

Human Health Risk Evaluation for Hydraulic Fracturing Fluid Additives

Prepared for

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Executive Summary

A. Hydraulic Fracturing Process Overview

Improvements in natural gas well development technology promise to expand the extraction of large reserves of natural gas from formerly uneconomical low-permeability shale gas formations. A key component of the gas well development process is the use of hydraulic fracturing (HF) procedures. Recent advances in well drilling techniques, especially the increased use of "horizontal" drilling in conjunction with high volume hydraulic fracturing, expand the capacity of 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 production and minimize the amount of land disturbance when developing the well network to extract natural gas from deep formations.

Hydraulic fracturing is a multi-step process aimed at opening up fractures within the natural gas bearing geologic formations and keeping fractures open to maximize the flow of natural gas to a gas production well. The HF process involves pumping the fluid into the target gas-bearing formation to create fractures, and then pumping proppants (*e.g.*, sand) into the induced fractures to prevent them from closing up. After the fracturing stage is complete, all readily recoverable HF fluid is pumped from the well to the surface; this is referred to as "flowback."

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 (NYSDEC, 2011; CRS, 2009; API, 2009).¹

The fluids 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. HF additives serve many functions in hydraulic fracturing. From limiting the growth of bacteria to preventing corrosion of the well casing, additives are needed to insure that the fracturing job is effective and efficient. The HF additives used in a given fracture treatment depend on the geologic conditions of the target formation.

¹ See also web resources:
<http://fracfocus.org/hydraulic-fracturing-process>
<http://www.energyindepth.org/>
http://www.halliburton.com/public/projects/pubsdata/hydraulic_fracturing/fracturing_101.html

B. Marcellus Shale Gas Deposits -- New York State

Natural gas exploration and production from the Marcellus Shale and other low-permeability reservoirs containing large reserves of natural gas are proposed in the southern portion of New York State (NYS). The New York State Department of Environmental Conservation (NYSDEC) published a revised draft Supplemental Generic Environmental Impact Statement (revised dSGEIS), dated September 2011 (NYSDEC, 2011), which contains generic permit requirements for the development of natural gas production wells in the Marcellus Shale formation using horizontal drilling and high-volume hydraulic fracturing techniques. The revised SGEIS has been updated based on public comment and further analysis by NYSDCE since it released the prior draft SGEIS (dSGEIS) in September 2009 (NYSDEC, 2009).

Concerns have been expressed over the potential exposure to HF additives that might potentially impact drinking water resources. Such concerns are noted in the revised dSGEIS in the event of spills of HF fluids:²

The overall risk of human health impacts occurring from hydraulic fracturing would depend on whether any human exposure occurs, such as, for example, in the event of a spill. If an actual contamination event such as a spill were to occur, more specific assessment of health risks would require obtaining detailed information specific to the event such as the specific additives being used and site-specific information about exposure pathways and environmental contaminant levels. (revised dSGEIS, p. 5-75)

This report, which Gradient has prepared on behalf of Halliburton Energy Services, Inc. (HESI) as a follow-up to our prior study (Gradient, 2009), presents our evaluation of the potential human health impacts of HF fluid leaks or 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 household drinking water purposes. In addition, concerns have been raised as to whether HF constituents pumped thousands of feet underground into the Marcellus Shale formation might plausibly migrate upward and contaminate shallow drinking water aquifers. We also address this concern in this report, although we note at the outset that NYSDCE and other stakeholders have evaluated this issue and concluded that it is not a plausible migration pathway. In our prior study (Gradient, 2009), we also concluded that upward migration of HF constituents from the Marcellus Shale formation to shallow aquifers was not a realistic migration pathway.

² There is no risk analysis presented in the revised dSGEIS that addresses these concerns.

C. Surface Spill Exposure Analysis

In this report, we examine several hypothetical uncontrolled surface HF fluid spill scenarios to assess whether such spills could pose possible human health risks to either groundwater or surface water that may be used as drinking water sources. Our risk analysis is based upon an examination of constituents in HF additives present in a range of typical HESI HF fluids that may be used during natural gas well development in the Marcellus Shale and other unconventional gas-bearing formations. We also examine potential health risks of constituents in flowback water, should spills occur during flowback handling. We examine two types of HF spill scenarios as summarized below.

"Diffuse" Spills

For this hypothetical spill scenario, we have assumed that leaks/spills could occur during HF fluid and flowback fluid handling that are relatively small at any one time, but that could perhaps occur throughout the year during HF activities. Furthermore, the leaks are assumed to occur potentially from multiple fluid handling locations, such that the leaks/spills could cause contamination over a relatively large "footprint" of a well pad. For the diffuse spill scenario, we have assessed the possible impacts of releasing 10 gallons of fluid per day throughout the year (approximately 3,500 gallons per year), covering a surface area of 2 acres of the well pad. This is considered an upper-bound estimate of the total volume of small leaks/spills during a year that might go undetected. It should be emphasized that we have evaluated this as a hypothetical spill scenario, one that is not expected to occur in practice, especially at the assumed spill rates (*i.e.*, 10 gallons of fluid per day).

"Sudden" Spills

The second scenario, which we term a sudden spill, is one possibly caused by a sudden, hypothetical equipment malfunction during HF operations. Given the automated monitoring that is utilized during HF procedures, if malfunctions were to occur, it is anticipated that the HF pumping would be shut down quickly after detection of abnormal pressure drops or other signs of abnormal operating conditions. These automated detection procedures should limit the duration and magnitude of potential sudden spills. For these reasons, the sudden spill volumes we have assessed (outlined below) are considered reasonable ranges.

For the sudden spill scenario, we have evaluated potential fluid spill volumes ranging from 1,000 gallons to as large as 10,000 gallons over a short time period.³ We chose a range of sudden spill volumes for several reasons. First, the range of spill volumes provides perspective on how exposure and potential health risk could vary as a function of spill volume. In addition, different HF fluid systems use different overall fluid volumes, with some using approximately 30,000 gallons, whereas others use over 4,000,000 gallons. Therefore, it is not unreasonable to consider that those HF systems employing larger volumes have the potential for larger sudden spills than do the systems using smaller volumes. A summary of the surface spill scenarios is given below.

Spill Scenario	Spill Volume		Impacted Area
<i>"Sudden spill" during down-hole pumping:</i>	1,000 gal	HF fluid volumes ≤ 250,000 gal	0.1 acre
	10,000 gal	HF fluid volumes > 250,000 gal	1 acre
"Diffuse spills": small leaks during the year over a larger footprint	3,500 gal	~10 gal/day year-round	2 acres

Impacted areas vary as a function of the volume of a spill and the spill "thickness" described later in this report.

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, (i) 100% of the surface spill leaches to groundwater; and (ii) 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.

³ The 10,000 gallon spill represents several minutes of pumping at the high pressures used for fracturing. As noted, any spill or significant leak is likely to be detected quickly given the monitoring systems in place at a well site. Based on spill information relating to oil and gas exploration/production activities in West Virginia, for the period 1990 to 2011, of the 323 spill incidents logged (with quantified spill volumes) the median spill volume was 55 gallons, and the 95th percentile was 2,750 gallons (source: https://apps.dep.wv.gov/oog/svsearch_new.cfm).

Surface Spill Impacts to Groundwater

As one possible scenario for this study, surface spills of HF fluids along with their constituents could spread out and soak into the ground in a shallow zone at the soil's surface. The HF constituents in this surface zone would then be subject to leaching downward through unsaturated soils (here-in referred to as the "unsaturated zone") as rainfall percolates into the ground, "washing" the HF constituents downward with the percolating water. Given sufficient time, if the HF constituents do not adsorb to soil and/or degrade (both processes are likely to occur), the HF 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 HF 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 too would cause the concentration of HF constituents to diminish, or be diluted, as they mix within the groundwater. To account for these inherent dilution and attenuation mechanisms, we have adopted well established modeling approaches to provide conservative estimates of the degree of attenuation that would likely occur between the point of the surface spill and a downgradient drinking water well. These modeling approaches are outlined below.

For the saturated zone groundwater exposure analysis, we adopted "dilution attenuation factors" (DAFs) that were developed by US EPA (1996) when it derived risk-based chemical screening levels in soil that are protective of groundwater resources. 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 to a maximum of 300 feet). Using a probabilistic modeling approach to incorporate these types of variable conditions, US EPA determined groundwater DAFs as a function of contaminated "source areas." For example, US EPA determined that a chemical 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 DAFs decrease to 668-fold in 85% of scenarios and 60-fold in 90% of scenarios.

