$$C(x,t) = \frac{1}{2} C_o \left\{ erf\left[\frac{x + x_o - vt}{2\sqrt{Dt}} \right] - erf\left[\frac{x - vt}{2\sqrt{Dt}} \right] \right\} \tag{C.7}$$

where:

C(x,t) = concentration in leachate at depth *x* and time *t* (mg/L)
C_o = initial concentration in contaminated soil water (mg/L)
x_o = initial thickness of contaminated soil (m)

The above solution applies under the following initial and boundary conditions.

Initial Conditions:	$C = C_o$	$0 \le x \le x_o$	@ t = 0
	$C = 0$	$x > x_o$	@ t = 0
Boundary Condition:	$\partial C/\partial x = 0$	$x \to \infty$ @ $t \ge 0$	

Note that the x-direction represents the vertical depth, where x = 0 at the ground surface and increases with depth.

C.1.2 Peak Chemical Concentration at Water Table

The ADE can be solved to determine the maximum chemical concentration leaching into the groundwater, which is when the peak of the chemical pulse (or plume) arrives at the water table. The time it takes for the peak of the plume to reach the water table is:

$$t = x/v$$

In addition, as indicated in Equation C.6, the dispersion coefficient can be expressed as:

$$D = \alpha v$$

where α is the dispersivity. Substituting these into Equation C.7 yields the following reduced form of the ADE for the peak concentration at the water table:

$$\frac{C_{peak}}{C_o} = \frac{1}{2} erf\left[\frac{x_o}{2\sqrt{\alpha\, x_{wt}}}\right] \tag{C.8}$$

where:

x_{wt} = depth to the water table (m)

The unsaturated zone DF corresponding to the peak concentration is simply:

$$DF = \frac{1}{C_o/C_{peak}} = \frac{C_{peak}}{C_o}$$

Note that the DF associated with the peak concentration at the water table is the smallest DF for the unsaturated zone.

C.1.3 Model Parameters and Calculated Unsaturated Zone DFs

As shown in Equation C.8, the DF for the peak concentration at the water table is a function of the initial depth of contamination (x_o), the depth to the water table (x_{wt}), and the dispersivity (α). It is notable that the peak concentration at the water table is independent of the infiltration rate, although the time it takes for the peak concentration to reach the water table is a function of the infiltration rate. The values used in calculating the unsaturated zone DF are provided below.

Table C.1 Distribution Parameters for the Unsaturated Zone DF

Parameter Name and Symbol	Parameter Values	Distribution Type	Source/Notes
Porosity (ϕ)	0.43 cm^3/cm^3	fixed value	US EPA (1996)
Dispersivity (α)	log mean -1.0, log std. dev. 0.5	lognormal	Based on Gelhar *et al*. (1992)
Initial spill ponded thickness	1 cm to 5 cm	uniform	See text Section 5
Initial soil contamination depth (x_o)	2.3 cm to 11.6 cm	uniform	Function of spill thickness and soil porosity
Depth to water table (x_{wt})		lognormal	US EPA (1996)

Gelhar *et al*. (1992), found that under field conditions, the observed dispersivity was on the order of 10% of the "flow length" scale, although with variability of several orders of magnitude around this mean value. We treated dispersivity as a lognormal variable with a log mean of -1.0 (*e.g.*, $\log_{10}(0.1)$ is -1.0), and a standard deviation of 0.5 log units.

The initial soil contamination depth (x_o) is given by the spill thickness divided by the soil porosity. Given that the spill thickness was treated as a uniform random variable, the initial soil contamination thickness is also a uniform random variable ranging from 2.3 cm to 11.6 cm.

C.2 Saturated Zone DFs

In the US EPA (1996) Soil Screening Level (SSL) Guidance, US EPA derived groundwater DFs for wide range of climatological and hydrogeological conditions (*e.g.*, aquifer characteristics, distance to drinking water well, depth of drinking water well, *etc.*) in the US.[1] In order to address the widely varying conditions across the US, the US EPA used a Monte Carlo framework coupled to a chemical fate and transport model. The framework was implemented by selecting a spill area and then randomly selecting inputs for the fate and transport model repeatedly to produce a distribution of DF values for a given spill area. This procedure was repeated for a range of spill areas from 0.02 to 69 acres leading to a family of DF distributions for the different spill areas US EPA selected. US EPA reported the 85th, 90th, and 95th percentile lowest values from these distributions in Table 5 of its SSL guidance (US EPA, 1996).

Although US EPA considered a range of spill areas in its SSL guidance, it did not develop relationships between the parameters of DF distributions (*i.e.*, mean and standard deviation) and spill area. These relationships are needed to implement the probabilistic framework utilized in our risk assessment. This section describes the method for developing the needed relationships based on information in the US EPA SSL Guidance.

The three DF percentile values reported by US EPA (85th, 90th, and 95th) were used to estimate the mean and standard deviation of the probability distribution of DF as a function of area. The US EPA DF percentiles were fit to a lognormal distribution. Because the lower bound of a lognormal distribution is zero, whereas the minimum value of DF is 1, we fit the transformed variable (DF-1) to the lognormal distribution:

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[1] US EPA referred to them as "dilution attenuation factors" (DAFs). We use the term "dilution factors" because in our analysis, as was also the case in US EPA's DAF development, we have not accounted for "attenuation" processes such as chemical-soil adsorption, or biodegradation. These attenuation processes would further reduce the chemical concentrations in the environment in the event of a spill (*e.g.*, leading to larger dilution factors if included).

$$P\ (Y \leq y) = 0.5 + 0.5erf\left[\frac{ln(y)-\mu}{\sqrt{2\sigma^2}}\right] \qquad \text{(C.9)}$$

where:

$P(Y \leq y)$ = cumulative probability of any value y from the distribution of the random variable Y
y = transformed variable (DF-1)
μ = mean of $\log_e$(DF-1)
σ = standard deviation of $\log_e$(DF-1)

By sequentially fitting the mean and coefficient of variation (CV is the standard deviation divided by the mean, or σ/μ) to each percentile and area, we derived a best fit polynomial for μ and CV as a function of spill area.[2] The resulting polynomial equations for each are given below:

$$\mu = 0.1118x^4 - 0.6148x^3 + 1.3806x^2 - 4.9055x + 16.6892$$

$$CV = 0.0135x^2 + 0.0792x + 0.5792$$

where:

x = $\log_{10}$(area) for spill area in acres
μ = mean of $\log_e$(DF-1)
CV = coefficient of variation of $\log_e$(DF-1)

Table C.1 provides a summary of the US EPA-reported DAF percentiles as a function of source area and our best fit lognormal distribution parameters (natural logs).

Table C.2 Groundwater DF Distribution Parameters as a Function of Source Area

Area (acres)	US EPA Reported DAF Percentile			LN Mean DF	LN CV DF	LN Std. Dev. DF
	85th	90th	95th			
0.02	14,200,000	209,000	946	33.10	0.49	16.11
0.04	919,000	28,300	211	28.08	0.49	13.87
0.11	55,400	2,740	44	23.20	0.51	11.87
0.23	11,600	644	15	20.94	0.54	11.20
0.5	2,500	170	7	18.29	0.55	10.15
0.69	1,430	120	4.5	17.55	0.57	9.93
1.1	668	60	3.1	16.39	0.58	9.56
1.6	417	38	2.5	15.72	0.60	9.38
1.8	350	33	2.3	15.48	0.60	9.31
3.4	159	18	1.7	14.33	0.62	8.95
4.6	115	13	1.6	13.77	0.63	8.74
11.5	41	5.5	1.2	12.75	0.69	8.75
23	21	3.5	1.2	11.01	0.71	7.77
30	16	3.0	1.1	11.24	0.73	8.23
46	12	2.4	1.1	10.53	0.75	7.87
69	8.7	2.0	1.1	9.67	0.77	7.41

Note:
US EPA values from US EPA (1996) Table 5.

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[2] We used the scientific software program MATLAB to determine the polynomial best fit parameters.

Plots of the polynomial best fit for the lognormal mean and lognormal coefficient of variation (CV) are shown below in Figure C.1 and Figure C.2. The fitted cumulative probability distribution functions as a function of source area are shown in Figure C.3, which also shows the US EPA reported percentile values.

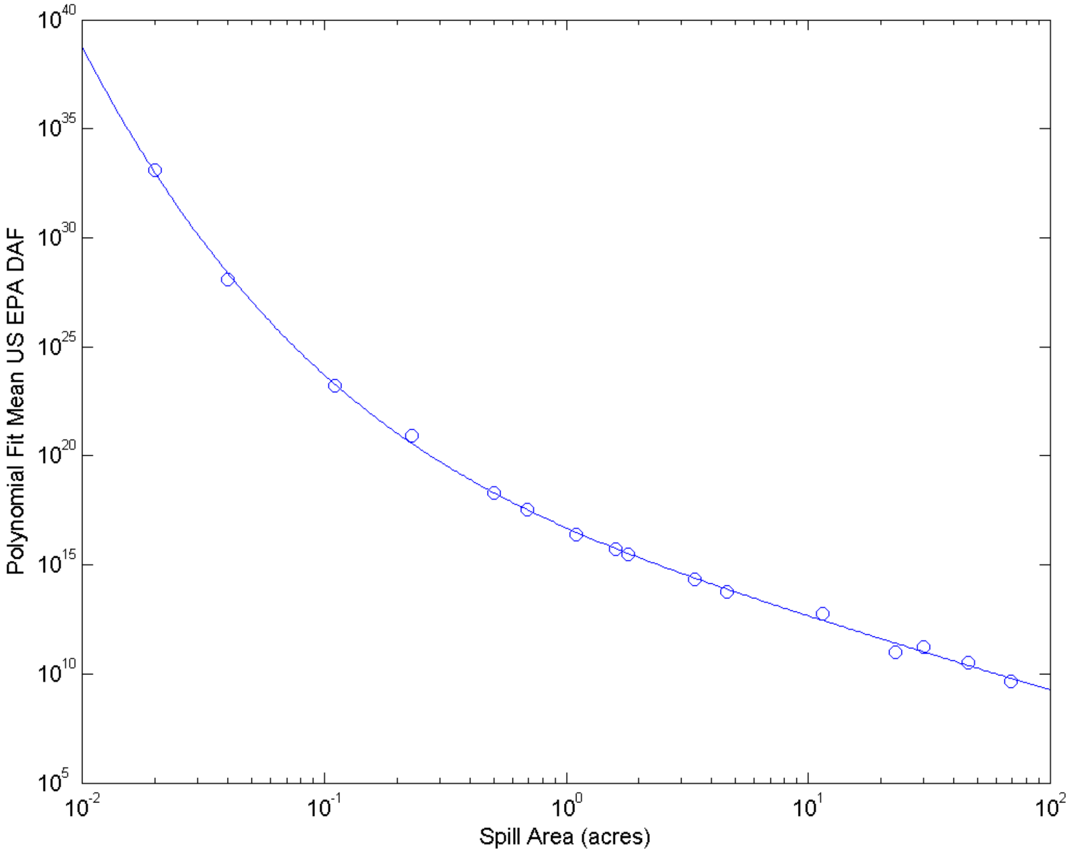

Figure C.1 Polynomial Best Fit Mean (natural log) DF Fit as a Function of Source Area for US EPA-reported DAF Percentiles