In the US EPA derivation of groundwater DAFs, simplifying and conservative assumptions were adopted that underestimate chemical dilution and attenuation in the soil and groundwater; these assumptions included that chemicals do not adsorb to soil, and that chemicals do not degrade. In addition, the chemical source was assumed to be "infinite." The US EPA adopted these assumptions as conservative measures, which effectively eliminate any consideration of attenuation in the unsaturated zone as

chemicals leach downward through the soil to the saturated zone (groundwater). While indeed conservative, clearly such assumptions are not realistic.

In this assessment we have not assumed an infinite source because the spill volumes used in our analysis are finite volumes considered to be reasonable upper-bound values. Consequently, we have accounted for attenuation of chemical concentrations in the unsaturated zone before reaching the groundwater table due to chemical spreading (dispersion) within the unsaturated zone.⁴ We used well-established, standard techniques (*i.e.*, a chemical advection-dispersion equation) to model constituent dilution and attenuation within the unsaturated zone. Our calculated unsaturated zone DAF values range from 50 to 150, where the larger DAF applies to diffuse spills (small leaks and spills distributed throughout the well pad) and the smaller DAF applies to a sudden spill (a one-time spill of larger volume).

Using this approach, we calculated an overall DAF for the soil-to-groundwater pathway by combining the US EPA-derived saturated-zone DAFs with the Gradient-derived unsaturated-zone DAFs. We emphasize that the soil-to-groundwater pathway DAFs used in this analysis are more likely to underestimate than overestimate dilution and attenuation because both the saturated- and unsaturated-zone DAFs were derived assuming no chemical adsorption⁵ or degradation. The assumption of no chemical adsorption or degradation 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 DAFs we used to assess the potential surface spill impacts to a shallow drinking water aquifer are summarized below.

Dilution Factors (DAF) For Surface Spill Migration to Drinking Water Well

Spill Volume	Saturated Zone DAF (US EPA 90 th Percentile)	Unsaturated Zone DAF	Overall DAF
<i>Sudden Spills</i>			
1,000 gal (0.1 acre)	2,740	50	137,000
10,000 gal (1 acre)	60	50	3,000
<i>Diffuse Spill</i>			
3,500 gal (2 acres)	33	150	5,000

⁴ 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.

⁵ In Gradient's 2009 analysis soil adsorption was included as an attenuation mechanism for all chemicals. In this updated analysis, we dropped that approach for all but three chemicals as noted later in this report.

The approach for estimating the DAFs for the soil-to-groundwater pathway described herein is based on the same conceptual framework as that used in Gradient's 2009 risk evaluation, with several refinements. In our 2009 evaluation, we used the same advection dispersion equation to estimate unsaturated-zone DAF values, with one change. In our earlier analysis, we had included the influence of chemical adsorption to soil within the unsaturated zone as an additional attenuation mechanism. For our current analysis, as a conservative measure we no longer generally consider chemical adsorption.⁶ This revised approach leads to less attenuation of the HF or flowback constituents potentially migrating to groundwater (*i.e.*, the revised analysis is even more health-protective as it results in lower DAFs). In addition, our earlier derivation of saturated-zone DAFs relied upon a mass-balance mixing model presented in the US EPA (1996) Soil Screening Guidance – the same guidance from which we now have adopted US EPA derived saturated-zone DAF values. That prior DAF estimation method required selecting specific drinking water well depths, as well as a particular groundwater flow rate. In the current analysis, we have instead chosen to use the probabilistic DAF values derived by US EPA (1996) because they represent a broader range of hydrologic conditions (well depth, groundwater flow rates, *etc.*) than we had previously evaluated in our 2009 study. Although the derivation of DAFs differ somewhat between our 2009 study and the current one, our previously derived DAFs are comparable to the probabilistic DAFs US EPA derived.⁷

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 DAFs assuming "low flow" mixing conditions in streams hypothetically impacted by surface spills. We based our analysis on the Lowest Annual Mean Daily Discharge (LAMDD) for streams in the Marcellus Shale region of New York. From a data set of 141 United States Geological Survey (USGS) stream gauging stations in this region, we selected the 10th percentile LAMDD value of 5.2 MGD to estimate surface water dilution factors for the surface water exposure scenarios. This is a conservative (health-protective) approach because the low flow values represent minimal dilution (*i.e.*, worst case conditions) as compared to more typical (annual mean daily discharge) flow conditions. Our selection of the 10th percentile among the distribution of LAMDD flow values (LAMDD flow values differ based on different stream sizes) adds further conservatism to our analysis because the selected flow value is exceeded in the vast majority (90%) of streams. For example, the 50th percentile LAMDD value in the USGS data set is

⁶ We consider chemical adsorption for only three chemicals noted later in the report.

⁷ As a comparative analysis, we also calculated potential exposures to HF constituents using the DAF values we developed in our 2009 analysis. These calculations are presented in Appendix D.

53 MGD. Had we used this more central (median) value, it would have yielded 10-fold greater dilution than the 10th percentile value which we used to derive the surface water DAF.

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 a lower percentile flow, 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. For the purpose of undertaking this study, we evaluated surface water exposures for two scenarios: (1) the HF spill is washed off to a stream during the course of a year, mixing with the stream over a one-year flow period, and (2) the HF spill mixes with the stream during a shorter 10-day mixing period. The shorter term mixing period leads to much less dilution. In our 2009 risk analysis, we did not examine this shorter term mixing period, thus our current analysis includes an even more conservative (health protective) analysis relative to our prior risk analysis. The surface water dilution factors used in this analysis are summarized below.

Summary of Surface Water DAFs

Surface Water Dilution Factors	Sudden Spills		Diffuse Spills 3,500 gal
	1,000 gal	10,000 gal	
DAF – annual dilution	1,900,000	190,000	540,000
DAF – 10 day dilution	52,000	5,200	N/A

DAF values using 10th Percentile Low Annual Mean Daily Discharge (5.2 MGD). N/A = not applicable for the diffuse spill scenario which occurs during the course of a year.

D. Hypothetical Upward Migration of HF Constituents from the Marcellus Shale

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" (dSGEIS, p. 8-6). In its revised 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" (revised dSGEIS, p. 8-29).

Our earlier analysis (Gradient, 2009), and our further analysis in this report, reaffirm NYSDEC's conclusions that potential groundwater contamination as a result of migration from the underlying fracture zone is not plausible. 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 to potable aquifers. In addition, given the significant thickness of rocks (thousands of feet) overlying the Marcellus Shale and the natural mechanisms that inhibit fracture propagation, the fracturing pressures are not expected to result in interconnected fractures to overlying potable aquifers. 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. In any event, even if groundwater migration from the Marcellus Shale to a potable aquifer were hypothetically assumed, the rate of migration would be extremely slow and the resulting DAF would be greater than a million-fold. 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 DAF, this exposure pathway does not pose a threat to drinking water resources.

E. Toxicity Characterization

As presented in the revised dSGEIS, and 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. 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 HF constituents. Agency-established toxicity criteria (*e.g.*, drinking water standards, or risk-based benchmarks) were adopted when these were available. For HF 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; US EPA, 2011a,b).

F. Risk Evaluation Conclusions

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, 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.

Conservative Assumptions
100% of spill assumed to impact both surface water and groundwater
Surface water dilution for as short as 10-day flow period
10 th percentile lowest mean daily flow value used for dilution
Selected US EPA's lowest 10 th percentile groundwater dilution factor
Adsorption of chemicals in soil largely ignored
Degradation of chemicals in soil and groundwater ignored
Assumed very shallow depth to groundwater (5 to 10 meters)

Human health risks associated with potential surface spills of the typical HESI HF fluid additives are expected to be insignificant for all of the scenarios evaluated due to attenuation mechanisms which are expected to reduce concentrations in potable aquifers and surface waters to levels well below health-based drinking water concentrations in the event of surface spills. These findings address the possible human exposure and health risk concerns noted in the revised dSGEIS in the event of surface spills of HF fluids. Furthermore, NYSDEC-proposed setback requirements and mitigation measures, were not considered in our analysis. Our analysis suggests that the need for these setbacks has not been established on the basis of a formal exposure and risk analysis and the appropriateness of the NYSDEC-proposed setback requirements should be reevaluated based on our findings.

Our analysis of hypothetical upward migration of HF constituents from the Marcellus also confirms that migration of HF fluid additives from the Marcellus Shale 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. Even if such a pathway were hypothetically assumed, the rate of migration would be such that the dilution/attenuation of groundwater would be significant, thereby reducing the HF fluid constituent concentrations in drinking water (*e.g.*, in a shallow aquifer), to concentrations that are well below health-based standards, and that would not pose a threat to human health.

1 Introduction

Natural gas exploration from the Marcellus Shale and other low-permeability reservoirs are proposed in the southern portion of New York State (NYS) using horizontal drilling techniques. A key component of the gas well development process is the use of hydraulic fracturing (HF) – a well stimulation technique in which water, sand, and chemical additives are introduced into the target rock zone to open fractures and to keep them open using proppants (*e.g.*, sands) to enable flow of natural gas.

The New York State Department of Environmental Conservation (NYSDEC) published a revised draft Supplemental Generic Environmental Impact Statement (revised dSGEIS), dated September 2011 (NYSDEC, 2011), which contains generic permit requirements for the development of natural gas production wells in the Marcellus Shale formation using horizontal drilling and high-volume HF techniques. The revised SGEIS has been updated based on public comment and further analysis by NYSDEC since it released the prior draft SGEIS (dSGEIS) in September 2009 (NYDEC, 2009).

This report, which has been prepared on behalf of Halliburton Energy Services, Inc. (HESI), contains Gradient's evaluation of the potential human health risks associated with hypothetical spills of HF fluids during the HF process. Our evaluation addresses the chemical constituents in typical HF fluid systems developed by HESI that may be used in the Marcellus formation. Given that HESI has developed HF fluid systems that are potentially used in other geologic formations, for completeness we also included a number of those HF systems in our risk analysis under the hypothetical assumption they would be used in the Marcellus Shale in New York.

In addition, we evaluated health risks associated with potential surface spills of flowback water (water recovered from the fracture zone after fracturing) using data presented in the revised dSGEIS for flowback samples collected from the Marcellus Shale formation in Pennsylvania and West Virginia.

Finally, we examined the possibility that HF constituents pumped into the Marcellus formation might hypothetically migrate upward through the overlying bedrock strata into shallow overlying aquifers. This was an issue raised previously in the prior dSGEIS, and one that NYSDEC then concluded was an unlikely migration pathway of concern. Again in our updated study, we further examine the potential

upward HF constituent migration during both the HF pumping phase (when the HF fluids are pumped down the well and into the formation under high pressure), and the gas production phase after the fracturing has been completed and the gas wells are operating.

We provide an overview of the HF process, proposed NYSDEC restrictions and setback requirements when installing horizontal wells, and typical HF fluid volumes and constituents for a number of HESI HF fluid systems in Section 2. An overview of the geological and hydrological conditions in the Marcellus Shale region of New York is provided in Section 3. We present the conceptual model for our risk analysis, and discuss the potential migration pathways that were evaluated in this report in Section 4, followed in Section 5 by details of the modeling framework used to estimate potential exposure concentrations in drinking water for the spill scenarios and migration pathways evaluated. 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 this analysis in Section 8.

2 Hydraulic Fracturing Process

Hydraulic fracturing is a multi-step process aimed at opening up fractures within natural gas-bearing geologic formations to maximize the flow of natural gas to a gas production well. The HF process involves pumping a fluid and proppants (*e.g.*, sand) into the target gas-bearing formation. The fluids generally consist mostly of water with small amounts of chemical additives, typically comprising on the order of 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 in-place allowing the gas to be extracted from the formation. After the fracturing stage is complete, all readily recoverable portions of the HF fluid plus any naturally occurring fluids from the formation, referred to as "flowback", are then pumped out. 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 (NYSDEC, 2011; CRS, 2009; API, 2009).⁸ A brief overview is provided in this section, including information on typical HESI HF fluid systems.

2.1 HF Well Pad Spacing and NYSDEC Proposed Restrictions

Gas wells are sited 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 gas production. In the revised dSGEIS, New York has proposed minimum spacing requirements for horizontal wells that vary depending on whether a single *versus* multiple wells are drilled at an individual well pad (revised dSGEIS, p. 5-22):

- 40 acres for a single horizontal well installation; and
- 640 acres (1 square mile) for multiple horizontal wells installed at a common well pad.

⁸ See also web resources:

http://www.halliburton.com/public/projects/pubsdata/hydraulic_fracturing/fracturing_101.html
<http://fracfocus.org/hydraulic-fracturing-process>

As discussed in the revised dSGEIS, most common installations for production from the Marcellus Shale in New York will be multiple horizontal wells drilled at a common well pad. 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. It is anticipated that typical well pads for multiple well installations will be approximately 3.5 acres during the drilling phase, and approximately 1.5 acres during the gas production phase (revised dSGEIS, p. 5-11). Assuming well pads are square, average pad dimensions would be approximately 400 feet on a side for such multiple well installations during the drilling phase, and approximately 250 feet on a side during the production phase. Industry estimates indicate that up to four horizontal wells would be drilled per year for a multi-well installation (revised dSGEIS, p. 6-104).

NYSDEC has proposed a number of restrictions and setback requirements for horizontal gas wells and well pads to protect drinking water wells and important water resources (Table 2.1). NYSDEC proposes that the top of the fracturing zone be 2,000 feet bgs and at least 1,000 feet below the base of the nearest drinking water aquifer. In addition, NYSDEC proposes that gas wells be at least 500 feet (laterally) from any designated principal aquifer boundaries and tributaries feeding public water supplies and at least 150 feet from any watercourse, including intermittent and perennial streams, storm drains, lakes, and ponds. Any variances to these proposed restrictions would require a site-specific evaluation or Environmental Impact Statement (EIS) to demonstrate that the setback size is unwarranted. In addition, the revised dSGEIS proposes a series of prohibited locations where horizontal well development cannot occur. For example, NYSDEC proposes that pads for horizontal wells be prohibited within 500 feet of domestic wells and springs, unless the well owner waives this restriction. Horizontal well development would be prohibited within the watersheds that feed the public water supplies for New York City and Syracuse (including a 4000 foot buffer setback). Similarly, NYSEC proposes that HF development be prohibited within "primary aquifers" or public supply wells and reservoirs, including a 2000 foot buffer zone surrounding these water resources. These proposed setbacks and restrictions are subject to public comment prior to the issuance of a final SGEIS.

In order to be conservative, our exposure and risk analysis does not take the proposed setbacks from surface water bodies and drinking water wells into account. Our conclusion is that even in the absence of setbacks to surface water and drinking water wells, the potential human health risks associated with potential environmental spills of HESI HF constituents (surface spills and hypothetical upward migration of constituents from the Marcellus formation) is expected to be insignificant. This analysis suggests that the need for these setbacks has not been established on the basis of a formal exposure and risk analysis.

Table 2.1 NYSDEC Proposed Setback Restrictions for Horizontal Wells^[a]

HF Well Restriction	Setback^[b]
Projects Requiring Site-Specific Permit Determinations	
Top of Fracture zone	2000 ft
Base of Drinking Water Aquifer	1000 ft
Principal aquifer boundaries	500 ft
Tributary to public water supply	500 ft
Tributaries not contributing to public water supplies	150 ft.
Prohibited Locations	
NYC and Syracuse watersheds	4000 ft
Primary aquifer boundaries	2000 ft
Public Supply Wells and reservoirs	2000 ft
Domestic wells or springs	500 ft
Within 100 year floodplains	(not allowed)

^[a] revised dSGEIS, p. 3-14 to 3-16.

^[b] Setback distances would be measured from the edge of the well pad (except top of fracture zone and base of drinking water aquifer restrictions).

2.2 Gas Well Design and Installation

Gas wells are drilled with care to prevent drilling fluids, HF fluids, or natural gas from leaking into permeable aquifers. The upper portion of the well (*i.e.*, overlying the target zone) is drilled using vertical drilling techniques. Within the target zone, horizontal drilling techniques are often utilized to maximize the well's capture zone for natural gas withdrawal. In addition, it is common to install multiple horizontal wells at a single "well pad" in order to maximize gas production and minimize the amount of land disturbance when developing the well network to extract the natural gas. The drilling phase for a single horizontal well typically lasts 4 to 5 weeks, including drilling, casing, and cementing the well (revised dSGEIS, p. 5-27), whereas the gas production phase persists for years to decades.

Care is taken in the design and installation of gas wells to protect drinking water aquifers and to isolate the gas producing zone from overlying hydrogeologic units. In addition to minimizing environmental impacts, it is critical for the gas well to be completely isolated from overlying drinking water aquifers and other non-potable aquifer units (referred to as "zonal isolation") in order to economically produce natural 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 gas wells (API, 2009).