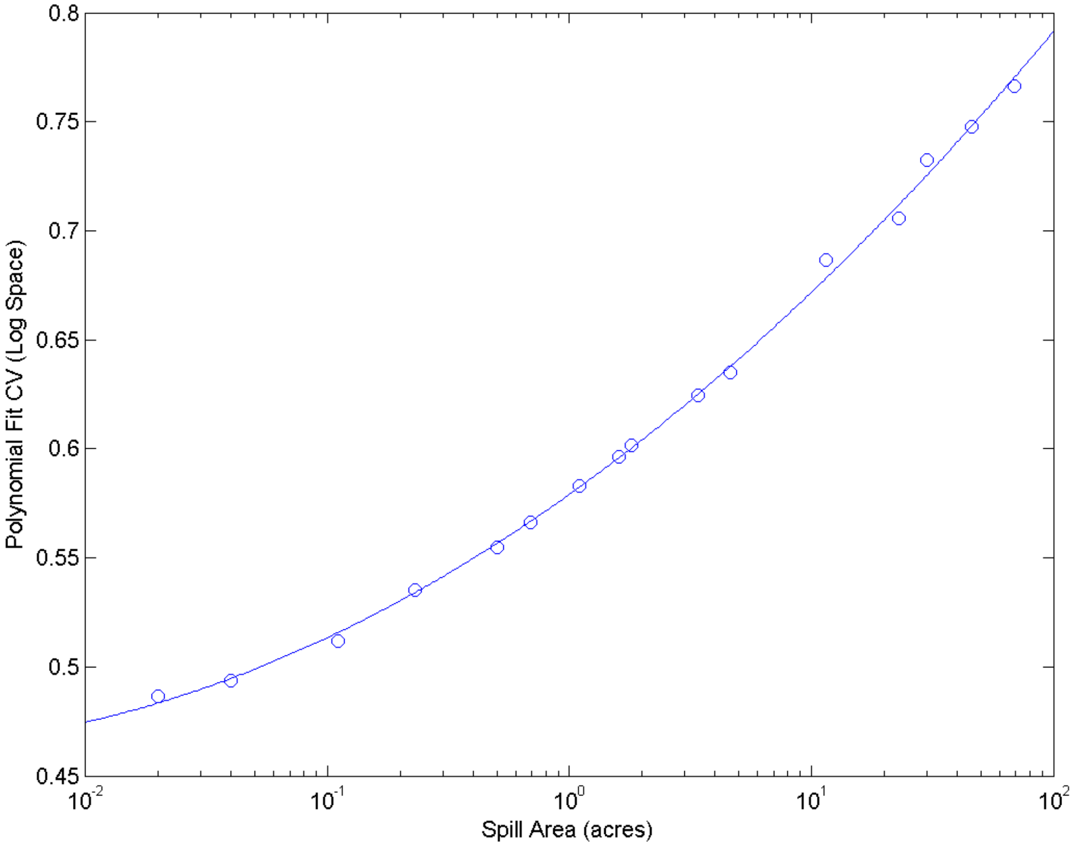

Figure C.2 Polynomial Best Fit Coefficient of Variation (natural log) DF Fit as a Function of Source Area for US EPA-reported DF Percentiles

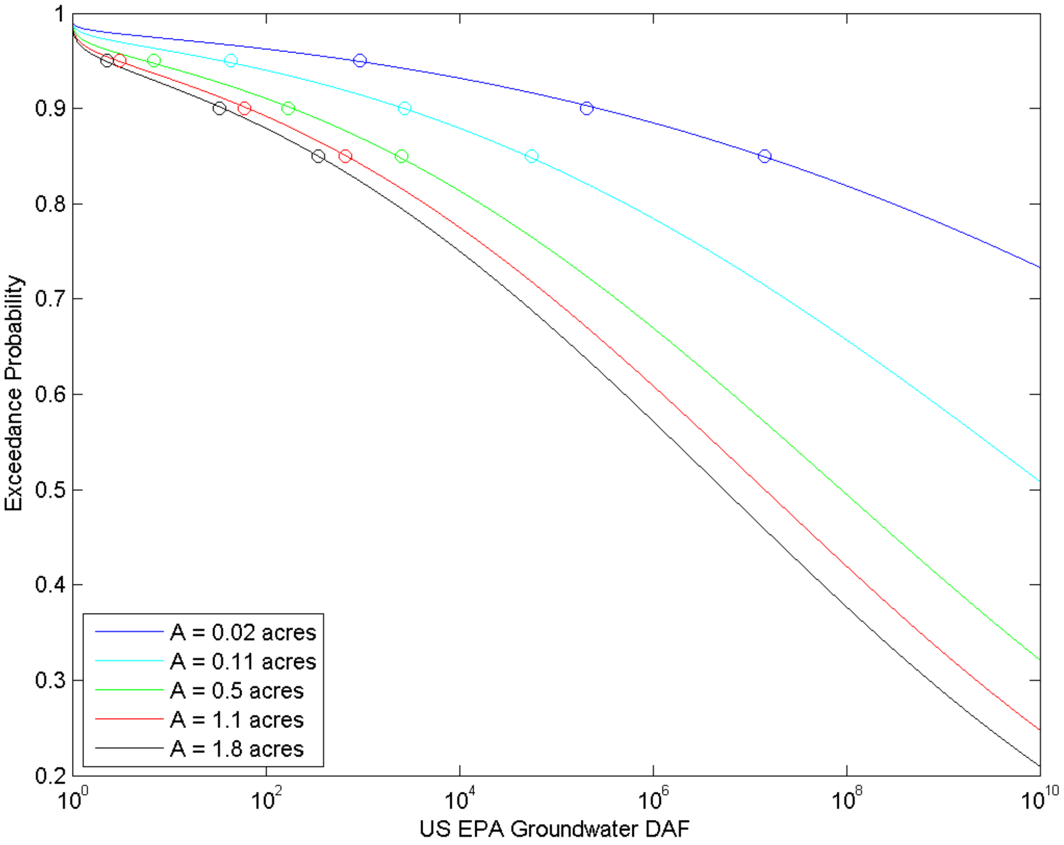

Figure C.3 Fitted Cumulative Distribution Functions of US EPA Groundwater DAF Values and Corresponding US EPA-reported Percentiles

As Figure C.4 shows below, there is a very close fit of the fitted DFs (using the above polynomial curve fitting method) and the US EPA-reported DF percentiles. As further verification that our procedures provided a reliable means to estimate the groundwater DFs (*e.g.*, matching the high-end DFs reported by US EPA, we plotted our "fitted DFs" *versus* those reported by US EPA.

To generate samples from the full distribution of DFs as a function of spill area (*e.g.*, rather than just the percentiles reported by US EPA), the following equation was used:

$$DF_{gw} = e^{(Z\sigma+\mu)} + 1 \qquad \text{(C.10)}$$

where Z is a randomly generated standard normal variate (mean of 0 and standard deviation of 1) with associated probability, and $\sigma = CV \times \mu$. Any particular percentile of the distribution can be calculated using Equation C.10 by substituting the associated value of Z_α in this equation, where α corresponds to the probability (percentile) of interest (see below).[3]

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[3] The US EPA percentiles are reported the DF percentiles as the "complimentary" cumulative distribution function, which is simply 1 – P(y), where P(y) is the cumulative distribution function (CDF). These "upper" percentiles of the complimentary CDF represent the 1-pth lower percentile values of the CDF, *i.e.*, the upper 85th percentile of the complimentary CDF is the lower 15th percentile of the CDF, the 90th percentile is the lowest 10th percentile, and the 95th percentile is the lowest 5th percentile, respectively.

Percentile (α)	15th = 1 - 85th	10th = 1 - 90th	5th = 1 - 95th
Z_α	-1.0364	-1.282	-1.645