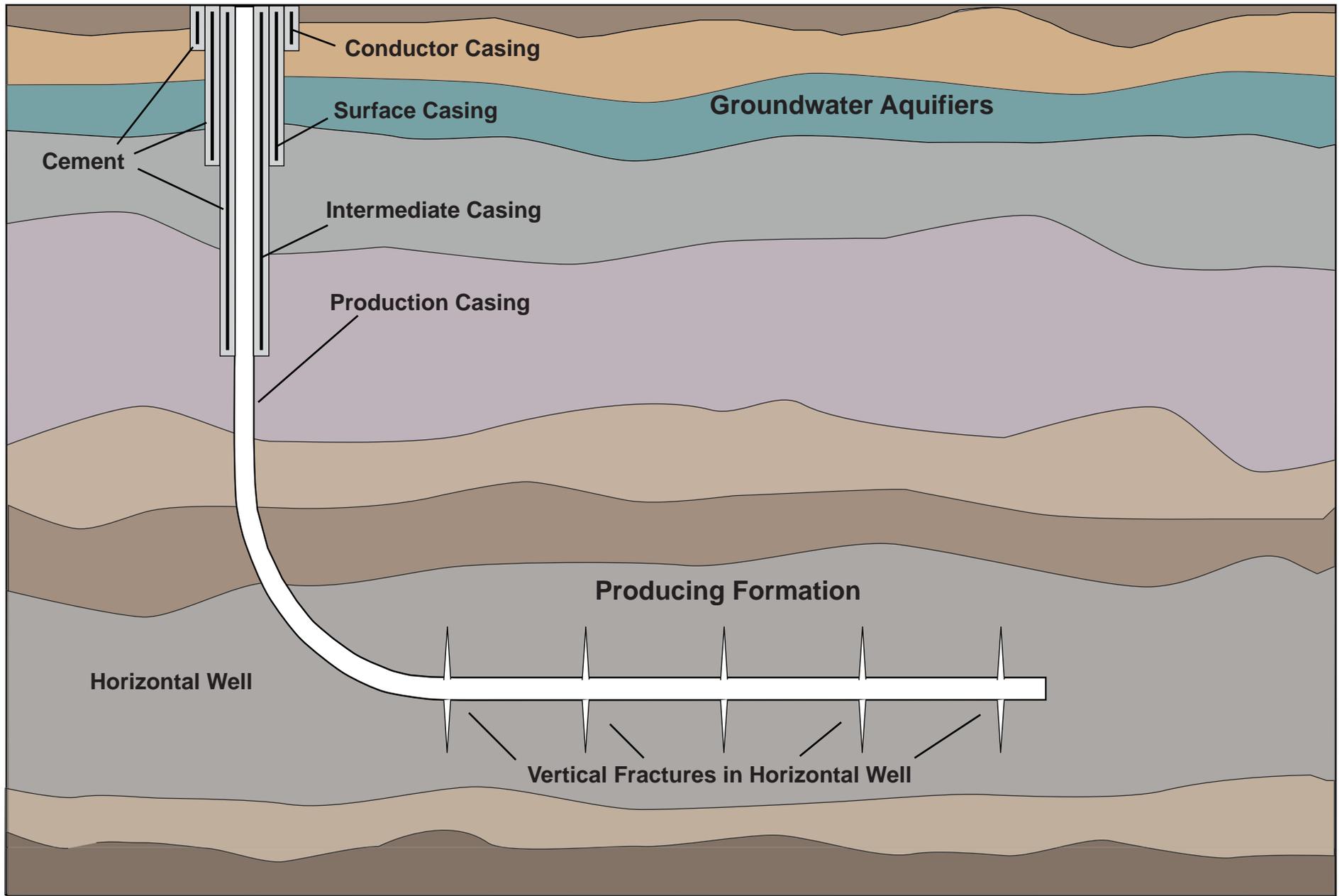
The following elements are included in the design and installation of gas wells to ensure well integrity, *i.e.*, that the well is only in communication with the hydrocarbon-bearing unit and not with other overlying units. These well installation and design elements reflect the current state of the art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

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 gas wells, such as those anticipated to be installed in the Marcellus Shale formation, 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), also a NYSDEC requirement (NYSDEC, 2009c).
- *Surface Casing* – After the conductor casing has been drilled and cemented, the surface casing is installed to protect potable aquifers. NYSDEC (2009c) regulations require that the casing be set to a depth of 75 feet below the deepest potable aquifer or 75 feet into competent bedrock, whichever is deeper. 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 – to test whether the casing integrity is adequate (*i.e.*, no leaks or zones of weakness) for meeting the well's design objectives; 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.



File Path: C:\Projects\210116_HESI\Graphics\NonCAD\Figure 2.1.ai

REFERENCE: API, 2009.



Typical Horizontal Well Design

FIGURE 2.1

Date: 1/9/2012

- *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; however, NYSDEC is proposing to require the use of intermediate casing in all horizontal wells in the Marcellus shale. 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 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 performing the hydraulic fracturing stage.

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.

Cement Bond Logging

Cement bonds play a critical role in isolating the 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, gas wells are carefully designed, with a number of key design and monitoring elements (*e.g.*, multiple well casings/cement bonds, cement bond logging, and pressure integrity testing). These practices protect drinking water aquifers by achieving full zonal isolation of the gas well from overlying formations.

After the well has been installed and its integrity has been tested, the last step in the process is the perforation of the horizontal section of the well in the gas production zone. During this process sections of the well casing are successively perforated. 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 natural gas during the gas production phase.

2.3 Hydraulic Fracturing Stages

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 stages and fluids used are tailored to the particular conditions of the particular formation being fractured. The selection of site-specific fracturing steps and fluids is determined during an HF pre-planning step. Therefore, while the HF process outlined below applies generally, the sequencing of particular HF stages may change depending upon specific local conditions. We describe a typical sequence of fracturing stages 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 halt the HF process. The key HF planning and monitoring elements include (API, 2009):

HF Pre-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 utilizing 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.
- 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.

- Often, 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 establish baseline conditions, refine the HF execution, and minimize the likelihood of any fluid spills during the HF process.

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 well 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 gas 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, spilled 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 fracture geometry in the subsurface is consistent with the frac 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 pre-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.

2.3.2 HF Fracturing Stages and Role of Chemical Additives

Hydraulic fracturing is conducted in stages, with discrete sections of the well "fractured" at a time. HF fluid properties are adjusted during each phase of the well development to enhance the effectiveness of the HF process. 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 stage* 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 gas-bearing zone.
2. *Fracturing stage*, during which the fractures are induced in the target formation after which proppants are pumped into the fracture network to "prop" the fractures so that they remain open.
3. *Flush stage* to clean out the well after fracturing, including removing excess proppant materials.

Chemicals serve many functions in hydraulic fracturing. From limiting the growth of bacteria to preventing corrosion of the well casing, chemicals are needed to insure that the fracturing job is effective and efficient. The chemical additives used in a typical fracture treatment depend on the geologic conditions of the formation being fractured.

As noted in the revised dSGEIS, and summarized in Table 2.2, HF fluid is predominantly water (~90%), with proppants (*e.g.*, sand, ceramic beads, etc.) comprising approximately 9% of the HF fluid by weight, and the HF additives comprising the remainder (~0.5%) of the HF fluid by weight. Each HF chemical component 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. In addition, other additives include: 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 HF additives that may be used in the Marcellus formation is given in Table 2.2.

Table 2.2 Example HF Fluid Components for Marcellus Shale

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: revised dSGEIS, Figure 5.4

2.3.3 Flowback Water Recovery

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. In the Marcellus Shale, the volume of fluid that is recovered as flowback fluid is expected to be on the order of 20% of the amount pumped into the formation. This expected recovery rate is within the range reported for the Marcellus formation in northern Pennsylvania (9% to 35%). In addition, the Susquehanna River Basin Commission (SRBC) has reported the average flowback recovery to be 18% (SRBC, 2009).

Flowback water is either recycled for re-use in subsequent HF stages, or disposed of by HF operators. Operators indicate that recovered flowback fluids will be stored in tanks prior to reuse or disposal (revised dSGEIS, p. 1-2, p. 5-100). While lined impoundments had been contemplated in the 2009 dSGEIS, should operators use impoundments for managing flowback fluids, any such impoundments would require a site specific permit application for approval by NYSDEC (revised dSGEIS, p. 1-2). Depending on local conditions and regulations, flowback disposal options may include deep well injection and treatment at a publicly-owned treatment works (POTWs) or a private treatment facility.

Flowback fluid constituents reported in the revised dSGEIS are based on fluid samples collected from horizontal gas wells installed in the Marcellus Shale formation in Pennsylvania and West Virginia.. A summary of the flowback constituents is provided in Table 2.3. These constituents that have been identified in flowback do not necessarily derive from HF additives; in many if not most cases these constituents occur naturally in the formation being hydraulically fractured. In addition, it is not clear where these flowback samples were collected (*e.g.*, at/near a wellhead or from a surface impoundment), and whether proper sample collection and laboratory quality assurance/quality control procedures for generating reliable environmental data were utilized. Nonetheless, irrespective of origin and data quality, we evaluated the potential human health risks associated with flowback constituents reported in the revised dSGEIS.