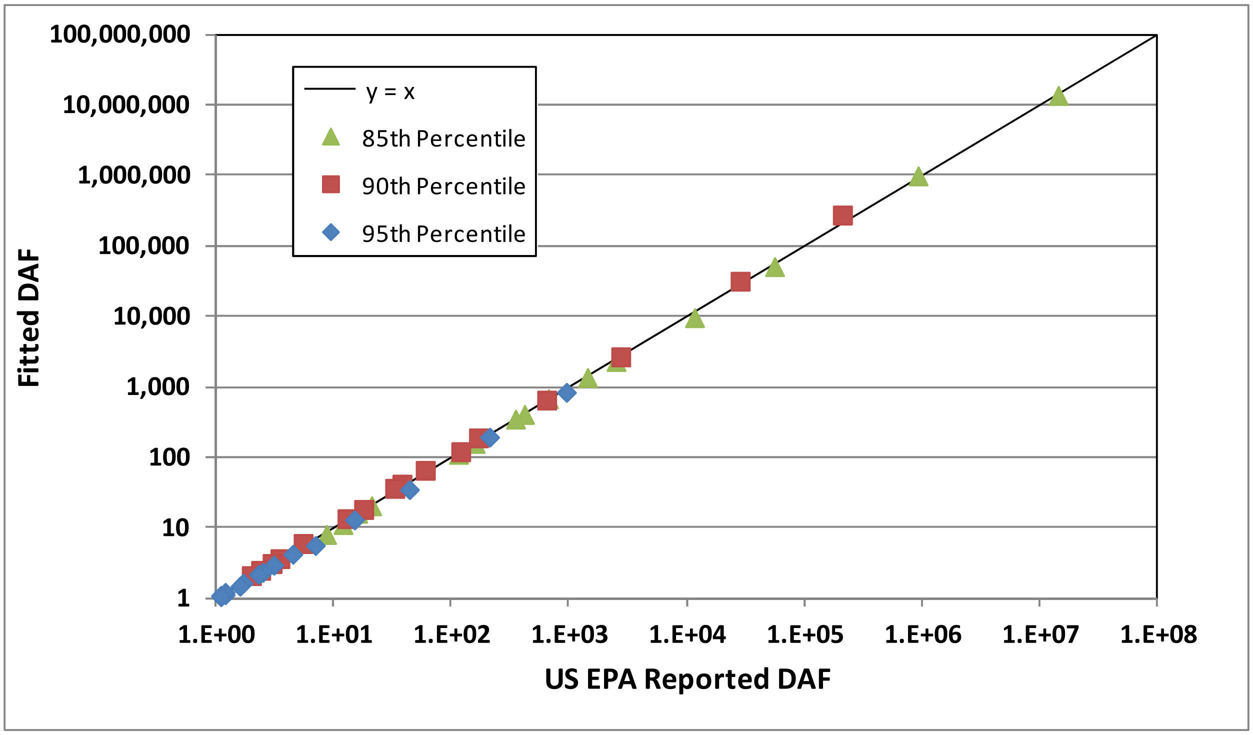

Figure C.4 Comparison of Fitted Groundwater DF Percentiles and US EPA-reported DAF Percentiles

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Appendix D

Drinking Water Human Health Risk Based Concentrations (RBCs) for HF Additives

List of Tables

Abbreviations

AI	Adequate Intake
AIM	Analog Identification Methodology
ATSDR	Agency for Toxic Substances and Disease Registry
CalEPA	California Environmental Protection Agency
DRI	Dietary Reference Intake
GRAS	Generally Recognized as Safe
FAO	Food and Agriculture Organization
HEAST	Health Effects Assessment Summary Tables
HF	Hydraulic Fracturing
HPV	High-Production Volume
HSDB	Hazardous Substances Data Bank
IPCS	International Programme on Chemical Safety
IRIS	Integrated Risk Information System
JEFCA	Joint FAO/WHO Expert Committee on Food Additives
LOAEL	Lowest Observed Adverse Effect Level
MCL	Maximum Contaminant Level
MRL	Minimum Risk Level
NOAEL	No Observed Adverse Effect Level
NSF	National Sanitation Foundation
OPP	Office of Pesticides Program
PPRTV	Provisional Peer Reviewed Toxicity Value
RBC	Risk-Based Concentration
RDA	Recommended Daily Allowance
RfD	Reference Dose
RfC	Reference Concentration
RSL	Regional Screening Level
RTECS	Registry of Toxic Effects of Chemical Substances
TPHCWG	Total Petroleum Hydrocarbon Criteria Working Group
UF	Uncertainty Factor
UL	Tolerable Upper Intake Levels
US EPA	United States Environmental Protection Agency
US FDA	United States Food and Drug Administration
WHO	World Health Organization

Overview

This appendix describes the sources of chemical hazard (toxicity) information and methods we relied upon to develop health protective drinking water risk-based concentrations (RBCs) for constituents in hydraulic fracturing (HF) fluid additives and flowback water. These RBCs, developed in accordance with United States Environmental Protection Agency (US EPA) risk assessment guidelines and methods (US EPA, 1996, 2009a, 2012a) reflect chemical concentrations in drinking water that would not be expected to pose human health risks.

Our approach involved using agency-established health-protective drinking water limits and toxicity factors when available, such as maximum contaminant levels (MCLs), regional screening levels (RSLs), and reference doses (RfDs). When such information was not available, we investigated chemical-specific toxicity information *via* the oral route of exposure. If repeated dose oral toxicology information was available, we used this information to develop quantitative toxicity factors using a methodology consistent with US EPA guidance. In the absence of any chemical-specific oral toxicity information we identified toxicity information for a chemical surrogate and used that information to develop an RBC. For compounds where we could not locate an appropriate chemical surrogate, we performed a qualitative hazard assessment based on one of several different evaluations performed by the United States Food and Drug Administration (US FDA) or US EPA.

D.1 Sources of Chemical Hazard Information for Use in HF Risk Analysis

As summarized here, and reflected in the HESI HF fluid systems, a wide variety of additives and their associated chemical constituents could be used in hydraulic fracturing. The sources of hazard information we examined to determine RBCs for these constituents are described below and summarized in Table D.1.

- Chemical-Specific, Quantitative Toxicity Factors: US regulatory agencies and other scientific institutions are important sources of quantitative toxicity information. In particular, the US EPA has developed MCLs and tap water RSLs, which use established toxicity factors with generic exposure assumptions to develop chemical concentrations in drinking water that are safe to consume over a lifetime. Other agencies, including US FDA and the Joint FAO/WHO Expert Committee on Food Additives (JEFCA), also quantify a chemical dose that is safe to consume over a lifetime. This "safe" dose can subsequently be combined with exposure information to calculate safe drinking water concentrations. As discussed in Section D.2, we used these established values preferentially as RBCs.
- Quantitative Toxicity Factors Derived Using Chemical-Specific Toxicity Information: When established toxicity factors were not available, but there was adequate information from long-term toxicology studies, we developed toxicity factors and associated RBCs *de novo*. This was accomplished using well-accepted methodologies that properly account for uncertainties.
- Quantitative Toxicity Factors Derived Using Information on a Chemical Surrogate: In the absence of chemical-specific information, we used the US EPA's Analog Identification Methodology (AIM) in conjunction with professional judgment to identify compounds that would be expected to have similar toxicity to the compound of interest because of shared structural

features. Once an appropriate chemical surrogate was identified, we used existing criteria or toxicity information on the surrogate compound to develop a health-protective RBC.

- Qualitative Toxicity Information on Hazard Potential: Several available data sources have evaluated the potential for a chemical to pose a public health concern. While this information is not quantitative, we used this information to understand whether a compound is likely to have a low potential to pose a human health risk.

Table D.1 Sources of Hazard Information Used in the HF Risk Evaluation

Information Type	Specific Examples
Chemical-Specific, Quantitative Toxicity Factors	
	MCLs RSLs US EPA values (IRIS, PPRTV, HEAST, OPP) CalEPA values ATSDR MRLs Dietary Reference Intakes NSF RfDs TPHCWG criteria JECFA Safe Intake Levels
Sources of Chemical-Specific or Surrogate Information Used to Develop Toxicity Factors	
	ACToR TOXNET Hazardous Substances Data Bank RTECS International Programme on Chemical Safety INCHEM JECFA - Monographs and Evaluations Joint Meeting on Pesticide Residues (JMPR) - Monographs and Evaluations Screening Information Data Set (SIDS) for High Production Volume Chemicals
Qualitative Toxicity Information on Hazard Potential	
	US FDA Generally Recognized as Safe Evaluation US EPA Low Hazard Polymer Exemption Guidance US EPA Tolerance Exempt Chemical Lists

D.2 Hierarchy for Selecting Risk Based Criteria

Given the large number of HF constituents in the typical HESI HF fluid systems, it was necessary to examine multiple sources of toxicology information in order to establish the drinking water RBCs. We used a tiered approach to identify or develop health-protective RBCs for the HF and flowback constituents. This tiered hierarchy incorporates standard risk assessment practice and US EPA guidance (US EPA, 1996, 2009a, 2012a). This sequential methodology is described below (see also Figure 6.1 in the body of the report):

- We preferentially used promulgated chemical-specific drinking water MCLs as RBCs where available (US EPA, 2009a), as the MCLs represent federally established acceptable drinking water concentrations for public water supplies.

- For chemicals lacking an MCL, we used risk-based "tap water" RSLs published by the US EPA (2012b) as the RBC, where they were available. These RSLs are based on the long-term drinking water consumption of children (*i.e.*, 15-kg child ingesting 1 L/day of water).
- If MCLs and RSLs were not available, we used quantitative oral toxicity factors published by various regulatory agencies to calculate health-protective RBCs. The RBCs calculated in this manner were based on exposure assumptions consistent with US EPA's RSL methodology (*i.e.*, 15-kg child ingesting 1 L/day of water; US EPA, 2012c). We preferentially used sources of toxicity factors in the following order:
  - IRIS database → DRI →PPRTVs → MRL List→ CalEPA → HEAST → NSF → US EPA's OPP → GRAS database and JEFCA information → Toxicology Working Group Values (*e.g.*, TPHCWG, HERA, *etc.*)
- For compounds that did not have an MCL, RSL, or an agency-established oral toxicity factor, we obtained primary repeated dose oral toxicity data (*i.e.*, a study duration of at least 28 days), and derived a "chronic RfD" *de novo* using methods to account for uncertainty that are consistent with US EPA methods for deriving RfDs in the Integrated Risk Information System (IRIS).
- If repeat-dose oral toxicity information was not available, we used US EPA's AIM, in conjunction with professional judgment, to select a surrogate compound that, because of shared structural features, would be expected to have similar toxicity as the compound being evaluated. Also, in the cases of salts that readily dissociate, if toxicity information on the salt was not available, we used toxicity information on the individual ions to develop RBCs. As a conservative measure, we used the ion with higher toxicity to calculate the RBC. For example, magnesium chloride hexahydrate dissolves completely in water, such that only magnesium and chloride ions remain in solution. We used hazard data for magnesium, the more toxic ion, to develop an RBC for this constituent.
- For HF and flowback components that did not have chronic oral toxicity information, it was not possible to quantitatively evaluate the chemical of interest in this risk evaluation. For these chemicals we performed a qualitative assessment and cross-referenced the component against government regulatory lists indicating if the chemical was Generally Recognized as Safe (US FDA), an inert pesticide ingredient (US EPA), or met the requirements for determination of a "low risk" polymers (US EPA).

A summary of the RBCs used in this risk evaluation is presented in Table D.2a,b. Additional information describing the sources of this information is provided in the following sections.

D.3 Hazard Identification Approach

This section describes the specific sources of information we used to determine the RBCs for the HF and flowback constituents.

D.3.1 Maximum Contaminant Levels

US EPA establishes enforceable drinking water standards called MCLs for approximately 70 inorganic and organic compounds. An MCL considers chemical toxicity, and factors such as technical water treatment feasibility and the cost of compliance. According to US EPA, the MCLs "reflect both the level [in drinking water] that protects human health and the level that water systems can achieve using the best available technology" (US EPA, 2009b, 2012b). For HF constituents with a promulgated MCL, we selected the MCL as the RBC.

D.3.2 US EPA Regional Screening Levels

Regional US EPA offices have independently developed risk-based screening levels for drinking water (for both residential and industrial scenarios). At one time, each region developed and relied on different sets of screening criteria, but recently these analyses have been harmonized into a common set of criteria called RSLs (US EPA, 2012b). Unlike MCLs, RSLs are not enforceable drinking water standards. According to the regional US EPA offices (US EPA, 2012c):

> SLs [Screening Levels] are not de facto cleanup standards and should not be applied as such. The SL's role in site "screening" is to help identify areas, contaminants, and conditions that require further federal attention at a particular site…. Chemical concentrations above the SL would not automatically designate a site as "dirty" or trigger a response action; however, exceeding a SL suggests that further evaluation of the potential risks by site contaminants is appropriate.

Many more chemicals have RSLs than MCLs (some chemicals have both). This is because an RSL can readily be calculated for any compound with a US-agency approved RfD and/or cancer slope factor. RSLs consider potential health risks associated with both cancer and non-cancer endpoints; the RSL is ultimately based on the endpoint that results in the more restrictive level (typically the cancer health endpoint). The US EPA derives the residential RSLs assuming the risks to a child based on a 30-year daily exposure to chemicals in drinking water. For non-cancer endpoints, this long term daily intake is averaged over the exposure period (*i.e.*, 30 years), whereas for cancer endpoints, the daily intake is averaged over a lifetime. For HF constituents lacking an MCL, but for which a published drinking water RSL existed, we used the residential RSL as the RBC.

D.3.3 RBCs Derived Using Agency-Established Toxicity Factors

Oral toxicity criteria can be used to develop safe levels of chemical concentrations (*i.e.*, an RBC) in drinking water. US EPA as well as several other US agencies and leading scientific institutions have developed chemical-specific oral toxicity values. These toxicity values were used to calculate an RBC utilizing the approach employed by US EPA to calculate a tap water RSL (US EPA, 2012b). Specific toxicity resources used in this evaluation are summarized below.

D.3.3.1 US EPA Toxicity Factors

The preferential source for quantitative human health risk assessment criteria is the US EPA's IRIS (US EPA, 2013a). US EPA develops toxicity criteria known as RfDs to evaluate non-cancer risks. As defined by US EPA, an RfD is intended to represent "[a]n estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime" (US EPA, 2002). According to US EPA methodology, to derive an RfD, the chemical-specific threshold dose must be defined. This is accomplished by identifying a LOAEL and/or a NOAEL, from either human epidemiology or laboratory animal toxicology studies. After determining the NOAEL or LOAEL, this dose is divided by uncertainty factors (UFs) to account for potential uncertainties (including inter- and intra-species differences in sensitivity, insufficient study durations, use of a LOAEL instead of a NOAEL, and data deficiencies) to arrive at a final RfD. The application of UFs in the derivation of the RfD helps ensure that the RfD is health-protective. It should be noted, however, that according to US EPA, "it should not be categorically concluded that all doses below the RfD are 'acceptable' (or will be risk-free) and that all doses in excess of the RfD are 'unacceptable' (or will result in adverse effects)" (US EPA, 1993).

D.3.3.2 Non-US EPA Toxicity Factors

For constituents lacking toxicity criteria in the IRIS database, we considered toxicity information published by other authoritative agencies that have developed comparable criteria. In general, toxicity criteria developed by these organizations are analogous to RfDs developed by US EPA, both in their derivation, and in their representation of a dose associated with negligible risk to the general population, including sensitive subpopulations, from lifetime exposures. Additional sources of quantitative toxicity information used to calculate health-based drinking water concentrations (*i.e.*, RBCs) are as follows:

- **Dietary Reference Intakes**: Under the umbrella of the National Academies of Science, the Institute of Medicine has established dietary reference intakes (DRIs) (NAS, 2013). DRIs can encompass several different types of reference values, including Recommended Dietary Allowances (RDAs), Adequate Intakes (AIs), and Tolerable Upper Intake Levels (ULs). In the present analysis, we used ULs when available. A UL is defined as "the highest average daily nutrient intake level that is likely to pose no risk of adverse health effects to almost all individuals in the general population" (IOM, 2005). If a UL was not available we used an RDA. If an RDA was not available, we used an AI.
- **Criteria Developed Under US EPA's Office of Pesticides Program (OPP)**: Under the US EPA pesticide registration program, OPP develops quantitative toxicity factors to evaluate potential risk associated with pesticide use. These values appear in the re-registration eligibility decision documents for specific pesticides (US EPA, 2013b).
- **Safe Intake Levels Under US FDA Generally Recognized as Safe (GRAS) Program**: Under this program, a compound is considered "GRAS" if the substance is generally recognized, among qualified experts, as having been adequately shown to be safe under the conditions of its intended use (US FDA, 2013). In certain cases, chemical intake that is unlikely to be associated with adverse effects has been established.
- **JECFA Evaluations**: JECFA is an international scientific expert committee that is administered jointly by the Food and Agriculture Organization of the United Nations and the World Health Organization. JECFA has published monographs that quantify safe intakes of food additives and constituents.
- **Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) Values**: The TPHCWG is a scientific panel specifically convened to establish toxicity factors for petroleum fractions for use in risk assessment. The working group's stated purpose is: "To develop scientifically defensible information for establishing soil cleanup levels that are protective of human health at hydrocarbon contaminated sites" (TPHCWG, 1997).

D.3.3.3 RBC Calculation Approach

The approach used by US EPA for calculating a tap water RSL (US EPA, 2012c) was used to calculate a RBC for constituents that lacked an MCL or RSL. The RBC value was calculated by combining the toxicity value (obtained from an agency source or derived *de novo* using toxicity studies) together with standard US EPA exposure assumptions (US EPA, 2012c) in the following equation:

$$\text{Risk Based Concentration}\left(\frac{\mu g}{L}\right) = \frac{\text{RfD}\left(\frac{mg}{kg-day}\right) \times \text{BW (kg)} \times \text{CF}\left(\frac{\mu g}{mg}\right)}{\text{IR}\left(\frac{L}{day}\right)}$$

where:

RfD = chronic oral reference dose (mg/kg-day)
BW = body weight (15 kg for a child)
IR = drinking water ingestion rate (1 liter/day for a child)
CF = conversion factor (1,000 µg/mg)

The RfD values used and the calculated RBC values are presented in Table D.2a.

D.3.4 RBCs Derived Using Repeat-Dose Toxicology Studies

In the absence of an existing toxicity criterion from the above agency sources, we developed chemical-specific toxicity factors *de novo* using an approach consistent with the US EPA IRIS methodology (US EPA, 1993). Adopting this approach allowed us to include HF additive chemicals that would otherwise not have been included in the risk evaluation due to a lack of agency-established toxicity criteria. Similar to US EPA's RSLs, these *de novo* RBCs were developed to evaluate long-term exposure for children. A chronic toxicity criterion (*i.e.*, reference dose) was developed using the following equation:

$$\text{Calculated Reference Dose (RfD)}\left(\frac{mg}{kg-day}\right) = \frac{\text{NOAEL or LOAEL}\left(\frac{mg}{kg-day}\right)}{(UF_{AH} \times UF_{HH} \times UF_{SbC} \times UF_{LN} \times UF_{DB})}$$

where:

NOAEL = no observed adverse effect level from a subchronic or chronic oral study (mg/kg-day)
LOAEL = lowest observed adverse effect level from a subchronic or chronic oral study (mg/kg-day)
UF_{AH} = interspecies uncertainty factor (animal to human)
UF_{HH} = intraspecies uncertainty factor (human to human)
UF_{SbC} = subchronic to chronic uncertainty factor
UF_{LN} = LOAEL to NOAEL uncertainty factor
UF_{DB} = database uncertainty factor

Uncertainty values used in the RfD calculations are summarized in Table D.3 below.

In an effort to be comprehensive and evaluate as many chemicals as possible, we conducted an extensive review of toxicology information for all HF constituents[1] that did not have existing quantitative toxicity criteria. We identified chemical-specific toxicity studies involving repeated exposures (*i.e.*, studies assessing at least a 28-day exposure) and used this information in conjunction with US EPA methodology to develop quantitative estimates of a "chronic RfD" (US EPA, 1993). This approach was also taken for

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[1] As a conservative measure, when evaluating chemicals that would disassociate in water, we preferentially selected the ion with higher toxicity when calculating the RBC. For example, magnesium chloride hexahydrate dissolves completely in water, such that only magnesium and chloride ions remain in solution; in this case, we based the RBC on the magnesium ion.

an appropriate chemical surrogate if chemical-specific toxicity information was not available. The sources of information we used to identify relevant toxicological studies are listed below:

- **ACToR** (http://actor.epa.gov/actor)

  ACToR is a database of publicly available chemical toxicity data that was recently compiled by US EPA's National Center for Computational Toxicology. The online site aggregates data from over 500 public sources, on over 500,000 environmental chemicals. Information on chemicals is searchable by chemical name, chemical structure, and various other chemical identifiers.

- **TOXNET (**http://toxnet.nlm.nih.gov/)

  TOXNET is a collection of databases covering toxicology, hazardous chemicals, environmental health, and related areas. It is managed by the Toxicology and Environmental Health Information Program in the Division of Specialized Information Services of the National Library of Medicine. For this evaluation we relied mainly on information presented in HSDB® (Hazardous Substances Data Bank). HSDB is a factual TOXNET database focusing on the toxicology of over 5,000 potentially hazardous chemicals. In addition to toxicity data, HSDB provides information in the areas of emergency handling procedures, industrial hygiene, environmental fate, human exposure, detection methods, and regulatory requirements. The data are fully referenced and peer-reviewed by a Scientific Review Panel composed of expert scientists.