Table 2.3 Summary of Flowback Constituents in the 2011 SGEIS

CAS	Parameter ^[a]	N	Det	Flowback Concentration (µg/L)	
				Median	Max
7439-90-5	Aluminum	43	12	70	1,200
7664-41-7	Aqueous ammonia	48	45	44,800	382,000
7440-38-2	Arsenic	43	7	90	123
7440-39-3	Barium	48	47	1,450,000	15,700,000
7440-39-3	Barium-Dissolved	22	22	212,000	19,200,000
7440-42-8	Boron	23	9	2,060	26,800
24959-67-9	Bromide	15	15	607,000	3,070,000
7440-43-9	Cadmium	43	6	25	1,200
7440-70-2	Calcium	187	186	4,241,000	123,000,000
16887-00-6	CHLORIDE	193	193	56,900,000	228,000,000
7440-47-3	Chromium	43	9	82	760,000
7440-47-3	Chromium-Dissolved	19	10	539	7,810
7440-48-4	Cobalt	30	6	398	620
7440-50-8	Copper	43	8	25	157
7439-89-6	Iron	193	168	29,200	810,000
7439-89-6	Iron-Dissolved	34	26	63,250	196,000
7439-92-1	Lead	43	6	35	27,400
7439-93-2	Lithium	13	13	90,400	297,000
7439-93-2	Lithium-Dissolved	4	4	61,350	144,000
7439-95-4	Magnesium	193	180	177,000	3,190,000
7439-96-5	Manganese	43	29	1,890	97,600
7439-96-5	Manganese-Dissolved	22	12	2,975	18,000
7439-98-7	Molybdenum	34	12	440	1,080
7440-02-0	Nickel	43	15	30	137
7440-09-7	Potassium	33	17	125,000	7,810,000
7440-23-5	Sodium	42	41	23,500,000	96,700,000
7440-24-6	Strontium	36	36	1,115,000	5,841,000
7440-24-6	Strontium-Dissolved	22	21	629,000	7,290,000
14808-79-8	Sulfate	193	169	1,000	1,270,000
7440-66-6	Zinc	43	18	36	8,570,000
71-43-2	Benzene	35	14	480	1,950
100-41-4	Ethyl Benzene	38	14	54	164
108-88-3	Toluene	38	15	833	3,190
1330-20-7	xylenes	38	15	444	2,670
NORM ^[b]					Max (pCi/L)
	Ra-228	3	3		18.4
	Ra-226	3	3		33
	Cs-137	2	16		10.5

Note:

[a] Chemicals measured in Marcellus flowback samples reported in rSGEIS detected in more than 3 samples.

[b] Naturally occurring radioactive material.

2.4 HESI HF Fluid Systems and Constituents

HESI has developed HF fluid systems for fracturing in the Marcellus formation, as well as other oil and gas-bearing formations in other regions of the US. Designations for a number of typical HESI HF fluid systems, as well as the volume of fluids used during separate fracturing stages, are given in Table 2.4. 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.

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 on a fluid system in which some combination of Water Frac, linear Gel Frac and/or cross-linked Gel Frac may be used as part of the engineered fluid formulation. Linear Gel-Frac systems are those without the "cross-linking" agents that are used in some formations to enhance the transfer of proppants into the fractures.

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 gas-bearing zone

According to HESI, in the Marcellus Shale, a typical well is anticipated to use approximately 30,000 gal of fluid for the total pre-frac acid stage, and approximately 4,500,000 gal/well for the combined fracturing/flush phases—with the fracturing phase comprising the vast majority of the fluid volume. We note that one of the HESI formulations that may be used in the Marcellus Shale is a "foam frac" fluid,

which uses far smaller fluid volumes (less than 30,000 gallons for the frac and flush stages – see Table 2.4).⁹

Although only a subset of the typical HESI HF systems noted in Table 2.4 may be used in the Marcellus formation, to be inclusive and comprehensive, we have evaluated all of the HF constituents that are included in this list of typical HESI HF systems. The chemical constituents of the HF additives contained within these HF fluid systems are listed in Table 2.5.

The conceptual model used to evaluate possible environmental impacts to drinking water resources for these HESI HF constituents, and flowback water constituents, is presented in Section 4.

⁹ Note that the revised dSGEIS indicates approximately 5,000,000 gal of HF fluid per well. Given the generalized nature of our analysis, and its conservative assumptions, our risk analysis methods and results would not be altered had we used the dSGEIS value of 5,000,000 gal/well.

Table 2.4 Typical HESI Hydraulic Fracturing 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: Treated Water (TW), Linear Fluid (LF), Cross-Linked Fluid (XLF), Water Frac (WF)

*Systems designated for HF activities in Marcellus formation.

Table 2.5 HF Constituents in Typical HESI HF Fluid Systems

CAS No	Chemical
95-63-6	1,2,4 Trimethylbenzene
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	Attapulgate
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	HCl in 22 Baume Acid

Table 2.5 HF 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 2.5 HF 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
Note: CBI – Confidential Business Information. Gradient was provided chemical-specific CAS and chemical names and used this information to evaluate chemical-specific toxicity.	

3 Geologic Conditions and Drinking Water Resources

The Marcellus Shale underlies a large portion of the Appalachian Mountains from New York southward to West Virginia. In New York, the Marcellus Shale occurs only in the southern portion of the state, known as the Alleghany Plateau (Figure 3.1). The Plateau has moderate to highly sloping terrain and is dissected by numerous streams, rivers, ponds, and lakes. The region's topography and surface deposits were strongly influenced during the last ice age by glaciers, which both carved the landscape and deposited sand, gravel, silt, and clay on the land surface. As a result of these geological processes, the flow of surface water and the occurrence of groundwater (*i.e.*, the water resources of New York) are strongly controlled by these landscape characteristics.

3.1 Geologic Conditions

The land surface in southern New York is either exposed bedrock (outcrops) or soil. Soils primarily originated from glacial deposits, with the most commonly occurring soils being the following:

- Sand and gravel – deposited from glacial outwash and has high permeability; and
- Glacial till – a poorly sorted mixture of clay, silt, and larger soil grains with an overall low permeability.

In southern New York, glacial till is the dominant soil type at the land surface (Cadwell *et al.*, 1991a,b,c,d; Muller *et al.*, 1991). Often, glacial till is underlain by shallow bedrock, especially at higher elevations and on steeper slopes. Due to the high prevalence of bedrock at or just below ground surface (bgs) and the low permeability of glacial till, the overburden deposits for much of the Marcellus Shale region will not transmit water rapidly, *i.e.*, shallow overburden deposits are not a significant groundwater resource. Exceptions do occur, however, in the narrow stream valleys that dissect the landscape. In a number of these valleys (*e.g.*, portions of the Chemung and Susquehanna river valleys), thick deposits of sand and gravel have accumulated and these high permeability materials can transmit groundwater at very high rates.

At the base of overburden deposits is bedrock. The bedrock in the Alleghany Plateau consists of sedimentary rocks – consolidated sand (sandstone), silt (siltstone), and clay (shale) – that were deposited hundreds of millions of years ago when this area of New York was submerged under a large sea (USGS, 2009). As this sea went through multiple cycles of expansion and contraction over geologic times (millions of years), the depositional environment also went through cycles favoring the deposition of different sized particles (*i.e.*, sand, silt, or clay). As a result, the sedimentary bedrock in the Alleghany Plateau consists of multiple alternating layers of sandstone, siltstone, and shale (Figure 3.4). Interspersed in these layers is occasionally limestone, which was formed as a result of carbonate-rich water near the ancient sea floor.

The shales in the Alleghany Plateau fall into two general categories: gray shale and black shale. Both types are fine-grained and have low permeability, although black shales have much higher organic carbon content (giving them a black color). The organic matter in black shales transformed into petroleum compounds (natural gas and oil) over the course of millions of years as a result of the high temperatures and pressures associated with deep burial of the rock mass. Generally, black shales with organic carbon content greater than 2% are favorable for gas production (revised dSGEIS, p. 4-2). The Marcellus Shale is one of these deeply buried, organic rich (up to 12% organic carbon) black shales underlying portions of southern New York (revised dSGEIS, p. 4-16).