- **IPCS INCHEM** (http://www.inchem.org/)

  IPCS INCHEM is a collection of databases produced through cooperation between the International Programme on Chemical Safety (IPCS) and the Canadian Centre for Occupational Health and Safety. It offers quick and easy electronic access to thousands of searchable full-text documents on chemical risks and the sound management of chemicals. IPCS INCHEM contains data from the following 13 databases:

  - Concise International Chemical Assessment Document (CICADS)
  - Environmental Health Criteria (EHC) Monographs
  - Harmonization Project Publications
  - Health and Safety Guides (HSGs)
  - ARC Summaries and Evaluations
  - International Chemical Safety Cards (ICSCs)
  - IPCS/CEC Evaluation of Antidotes Series
  - JECFA – Monographs and Evaluations
  - Joint Meeting on Pesticide Residues (JMPR) – Monographs and Evaluations
  - KemI-Riskline
  - Pesticide Data Sheets (PDSs)
  - Poisons Information Monographs (PIMs)
  - Screening Information Data Set (SIDS) for High Production Volume Chemicals

After identifying relevant NOAELs and/or LOAELs from our extensive toxicological evaluation, we conservatively applied uncertainty factors to account for differences in species sensitivity, duration of the study, and adequacy of the available data according to the default recommended uncertainty factor approach provided by US EPA (US EPA, 2002). Table D.3 lists the default factors for each category of uncertainty. A value of 3,000 is the maximum UF recommended by US EPA guidance to derive a chronic toxicity factor (US EPA, 2002).

Table D.3 Summary of Uncertainty Factors

Uncertainty Factor (UF) Type [a]	Value
Interspecies UF	10
Intraspecies UF	10
LOAEL to NOAEL UF	10
Subchronic to Chronic UF	10
Database UF [b]	3 or 10
Maximum UF	3,000

Notes:
[a] Default values as reported by US EPA (2002).
[b] Default UFs for database adequacy can be reduced from 10 to 3 if sufficient studies defining reproductive and developmental effects (*e.g.*, 2-generation reproduction study or prenatal developmental study) are available in the toxicity database and consideration of the overall availability of toxicity information (US EPA, 2002).

For one compound, isopropanol, we were able to locate an RfD derivation in the primary scientific literature. Using pharmacokinetic modeling, Gentry *et al*. (2002) derived a chronic oral RfD of 10 mg/kg. We used this value in our analysis.

D.3.5 Qualitative Assessment of Chemicals Lacking Quantitative Data

For some chemicals, we were unable to locate credible quantitative oral toxicity information to reliably calculate an RBC. Therefore, we excluded these compounds from the quantitative risk consideration. Several of these compounds, however, have additional information that allows us to make qualitative judgments about the potential for a compound to pose a human health risk. Sources of information used in this qualitative assessment are provided below. The compounds that have no RBC were evaluated in a qualitative assessment described below.

D.3.5.1 Chemicals With US Government Tolerance Exemptions

Several US government agencies identify exemptions for the ingestion of certain chemicals. For example, US FDA has designated select chemicals as GRAS. Similarly, US EPA has classified certain pesticide ingredients as "minimal risk" (which are exempt from a tolerance and can be used without restriction in accordance with good agricultural practices), while others may have some use restrictions but are still exempt from tolerance requirements. While GRAS and inert pesticide ingredients not requiring a tolerance cannot necessarily be equated to a lack of toxicity, the lack of need for approval as a food additive or a tolerance limit provides an indication that the compound is considered less of a human health concern compared to compounds that do require such limits.

- **US FDA Generally Recognized as Safe**

US FDA has designated some chemicals added to food as GRAS. Under the mandates of the Federal Food, Drug, and Cosmetic Act, any substance that is intentionally added to food is a food additive that is subject to premarket review and approval by US FDA, "unless the substance is generally recognized, among qualified experts, as having been adequately shown to be safe under the conditions of its intended use, or unless the use of the substance is otherwise excluded from the definition of a food additive" (21 CFR 170.3(i); US FDA, 2013). Table D.2 lists HF constituents that have been determined to be GRAS by qualified experts, along with the conditions of the intended use (CFR 42, Title 21, Part 182). For example, the table lists the intended usage (*e.g.*, milk and cream), as well as if the chemical is a direct or indirect additive to the food (see RBC Basis Notes).

- **US EPA Inert Ingredients**

  US EPA has also identified several groups of chemicals that are exempt from the requirement to derive a tolerance level when used in food additives (US EPA refers to these chemicals as "inert ingredients"; US EPA, 2013c). The term "inert ingredient" is a legal definition as defined by the Federal Insecticide, Fungicide, and Rodenticide Act, which governs the use of pesticides. While an "active ingredient" in a pesticide formulation is the constituent that "prevents, destroys, repels, or mitigates a pest, or is a plant regulator, defoliant, desiccant or nitrogen stabilizer," the additional ingredients in the formulation are referred to as "inert ingredients" (US EPA, 2013c). These inert chemicals are broadly divided into different categories. "Minimal risk" ingredients are inert ingredients that do not have any use limitations other than being used in accordance with good agricultural and manufacturing practices. These include chemicals that are commonly consumed food commodities, animal feed items, edible fats and oils, or other substances specified in 40 CFR 180.950. Additionally, other inert compounds may be specified for food, non-food use, or both. Such compounds similarly do not require a tolerance limit, but there may be certain limitations or restrictions on use. Table D.2a indicates those HF additives that have been determined to be "minimal risk" or inert ingredients approved for food, fragrance, or non-food use. US EPA designated inert chemicals were located using the following resource:

- **US EPA InertFinder** (http://iaspub.epa.gov/apex/pesticides/)

  The US EPA InertFinder database is a listing of both "active" and "inert" pesticide ingredients. This online database lists the status of an inert ingredient on 40 CFR part 180 (including uses and limitations, if any), as well as its status as a food ingredient, nonfood use inert ingredient, or status as a component of a fragrance (*i.e.*, inclusion on the OPP Fragrance Ingredient List).

D.3.5.2 US EPA Polymer Assessment

In addition to the above analyses, we reviewed the polymers in HF additives for those that can be classified as low toxicity substances according to US EPA guidelines. US EPA (2001) states:

> polymers with molecular weights greater than 400 generally are not absorbed through the intact skin and substances with molecular weights greater than 1,000 generally are not absorbed through the gastrointestinal tract (GI). Chemicals not absorbed through the skin or GI tract generally are incapable of eliciting a toxic response. Therefore, there is no reasonable expectation of risk due to cumulative exposure.

The specific criteria for determining low risk polymers according to US EPA guidance are as follows (US EPA, 2009c):

1. "The polymer is not a cationic polymer nor is it reasonably anticipated to become a cationic polymer in a natural aquatic environment.
2. The polymer does contain as an integral part of its composition the atomic elements carbon, hydrogen, and oxygen.
3. The polymer does not contain as an integral part of its composition, except as impurities, any element other than those listed in 40 CFR 723.250(d)(2)(ii).
4. The polymer is neither designed nor can it be reasonably anticipated to substantially degrade, decompose, or depolymerize. The polymer is manufactured or imported from monomers and/or reactants that are already included on the TSCA [Toxic Substances Control Act] Chemical Substance Inventory or manufactured under an applicable TSCA section 5 exemption.
5. The polymer is not a water absorbing polymer with a number average molecular weight (MW) greater than or equal to 10,000 daltons.
6. Additionally, the polymer also meets as required the following exemption criteria specified in 40 CFR 723.250(e).
7. The polymer's number average MW is greater than 1,000 and less than 10,000 daltons. The polymer contains less than 10% oligomeric material below MW 500 and less than 25% oligomeric material below MW 1,000, and the polymer does not contain any reactive functional groups."

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Table D.2a Summary of Drinking Water Risk Based Concentrations (RBCs) for HF Constituents