The Marcellus Shale in New York is approximately 25 to 300 ft thick (revised dSGEIS, p. 4-16). It crops out in central New York and slopes southward to depths of up to 8,500 ft bgs (ICF, 2009). Gas wells in the formation are 4,000 to 8,500 ft bgs and at these depths, a thick sequence of rocks overlies the Marcellus Shale (CRS, 2009). The overlying rocks are highly stratified, alternating between layers of shales, sandstones, siltstones, and limestones (Figure 3.4). Figure 3.4 shows the location of the Marcellus Shale relative to other rock layers in NYS. Note, however, that the Marcellus Shale is significantly deeper (4,000 to 8,500 ft bgs) in the areas targeted for natural gas production than what is shown in this figure. Immediately overlying the Marcellus Shale is a layer of limestone followed by a layer of gray shale, collectively called the Skaneateles Formation (revised dSGEIS, p. 4-14). Because many of the layers above the Marcellus Shale are effectively impermeable, they have trapped natural gas and saline water within the Marcellus Shale for hundreds of millions of years.

The appeal of the Marcellus Shale as a gas reservoir starkly contrasts with its limited value as a drinking water resource. Groundwater in the Marcellus Shale (and adjoining rock layers) is not potable without extensive treatment due to its high salinity – on the order of 100,000 ppm salt, or several times saltier than

seawater (ICF, 2009) – and the unit yields little water due to its low hydraulic conductivity, high capacity to retain moisture, and small thickness. For these reasons and the formation's depth, the Marcellus Shale is not a viable source of drinking water. In fact, the portion of the Marcellus Shale targeted for gas production lies thousands of feet below the nearest potable aquifer in New York (ICF, 2009). These deep saline waters are isolated from shallow higher quality groundwater by numerous impermeable rock layers, thus preventing commingling of water from the different formations.

3.2 Drinking Water Resources

Physical Setting and Watersheds

Many streams dissect the landscape of the Alleghany Plateau into watersheds of variable sizes. The key watersheds overlying the Marcellus Shale constitute the major drainage basins of large rivers and lakes in the region (Figure 3.2). Within these basins, streams range in size, from small ephemeral streams that only flow during particularly wet periods of the year to large rivers that convey large quantities of water perennially. The major basins overlying the Marcellus Shale in New York primarily drain to the north or south, with some basins draining to lakes (*e.g.*, Lake Erie and the Finger Lakes).

Streams occur in topographically low areas, serving as drainage points for the landscape. The water draining to streams is derived from precipitation and snow melt that travel downslope or down a hydraulic gradient through a combination of overland runoff and the much slower percolation of water through soils and surficial aquifers (groundwater flow). Overland runoff is expected to account for a significant component of stream flow in areas where bedrock outcrops or other relatively impermeable deposits are present. Conversely, groundwater may contribute the majority of water to streams in watersheds underlain by deep, transmissive aquifers, especially during dry conditions. Thus, the relative contributions to stream flow from overland runoff and groundwater flow are determined by the terrain and the surface geology, both of which vary throughout southern New York.

Annual Precipitation

Precipitation, the source of water to streams and aquifers, varies somewhat throughout southern New York, with cumulative annual averages ranging from less than 35 to more than 60 inches per year during the period 1961 to 1990 (USGS, 1998). Where the Marcellus Shale occurs, there is a band of lower precipitation that runs through west-central New York that separates regions of higher precipitation

farther to the east and west. The ultimate fate of precipitation is either to evaporate back to the atmosphere or to evolve as stream flow or groundwater recharge.

Drinking Water Sources

The portion of precipitation that flows through rivers and accumulates in ponds, lakes, and reservoirs constitutes the surface waters available for human use. New York relies upon surface water and groundwater for a variety of uses, *e.g.*, domestic water supply, power generation, recreation, mining, and other industrial activities. Water supply requires significant withdrawals from the State's water resources – approximately 9 to 10 billion gallons (gal) of water per day for the entire state (revised dSGEIS, p. 6-9). The majority of this water comes from surface water sources, such as rivers, lakes, and reservoirs (NYSDOH, 2009).

About 25 percent of New Yorkers draw their drinking water from underground sources (aquifers) (revised dSGEIS p. 2-20). Although groundwater resources occur in many areas throughout the state (Figure 3.3), the most productive aquifers overlying the Marcellus Shale are confined to stream and river valleys filled with glacial sand and gravel deposits (CRS, 2009). Some of these aquifers are extremely productive due to their high permeability and substantial thickness. New York classifies these groundwaters as either Primary or Principal Aquifers, depending on whether they are currently being used (Primary Aquifers), or are not used currently, but have the potential to supply major municipal systems (Principal Aquifers). Except for these highly productive aquifers, shallow groundwater aquifers throughout the rest of the state may be used as sources of drinking water for small communities and individual systems due to their small size and low yields (revised dSGEIS, p. 2-22).

The thickness of aquifers in New York varies, but the maximum depth of potable water is approximately 850 feet (ft) bgs. At greater depths, groundwater is often undrinkable due to high salinity. There are isolated cases, however, where saline groundwater is shallower than 850 ft bgs or where potable groundwater is deeper than 850 ft bgs. Since these cases are isolated (*i.e.*, uncommon), the practical benchmark for maximum potable aquifer depth is 850 ft bgs (revised dSGEIS, p. 2-23).

File Path: G:\Projects\210116_HESI\Graphics\CAD\GIS\100210116_100-01.dwg

Legend

- Depth to the Top of the Marcellus Shale
- ▨ Marcellus Shale and Hamilton Group Outcrop
- Extent of the Marcellus Shale in New York

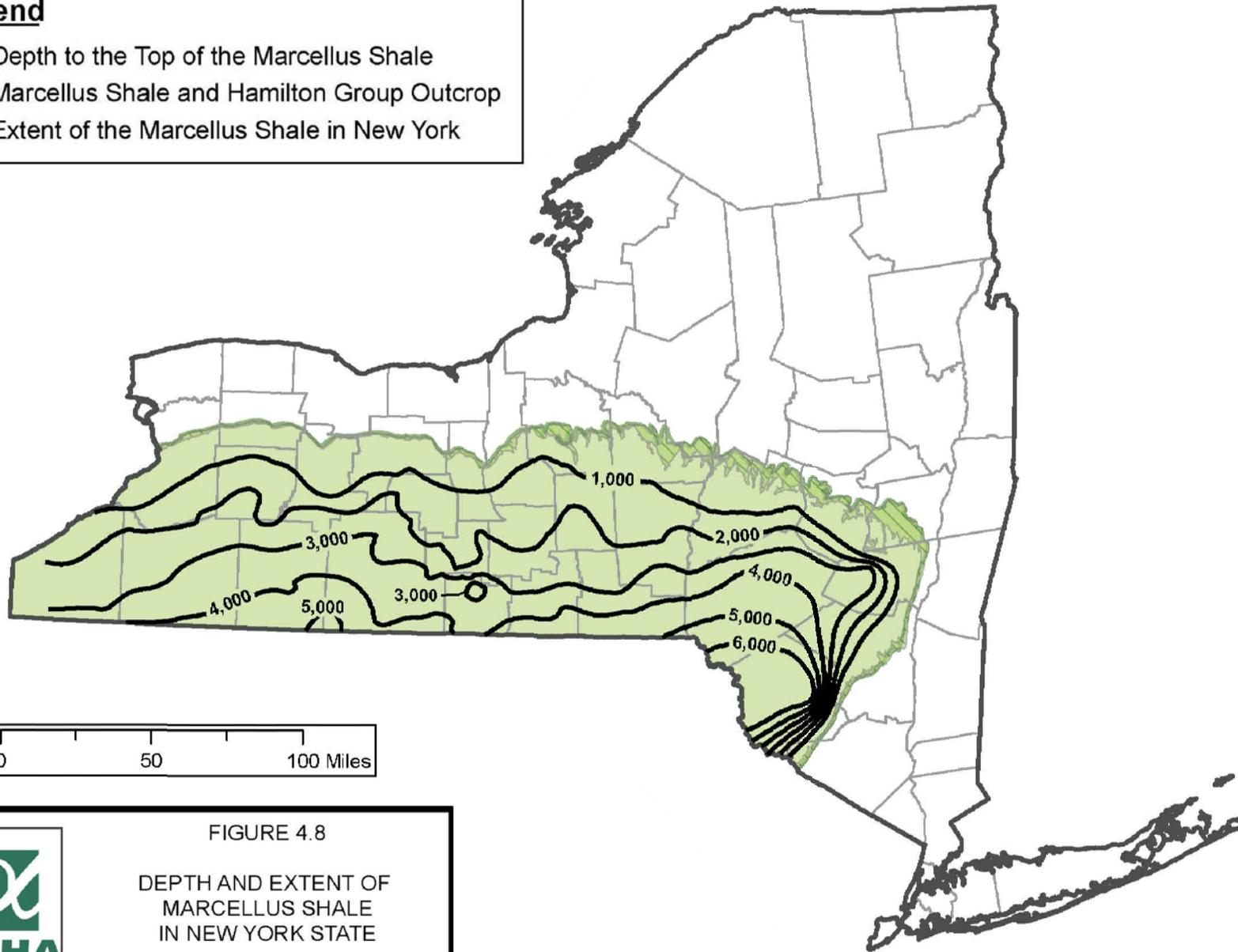


FIGURE 4.8

DEPTH AND EXTENT OF MARCELLUS SHALE IN NEW YORK STATE

Technical Support Document to the Draft Supplemental Generic Environmental Impact Statement



Source: - New York State Museum - Reservoir Characterization Group (Leone, 2009).