CAS	Chemical Name	CAS RBC Chem	RBC Chemical (if different than chemical name)	RBC (µg/L)	RBC Basis Notes	RBC Note[a]
95-63-6	1,2,4 Trimethylbenzene			15	US EPA ingestion RSL	A
52-51-7	2-Bromo-2-nitro-1,3-propanediol			1,500	Existing OPP toxicity factor (US EPA, 1995)	A
64-19-7	Acetic acid			214,200	Quantitative JEFCA information (JEFCA, 1974)	B
108-24-7	Acetic anhydride	64-19-7	Acetic acid	214,200	Quantitative JEFCA information for surrogate chemical (JEFCA, 1974)	D
68551-12-2	Alcohols, C12-16, ethoxylated		Ethoxylated alcohols	5,625	Working group derived toxicity factor (HERA, 2009)	B
68951-67-7	Alcohols, C14-C15, ethoxylated		Ethoxylated alcohols	5,625	Working group derived toxicity factor (HERA, 2009)	B
CBI	Aldehyde			1,250	Repeat-dose reproductive toxicity study	C
CBI	Alkyl sulfonate			5,000	Repeat-dose toxicity study	C
61791-14-8	Amines, coco alkyl, ethoxylated			3,750	Repeat-dose toxicity study (US EPA, 2013)	C
631-61-8	Ammonium acetate			300	Repeat-dose toxicity study (US EPA, 2008)	D
12125-02-9	Ammonium chloride			3,420	Repeat-dose toxicity study (OECD, 2003a)	C
7727-54-0	Ammonium persulfate			205	Repeat-dose toxicity study (OECD, 2005)	C
7722-76-1	Ammonium phosphate			30,000	US EPA (2006b) Lifetime health advisory level	A
12174-11-7	Attapulgite			1,920,000	Prescription drug use information (MedicineNet, 1999)	B
121888-68-4	Bentonite, benzyl(hydrogenated tallow alkyl) dimethylammonium stearate complex			5,000	Repeat-dose toxicity study (OECD, 2007)	C
CBI	Borate salt			3,100	US EPA ingestion RSL for surrogate chemical	D
3468-63-1	C.I. Pigment Orange 5		CI Pigment Red	125	Repeat-dose toxicity study for surrogate chemical (CPMA, 2006)	D
10043-52-4	Calcium chloride			50,000	Repeat-dose toxicity study (OECD, 2002d)	C
CBI	Carbohydrate			105,000	Dietary Reference Intake Value	A
15619-48-4	Chloromethylnaphthalene quinoline quaternary				Unable to locate relevant quantitative chronic toxicology information	E
7758-19-2	Chlorous acid, sodium salt			1,000	Drinking water MCL	A
94266-47-4	Citrus, extract				Unable to locate relevant quantitative chronic toxicology information. US EPA Inert Chemical approved for non-food and fragrance use. US FDA Food Additives Generally Recognized as Safe (21 CFR 182.20)	E
71-48-7	Cobalt acetate	7440-48-4	Cobalt	4.7	US EPA ingestion RSL	A
14808-60-7	Crystalline silica, quartz		Silicas/silicates	37,500	Repeat-dose toxicity study (OECD, 2004b)	C
CBI	Cured acrylic resin				Unable to locate relevant quantitative chronic toxicology information. US FDA Indirect Food Additives (21 CFR 175.105, 175.320, 176.170, 177.1200, 175.320). Very low acute toxicity (Oral LD50 Rat > 2,000 mg/kg).	E
111-46-6	Diethylene glycol			1,500	Repeat-dose toxicity study (Wagner, 2006)	C
111-40-0	Diethylenetriamine			350	Repeat-dose toxicity study (AP&G, 2003)	C
CBI	EDTA/Copper chelate			630	Agency-derived value	A
64-17-5	Ethanol			12,000	Repeat-dose toxicity study (OECD, 2004a)	C
CBI	Ethoxylate fatty acid			28,625	Repeat-dose toxicity study for surrogate chemical	D
CBI	Ethoxylate fatty acid	5117-19-1/25322-68-3	PEG-8	15,000	Repeat-dose toxicity study for surrogate chemical	D
78330-21-9	Ethoxylated branched C13 alcohol		Ethoxylated alcohols	5,625	Working group derived toxicity factor (HERA, 2009)	B
CBI	Ethoxylated fatty acid	5117-19-1/25322-68-3	PEG-8	15,000	Repeat-dose toxicity study for surrogate chemical	D
111-76-2	Ethylene glycol monobutyl ether			1,600	US EPA ingestion RSL	A
CBI	Fatty acid ester			9,000	Repeat-dose toxicity study	C
CBI	Fatty acid tall oil			125,000	Repeat-dose toxicity study	C
CBI	Fatty acid tall oil amide		Amides, coco, N,N-bis(hydroxyethyl)	500	Repeat-dose toxicity study for surrogate chemical	D
9043-30-5	Fatty alcohol polyglycol ether surfactant				Unable to locate relevant quantitative chronic toxicology information. US EPA Inert Chemical approved for	E
CBI	Fatty acid ester ethoxylate			5,000	Repeat-dose toxicity study	C
50-00-0	Formaldehyde			3,100	US EPA ingestion RSL	A
56-81-5	Glycerine			400,000	Repeat-dose toxicology study (ECA, 2011)	C

Table D.2a Summary of Drinking Water Risk Based Concentrations (RBCs) for HF Constituents

CAS	Chemical Name	CAS RBC Chem	RBC Chemical (if different than chemical name)	RBC (µg/L)	RBC Basis Notes	RBC Note[a]
9000-30-0	Guar gum			81,413	Repeat-dose toxicity study (NTP, 1982)	C
CBI	Guar gum derivative	9000-30-0	Guar gum	81,413	Repeat-dose toxicity study for surrogate chemical	D
64742-94-5	Heavy aromatic petroleum naphtha		Petroleum distillate	600	Working group derived toxicity factor (TPHCWG, 1997)	B
9012-54-8	Hemicellulase enzyme			600	Repeat-dose reproductive toxicity study	C
7647-01-0	Hydrochloric acid			7	Repeat-dose toxicity study (Upton and L'Estrange, 1977)	C
64742-47-8	Hydrotreated light petroleum distillate		Petroleum distillate	1,500	Working group derived toxicity factor (TPHCWG, 1997)	B
CBI	Inorganic salt			50,000	Repeat-dose toxicity study	C
67-63-0	Isopropanol			150,000	Repeat-dose toxicity study (Gentry *et al.* , 2002)	C
7791-18-6	Magnesium chloride hexahydrate	7439-95-4	Magnesium	75,000	Dietary Reference Intake Value (IOM, 2001)	A
67-56-1	Methanol			7,800	US EPA ingestion RSL	A
64742-48-9	Naphtha, hydrotreated heavy		Petroleum distillate	1,500	Working group derived toxicity factor (TPHCWG, 1997)	B
91-20-3	Naphthalene			310	US EPA ingestion RSL	A
68410-62-8	Naphthenic acid ethoxylate		Napthenic acids	500	Repeat-dose toxicity study for surrogate chemical (API, 2012)	D
127087-87-0	Nonylphenol ethoxylated			10,000	Repeat-dose toxicity study (DOW, 2007)	C
CBI	Olefin		C16/C18 compound	5,000	Repeat-dose toxicity study for surrogate chemical	D
CBI	Olefin			500	Repeat-dose toxicity study for surrogate chemical	D
CBI	Olefin		C16/C18 compound	5,000	Repeat-dose toxicity study for surrogate chemical	D
CBI	Olefin			500	Repeat-dose toxicity study for surrogate chemical	D
CBI	Organic phosphonate				Unable to locate relevant quantitative chronic toxicology information.	E
CBI	Oxylated phenolic resin				Unable to locate relevant quantitative chronic toxicology information. US EPA Low Hazard Polymer.	E
CBI	Oxylated phenolic resin				Unable to locate relevant quantitative chronic toxicology information.	E
CBI	Polyacrylamide copolymer				Unable to locate relevant quantitative chronic toxicology information.	E
61791-26-2	Polyoxylated fatty amine salt			1,080	Repeat-dose toxicity study (Cosmetic Ingredient Review Expert Panel, 2012)	C
584-08-7	Potassium carbonate	7440-09-7	Potassium	1,005,000	Dietary Reference Intake Value (IOM, 2005)	A
590-29-4	Potassium formate	141-53-7	Sodium formate	64,600	Repeat-dose toxicity study for surrogate chemical (ECA, 2013a)	D
1310-58-3	Potassium hydroxide	7440-09-7	Potassium	1,005,000	Dietary Reference Intake Value (IOM, 2005)	A
13709-94-9	Potassium metaborate	7440-42-8	Boron	3,100	US EPA ingestion RSL for surrogate chemical	D
71-23-8	Propanol			43,575	Repeat-dose toxicity study (Wagner, 2005)	C
107-19-7	Propargyl alcohol			31	US EPA ingestion RSL	A
CBI	Proprietary			9,000	Repeat-dose toxicity study	C
CBI	Quaternary ammonium compound			6,600	Repeat-dose toxicity study	C
68953-58-2	Quaternary ammonium compounds, bis(hydrogenated tallow alkyl) dimethyl, salts with bentonite			62,500	Repeat-dose toxicity study (OECD, 2007)	C
CBI	Quaternary ammonium salt				Unable to locate relevant quantitative chronic toxicology information.	E
68527-49-1	Reaction product of acetophenone, formaldehyde, thiourea and oleic acid in dimethyl formamide				Unable to locate relevant quantitative chronic toxicology information.	E
112926-00-8	Silica gel		silicas/silicates	37,500	Repeat-dose toxicity study (OECD, 2004b)	C
7631-86-9	Silica, amorphous -– fumed		silicas/silicates	37,500	Repeat-dose toxicity study (OECD, 2004b)	C
144-55-8	Sodium bicarbonate			856,500	Over the counter drug use information (OECD, 2002b)	C
9004-32-4	Sodium carboxymethyl cellulose			585,000	Repeat-dose toxicity study (Rowe et al., 1944, as cited in JECFA, 1990)	C
7647-14-5	Sodium chloride			1,243,500	Dietary Reference Intake Value (IOM, 2001)	A
2836-32-0	Sodium glycolate			3,750	Repeat-dose toxicity study (Andersen, 1998)	C
1310-73-2	Sodium hydroxide	7440-23-5	Sodium	492,857	Dietary Reference Intake Value (IOM, 2005)	A
7681-52-9	Sodium hypochlorite			475	Repeat-dose toxicity study (Kurokawa *et al.* , 1986 (as cited in US EPA, 2003)	C

Table D.2a Summary of Drinking Water Risk Based Concentrations (RBCs) for HF Constituents

CAS	Chemical Name	CAS RBC Chem	RBC Chemical (if different than chemical name)	RBC (µg/L)	RBC Basis Notes	RBC Note[a]
7681-82-5	Sodium iodide	7553-56-2	Iodine	160	US EPA ingestion RSL	A
10486-00-7	Sodium perborate tetrahydrate			5,000	Repeat-dose toxicity study (HERA, 2002)	C
7775-27-1	Sodium persulfate			455	Repeat-dose toxicity study (OECD, 2005)	C
7757-82-6	Sodium sulfate	14808-79-8	Sulfate	500,000	US EPA Health-Based Advisory; MCL Health Canada (sulfate)	A
7757-83-7	Sodium sulfite			7,200	Repeat-dose toxicity study (OECD, 2008)	C
7772-98-7	Sodium thiosulfate	14808-79-8	Sulfate	500,000	US EPA Health-Based Advisory; MCL Health Canada (sulfate)	A
CBI	Surfactant mixture		Ethoxylated alcohols	3,900	Repeat-dose toxicity study for surrogate chemical	D
CBI	Surfactant mixture			5,625	Working group derived toxicity factor	B
CBI	Terpenoid			12,500	Repeat-dose toxicity study for surrogate chemical	D
CBI	Terpenoid			12,500	Repeat-dose toxicity study for surrogate chemical	D
81741-28-8	Tributyl tetradecyl phosphonium chloride			43	Repeat-dose toxicity study (Malish, 2006)	C
101033-44-7	Triethanolamine zirconate				Unable to locate relevant quantitative chronic toxicology information	E
1319-33-1	Ulexite	7440-42-8	Boron	3,100	US EPA ingestion RSL for surrogate chemical	D
68909-34-2	Zirconium, acetate lactate oxo ammonium complexes				Unable to locate relevant quantitative chronic toxicology information	E

Table D.2b Summary of Drinking Water Risk Based Concentrations (RBCs) for Flowback Fluid Constituents

CAS	Chemical Name	CAS RBC Chem	RBC Chemical (if different than chemical name)	RBC (µg/L)	RBC Basis Notes	RBC Note[a]
7429-90-5	Aluminum			16,000	US EPA ingestion RSL	A
57-12-5	Amenable cyanide			9.4	US EPA ingestion RSL	A
7440-36-0	Antimony			6	Drinking water MCL	A
7664-41-7	Aqueous ammonia			30,000	US EPA (2012c) Lifetime health advisory level	A
7440-38-2	Arsenic			10	Drinking water MCL	A
7440-39-3	Barium			2,000	Drinking water MCL	A
24959-67-9	Bromide			2,000	WHO Guideline for Drinking-water (WHO, 2009)	A
7440-43-9	Cadmium			5	Drinking water MCL	A
7440-70-2	Calcium			2,505,000	Dietary Reference Intake Value (Upper Intake Level for 15 kg 4-8 yo child) (IOM, 2005)	A
7440-47-3	Chromium			100	Drinking water MCL	A
7440-50-8	Copper			1,300	Drinking water MCL	A
57-12-5	Cyanide, Total			9.4	US EPA ingestion RSL	A
7439-89-6	Iron			11,000	US EPA ingestion RSL	A
7439-92-1	Lead			15	Drinking water MCL	A
7439-93-2	Lithium			31	US EPA ingestion RSL	A
7439-95-4	Magnesium			75,000	Dietary Reference Intake Value (IOM, 2001)	A
7439-96-5	Manganese			380	US EPA ingestion RSL	A
7439-97-6	Mercury			2	Drinking water MCL	A
7439-98-7	Molybdenum			78	US EPA ingestion RSL	A
7440-02-0	Nickel			310	US EPA ingestion RSL	A
7440-09-7	Potassium			1,005,000	Dietary Reference Intake Value (IOM, 2005)	A
7782-49-2	Selenium			78	US EPA ingestion RSL	A
7440-22-4	Silver			78	US EPA ingestion RSL	A
7440-23-5	Sodium			1,905,000	Dietary Reference Intake Value (Upper Intake Level for 15 kg 4-8 yo child) (IOM, 2005)	A
7440-24-6	Strontium			9,400	US EPA ingestion RSL	A
14808-79-8	Sulfate			500,000	US EPA Health-Based Advisory; MCL Health Canada (sulfate)	D
7440-28-0	Thallium			0.16	US EPA ingestion RSL	A
7440-31-5	Tin			9,400	US EPA ingestion RSL	A
7440-32-6	Titanium			45,000	RfD derived through peer-reviewed process (NLM, 2013)	B
7440-66-6	Zinc			4,700	US EPA ingestion RSL	A
87-61-6	1,2,3-Trichlorobenzene			13	US EPA ingestion RSL	A
107-06-2	1,2-dichloroethane			16,000	US EPA ingestion RSL	A
108-67-8	1,3,5-Trimethylbenzene			160	US EPA ingestion RSL	A
105-67-9	2,4-Dimethylphenol			310	US EPA ingestion RSL	A
78-93-3	2-Butanone			9,400	US EPA ingestion RSL	A
91-57-6	2-Methylnaphthalene			63	US EPA ingestion RSL	A
95-48-7	2-Methylphenol			780	US EPA ingestion RSL	A
108-39-4	3/4-methylphenol	108-39-4	3-methylphenol	780	US EPA ingestion RSL	A
106-44-5	3/4-methylphenol	106-44-5	4-methylphenol	1,600	US EPA ingestion RSL	A
99-87-6	4-Isoproplytoluene			2,310	Repeat-dose toxicity study (Wolf et al., 1956)	D
83-32-9	Acenaphthene			940	US EPA ingestion RSL	A
67-64-1	Acetone			14,000	US EPA ingestion RSL	A
98-86-2	Acetophenone			1,600	US EPA ingestion RSL	A
71-43-2	Benzene			5	Drinking water MCL	A
100-51-6	Benzyl alcohol			1,600	US EPA ingestion RSL	A

Table D.2b Summary of Drinking Water Risk Based Concentrations (RBCs) for Flowback Fluid Constituents

CAS	Chemical Name	CAS RBC Chem	RBC Chemical (if different than chemical name)	RBC (µg/L)	RBC Basis Notes	RBC Note[a]
117-81-7	Bis(2-ethylhexyl)phthalate			4.8	US EPA ingestion RSL	A
107-92-6	Butyric Acid	71-36-3	n-butanol	625	Repeat-dose toxicity study for surrogate chemical (OECD, 2003b)	D
75-15-0	Carbon Disulfide			1,600	US EPA ingestion RSL	A
218-01-9	Chrysene			2.9	US EPA ingestion RSL	A
84-66-2	Diethyl phthalate			13,000	US EPA ingestion RSL	A
84-74-2	Di-n-butyl phthalate			1,600	US EPA ingestion RSL	A
117-84-0	Di-n-octyl phthalate			190	US EPA ingestion RSL	A
100-41-4	Ethyl Benzene			700	Drinking water MCL	A
107-21-1	ethylene glycol			31,000	US EPA ingestion RSL	A
206-44-0	Fluoranthene			630	US EPA ingestion RSL	A
86-73-7	Fluorene			630	US EPA ingestion RSL	A
64-18-6	formic acid			14,000	US EPA ingestion RSL	A
98-82-8	Isopropylbenzene (cumene)			1,600	US EPA ingestion RSL	A
75-09-2	Methylene Chloride			5	Drinking water MCL	A
71-36-3	n-Butanol			1,600	US EPA ingestion RSL	A
103-65-1	n-propylbenzene			530	US EPA ingestion RSL	A
95-47-6	o-xylene			10000	Drinking water MCL	A
85-01-8	Phenanthrene			600	Tolerable daily intake (NLM, 2013a)	B
108-95-2	Phenol			4,700	US EPA ingestion RSL	A
64743-03-9	Phenols	108-95-2	Phenol	4,700	US EPA ingestion RSL	A
79-09-4	Propionic Acid			2,585	Repeat-dose toxicity study (ECB, 2000b)	C
57-55-6	Propylene glycol			310,000	US EPA ingestion RSL	A
129-00-0	Pyrene			470	US EPA ingestion RSL	A
110-86-1	Pyridine			16	US EPA ingestion RSL	A
108-88-3	Toluene			1,000	Drinking water MCL	A
1330-20-7	xylenes			10,000	Drinking water MCL	A
	alpha (gross)			15 pCi/L	Drinking water MCL	A
	beta (gross)			4 mrem/yr	Drinking water MCL	A
	Cs-137			1.74 (pCi/L)	US EPA Preliminary Remediation Goal (PRG)	A
	Pb-212			2.12 (pCi/L)	US EPA Preliminary Remediation Goal (PRG)	A
	Pb-214			154 (pCi/L)	US EPA Preliminary Remediation Goal (PRG)	A
	Ra-226			5 (pCi/L)	Drinking water MCL (Ra-226/228)	A
	Ra-228			5 (pCi/L)	Drinking water MCL (Ra-226/228)	A
	U-235			0.737 (pCi/L)	US EPA Preliminary Remediation Goal (PRG)	A
	U-238			0.607 (pCi/L)	US EPA Preliminary Remediation Goal (PRG)	A

RBC Note Description (Table D.2)

RBC Note	Examples of Respective RBC Derivation
A	An authoritative agency has developed a risk criterion for the exact chemical of concern. The value has not been modified from the developed value (*e.g.* , US EPA Risk Screening Level [RSL]; IRIS RfD; OPP value). An authoritative agency has indicated that the COC is a nutrient, and there are sufficient quantitative data available to establish a "safe" intake level (*e.g.,* a dietary reference intake value).
B	The criterion or safe level was developed by a non-US governmental agency (*e.g.* , JECFA). The toxicological criterion was developed using a credible toxicological study* that was conducted, commissioned, or cited by an authoritative agency (*e.g.,* National Toxicology Program chronic bioassay). Gradient has used the best scientific judgment to select uncertainty factors, and (in some cases) the most appropriate endpoint to develop a criterion.
C	Toxicological criterion has been derived using an endpoint from a credible toxicological study cited in a reliable document (*e.g.,* peer-reviewed study, well-documented industry report). The study may have a duration less than 90 days. Gradient has used the best scientific judgment to select uncertainty factors and (in some cases) the proper endpoint.
D	The toxicological criterion was developed using a clearly-defined surrogate (*i.e.* , selected by the US EPA AIM program, or a similar transparent QSAR-based approach); a criterion must be developed based on toxicological information about the surrogate compound.
E	No data are available to evaluate the toxicological hazard of chronic exposure.

RBC Notes (cont):

*A credible toxicological study refers to an animal study that used an adequate number of animals, an adequate dose range, and established a no observed adverse effect level (NOAEL), or a lowest observed adverse effect level (LOAEL) for a sub-chronic or chronic duration.

†ADME = absorption, distribution, metabolism, and excretion.

COC = Chemical of Concern.

GRAS = Generally Regarded as Safe.

QSAR = Quantitative Structure Activity Relationship.

Toxicological Criterion = refers to the human equivalent dose or concentration that is being evaluated (*e.g* ., RBC µg/L).

US EPA Analog Identification Methodology (AIM) = a publically available online application that allows users identify experimental toxicity data on closely related chemical structures (http://aim.epa.gov).