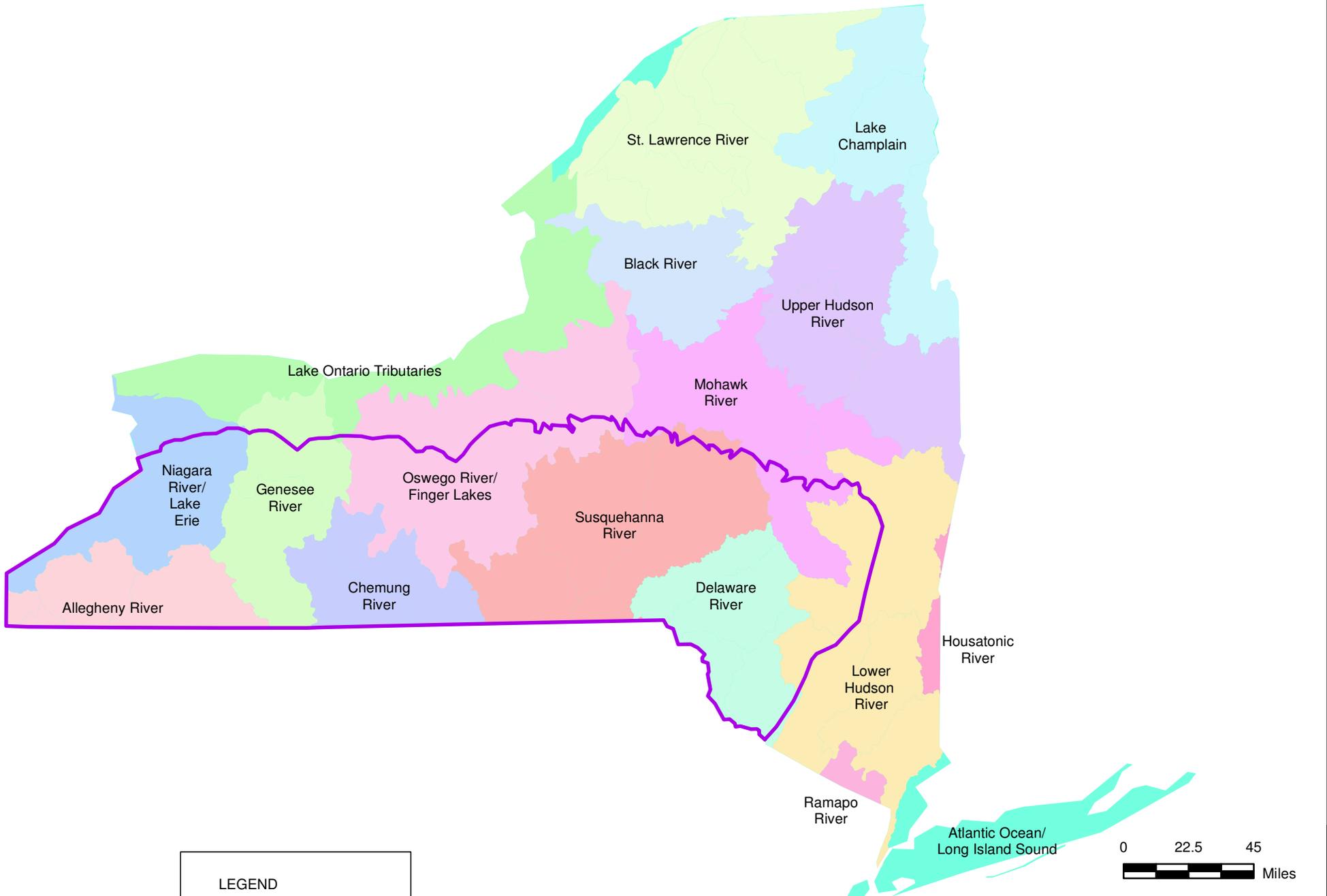
MAP REFERENCE: NYSDEC, 2009, Figure 4.8.



Depth and Extent of Marcellus Shale in New York

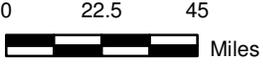
FIGURE 3.1

Date: 12/16/2011



LEGEND

 Marcellus Shale



MAP REFERENCE:
1) US EPA, 2011c.



Major Watersheds in New York

FIGURE
3.2

Date: 12/16/2009

Map No.	Aquifer Name	Number of Wells Within Mapped Aquifer Boundary		
		Gas Wells	Oil Wells	Other Wells*
1	Baldwinsville	37	0	3
2	Batavia	0	0	5
3	Corning	5	0	4
4	Cortland-Homer-Preble	0	0	2
5	Elmira-Horseheads-Big Flats	6	0	16
6	Endicott-Johnson City	0	0	3
7	Fulton	4	0	2
8	Jamestown	82	11	14
9	Lower Cohocton	4	0	24
10	Olean	7	310	81
11	Owego	0	0	2
12	Salamanca	14	2	6
13	Upper Cohocton	0	0	3
14	Waverly	0	0	1
	Principal Aquifer	1,664	749	1,344
	Total	1,823	1,072	1,510

Notes:

* - Other wells include storage, solution brms, dry hole, injection, stratigraphic, geothermal, and not listed well types.

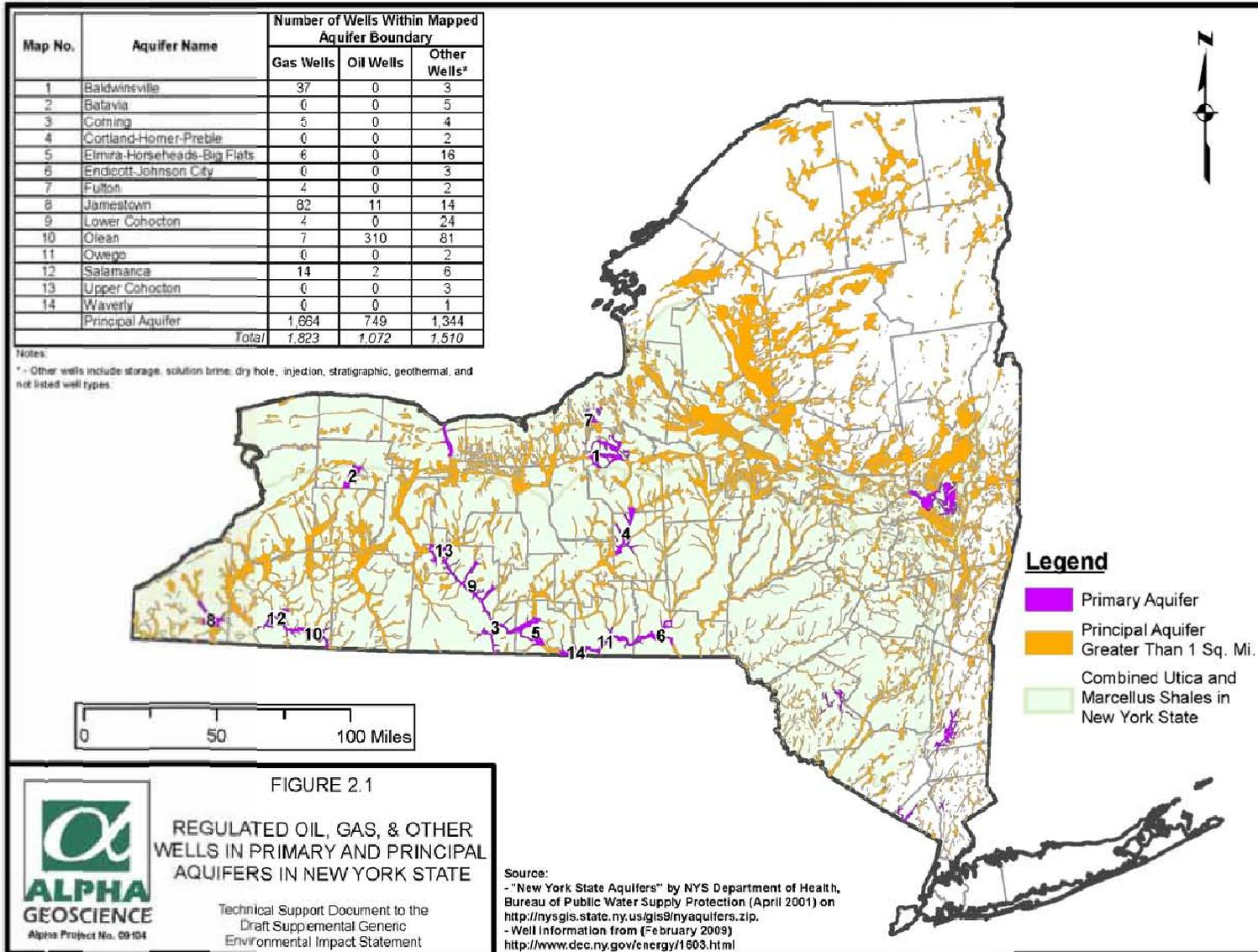


FIGURE 2.1



REGULATED OIL, GAS, & OTHER WELLS IN PRIMARY AND PRINCIPAL AQUIFERS IN NEW YORK STATE

Technical Support Document to the Draft Supplemental Generic Environmental Impact Statement