Examples of Authoritative Agencies:

Agency for Toxic Substances and Disease Registry (ATSDR)
California EPA (CalEPA)
Health Canada (HC)
International Programme on Chemical Safety (IPCS)
National Institute for Occupational Safety and Health (NIOSH)
National Toxicology Program (NTP)
Organisation for Economic Co-operation and Development (OECD)
Texas Commission on Environmental Quality (TCEQ)
U.S. Department of Energy (DOE)
US Environmental Protection Agency (US EPA)
US Food and Drug Administration (US FDA)
World Health Organization (WHO)

Appendix D – Table D.2 References

References – Table D.2

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Appendix E

Critique of Modeling Undertaken by Myers and Others

E.1 Introduction

The hypothesized upward migration of hydraulic fracturing (HF) fluid (or brine) from target formations to shallow potable aquifers is physically implausible, as we demonstrated in Section 5.2 and the two manuscripts submitted to peer-reviewed scientific journals (Flewelling and Sharma, Submitted; Flewelling *et al*., Submitted). Our findings are fundamentally at odds with two recently published studies (Myers, 2012; Rozell and Reaven, 2012), which have claimed that there are potential risks of groundwater contamination associated with the pumping of HF fluids into the Marcellus Shale. Both of these studies rely on unrealistic assumptions about the hydrogeological setting of tight formations, rock mechanics and seismological relationships that limit upward fracture growth, the physics of fluid motion, and the design and execution of HF stimulations. Overall, these studies are fundamentally flawed and do not provide any meaningful information that might contribute to the scientific debate regarding potential environmental impacts of the HF process and specifically the US EPA National HF Study (US EPA, 2012).

The following sections provide a brief discussion of the major shortcomings in the studies published by Myers (2012) and Rozell and Reaven (2012).

E.2 The Myers study is fundamentally flawed and unrealistic

The study by Myers (2012) used a standard United States Geological Survey (USGS) groundwater flow model called MODFLOW to simulate potential upward brine migration during a baseline period (*i.e.*, prior to HF activities) followed by simulations that predicted changes to potential upward fluxes of brine and HF fluid during and after an HF stimulation. We reviewed this study and noted numerous technical deficiencies that led to unrealistic modeling results that are not meaningful for assessing potential environmental impacts of the HF process. The following discussion of the Myers study focuses on a comparison of Myers' results to real world data that clearly demonstrates how unrealistic the Myers study is. We then provide a brief list of the major technical flaws that contributed to the misleading modeling results.

The simplest way to evaluate the modeling results presented in the Myers study is to compare the study's predictions during the baseline period (*i.e.*, prior to HF activities) to real world observations of groundwater conditions in the Marcellus Shale region. The Myers study calculates the natural rate of upward brine flux during the baseline period. Such fluxes can be evaluated with simple mass-balance mixing models (*e.g.*, Claassen and Halm, 1996). Over the long term, the total dissolved solids (TDS) concentration of shallow potable groundwater can be conceptualized as a mixture of precipitation derived recharge (freshwater) that percolates downward through the unsaturated zone to shallow potable groundwater and an upward flux of concentrated brine from depth. Water-rock interactions (*e.g.*, weathering and precipitation reactions) are typically the most important factors that govern groundwater TDS (Langmuir, 1997); however, ignoring these reactions and focusing solely on the potential contributions of brine to TDS produces a bounding limit for potential upward fluxes of brine and also provides a reality check on the upward brine fluxes predicted by Myers. For this bounding case, the mass-balance mixing model takes the following form:

$$C_{gw} = \frac{C_b F_b + C_r F_r}{F_b + F_r}$$

where, *C*s are TDS concentrations, *F*s are fluxes, and the subscripts gw, b, and r denote potable groundwater, brine, and precipitation-derived recharge, respectively. For simplicity, and to add more conservatism to this bounding calculation, we assume that the TDS concentration of precipitation-derived recharge (C_r) is zero. Thus, the mass-balance mixing equation simplifies to:

$$C_{gw} = \frac{C_b F_b}{F_b + F_r}$$

We use this relationship with observed brine TDS concentrations in the Marcellus Shale, natural upward brine fluxes modeled in the Myers study, and widely available information on recharge rates in the Marcellus Shale region published by the USGS. These estimated groundwater TDS concentrations that are a direct result of the upward brine fluxes predicted in the Myers study are then compared to measured groundwater TDS concentrations in potable aquifers throughout the Marcellus Shale region to evaluate whether the predicted TDS concentrations, and hence, Myers' predicted upward fluxes, are realistic.

The natural upward fluxes of brine predicted by the Myers study are between 0.0031 and 6.7 m yr^{-1} throughout the Marcellus Shale region. This range of upward fluxes is high in comparison to regional rates of groundwater recharge, which are about 0.3 m yr^{-1} (Cohen and Randall, 1998), suggesting that Myer's estimates are unrealistic at the outset. Brine TDS concentration in the Marcellus Shale is reported by Myers to be 350,000 ppm. Using these values and the simple mass-balance mixing equation indicates that shallow groundwater would have TDS concentrations in the range of 3,600 to 335,000 ppm – *i.e.*, salinity values that range between brackish water and 10-times saltier than seawater – if the natural brine fluxes modeled by Myers were correct. However, Myer's TDS range overestimates the average TDS of shallow groundwater and surface water in the Appalachian basin by orders of magnitude (*cf.*, Eckhardt and Sloto, 2012). Therefore the baseline (*i.e.*, natural or pre-HF) upward fluxes predicted by Myers are not realistic and all subsequently modeled HF impacts are invalid.

There are many factors to consider when evaluating fluid flow from black shales, so a closer look at Myers' work is needed to understand why the modeled predictions are unrealistic. While we do not attempt an exhaustive review, the following incorrect assumptions and/or model input values are the primary contributors to the unrealistic predictions presented in the Myers study:

- Myers selected an unrealistic range of permeabilities (10^{-15} to 10^{-10} m^2) for sedimentary rocks overlying the Marcellus Shale – a range based on the assumption that all rocks overlying the Marcellus were highly permeable sandstone. However, the overlying rocks are almost entirely low permeability shale (Ryder *et al.*, 2012). Additionally, as demonstrated by physical scaling functions presented by Flewelling and Sharma (Submitted), the settings under which upward brine migration is possible are inherently associated with very low permeability rocks (typically with permeability < 10^{-20} m^2). Thus, Myers used permeabilities in his modeling analysis that were 5 to 10 orders of magnitude higher than is physically possible.
- Myers did not account for the effect of density contrasts between freshwater and brine in his analysis. For example, an upward head gradient in excess of 0.23 would be required to move a parcel of brine at 350,000 ppm TDS (density of ~1,230 kg m^{-3}) upward through freshwater (density of ~1,000 kg m^{-3}) (Flewelling and Sharma, Submitted). The upward head gradient assumed by Myers (0.02) is over an order of magnitude lower, indicating that upward flow would not even be possible.
- Myers failed to account for the fact that the Marcellus Shale has no mobile water in it. The pore spaces are almost entirely filled with natural gas and an extremely small amount of water is present in the formation, bound to the porous shale matrix (Bruner and Smosna, 2011). Under these conditions of extremely low water saturation, any water (including water-based HF fluid)

> will be rapidly soaked up and bound in the formation, analogous to the way a dry sponge soaks up water (Engelder, 2012). This process, called imbibation, is largely responsible for the observation that only a fraction of HF fluid pumped into the Marcellus Shale is returned to the surface (typically 9-35%) after the HF process is complete.

We note that others have discussed the numerous technical shortcomings in the Myers study, including two letters to the editor of *Groundwater*, the journal in which the Myers study was published (Saiers and Barth, 2012 and Cohen *et al*., 2013). For example, Saiers and Barth (2012) stated:

> Myers' modeling framework neglects critical hydrologic processes, misrepresents physical conditions that drive groundwater flow, and is underpinned by simplifications that are too severe and unnecessary. Owing to these shortcomings, Myers' findings should not be interpreted as reasonable predictions of the response of groundwater flow and contaminant migration to hydraulic fracturing…. When taken together, these deficiencies are reflective of a model that is unconstrained by reality, making the model forecasts of frac-fluid transit times from the Marcellus to overlying drinking-water aquifers suspect.

We agree with Saiers and Barth (2012) and Cohen *et al.* (2013) that the Myers study is seriously flawed, does not comport with reality, and should not be used in any evaluation of potential impacts on potable aquifers associated with the HF process.

E.3 Potential risks presented by Rozell and Reaven are based on pure speculation and are unrealistic

Rozell and Reaven (2011) evaluated potential upward migration of HF fluid above the Marcellus Shale, to assess the likelihood of brine and HF fluid migration through induced fractures to shallow groundwater. They used a probabilistic approach (as opposed to Myers' numerical modeling simulations), where the volume leaked was assumed to be proportional to the probability of a fracture extending to an overlying aquifer (P_{FL}) and the portion of total HF fluid that would leak if such a pathway were to exist (P_{Fluid}). Neither P_{FL} nor P_{Fluid} were based on data or physical scaling analyses. Instead, Rozell and Reaven assumed that the probability of a fracture extending to an overlying aquifer (inferred to mean fracture heights over 1,000 m) was between 10^{-6} and 10^{-1}. Their selection of this range appears to be arbitrary, but there are data available for evaluating fracture height growth, as have been presented by Fisher and Warpinski (2011), Davies *et al.* (2012), and Flewelling *et al.* (submitted). The fracture height data compiled by these authors and the bounding relationships for fracture height developed by Flewelling *et al.* (Submitted) demonstrate that the probability of fractures reaching shallow potable groundwater is extremely small and perhaps even zero. These limits are discussed in more detail in Section 5.2 of our report. Of all the fracture height data compiled (for over 12,000 HF simulations in over 25 sedimentary basins across the US and Canada), there are no instances where fractures propagated upward to shallow potable groundwater (Fisher and Warpinski, 2011; Davies *et al.*, 2012; Flewelling *et al.*, Submitted). Thus, the likelihood of fracture heights reaching shallow potable groundwater is less than 1 in 12,000, *i.e.*, $< 8 \times 10^{-5}$ based on an extensive database of fracture heights and more likely to be orders of magnitude lower (or zero) based on the physical limits on fracture height growth (Flewelling *et al.*, Submitted). Thus, existing data and scaling functions suggest that the probability (p) of fractures propagating upward 1,000 m or more would be bounded by $0 \leq p < 10^{-5}$, rather than the range of $10^{-6} \leq p \leq 10^{-1}$ proposed by Rozell and Reaven (2011). Accordingly, Rozell and Reaven have overestimated the likelihood of upward fluid flux through fractures by orders of magnitude at best, and at worst, may have predicted risks associated with upward fluid migration when there may, in fact, be none. Due to the unsupported and somewhat arbitrary assumptions made in the Rozell and Reaven (2011) study, the conclusions of this work are unreliable and should not be considered in any evaluation of impacts on potable aquifers associated with the HF process.

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