Source:

- "New York State Aquifers" by NYS Department of Health, Bureau of Public Water Supply Protection (April 2001) on <http://nysgis.state.ny.us/gis9/nyaquifers.zip>.
 - Well information from (February 2009) <http://www.dec.ny.gov/energy/1603.html>

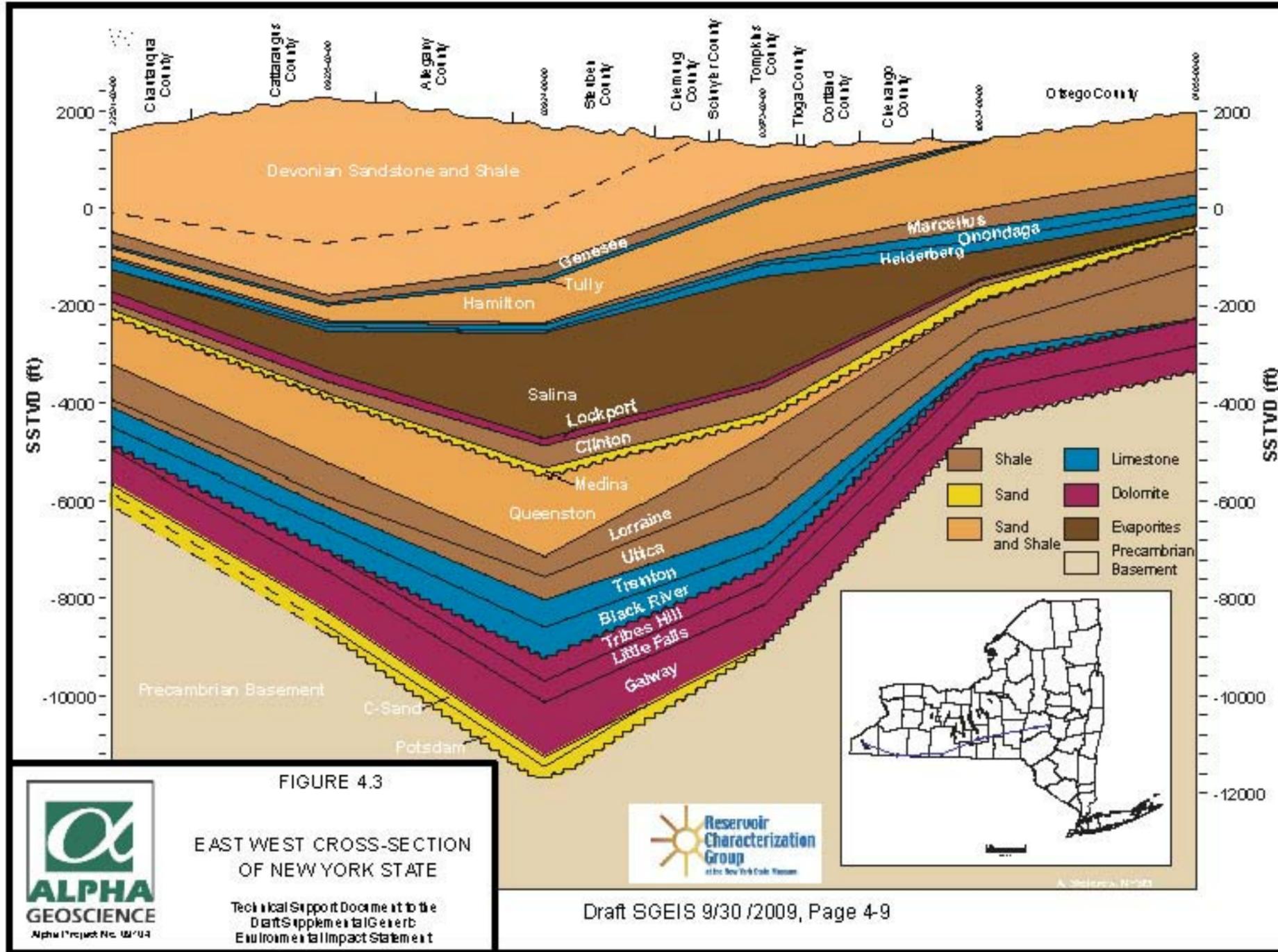


Primary and Principal Aquifers in New York

FIGURE 3.3

Date: 12/16/2011

MAP REFERENCE:
 NYSDEC, 2009, Figure 2.1.



Stratigraphic Column of New York; Oil and Gas Producing Horizons
(from D.G. Hill, T.E. Lombardi and J. P. Martin, 2002)

PERIOD	GROUP	UNIT	LITHOLOGY	THICKNESS (feet)	PRODUCTION	
PENNSYLVANIAN	Pottsville	Olean	Ss, cgl	75 - 100		
MISSISSIPPIAN	Pocono	Knapp	Ss, cgl	5 - 100		
	Conewango	Riceville	Sh, ss, cgl	70		
DEVONIAN	UPPER	Conneaut	Sh, ss	700		
		Undiff	Sh, ss		Oil, Gas	
		Canadaway	Perrysburg-Dunkirk	Sh, ss	1,100 - 1,400	Oil, Gas
		West Falls	Java	Sh, ss		
		Nunda	Sh, ss	365 - 125	Oil, Gas	
		Rhinestreet	Sh			
	MIDDLE	Sonyea	Middlesex	Sh	0 - 400	Gas
		Genesee	Genesee	Sh	0 - 450	Gas
		Tully	Ls	0 - 50	Gas	
		Hamilton	Moscow	Sh		
			Ludlowville	Sh		
			Skaneateles	Sh	200 - 600	
Marcellus	Sh			Gas		
LOWER	Onondaga	Ls	30 - 235	Gas, Oil		
	Tristates	Oriskany	Ss	0 - 40	Gas	
	Helderberg	Manlius	Ls	0 - 10		
		Rondout	Dol			
SILURIAN	UPPER	Akron	Dol	0 - 15	Gas	
		Salina	Camillus	Sh, gyp		
		Syracuse	Dol, sh, silt	450 - 1,850		
		Vernon	Sh		Gas	
		Lockport	Dol	150 - 250	Gas	
	LOWER	Rochester	Sh	125	Gas	
		Irondequoit	Ls			
		Sodus/Oneida	Sh/cgl		Gas	
		Reynales	Ls	75		
		Thorold	Ss			
ORDOVICIAN	UPPER	Medina	Grimsby	Sh, ss	75 - 150	Gas
		Whirlpool	Ss	0 - 25	Gas	
		Queenston	Sh		Gas	
	MIDDLE	Oswego	Ss	1,100 - 1,500	Gas	
		Lorraine	Sh			
	LOWER	Utica	Sh	900 - 1000	Gas	
Trenton-Black River		Trenton	Ls	425 - 625	Gas	
Black River		Ls	225 - 550	Gas		
CAMB.	UPPER	Beekmantown	Tribes Hill-Chuctanunda	Ls	0 - 550	
		Little Falls	Dol	0 - 350		
PRECAMBRIAN		Galway	Dol, ss	575 - 1,350	Gas	
		Potsdam	Ss, dol	75 - 500	Gas	
			Geiss, marble, quartzite			

NOTE:
This figure shows the relative position of the Marcellus shale to other rock layers in New York. However, the Marcellus shale is significantly deeper (4000 to 8500 feet below ground surface) in the areas targeted for natural gas production than what is shown in this drawing.

MAP REFERENCE:
NYSDEC, 2009, Figures 4.2 and 4.3.

FIGURE 4.3
EAST WEST CROSS-SECTION OF NEW YORK STATE
Technical Support Document to the Draft Supplemental General Environmental Impact Statement

Reservoir Characterization Group
of the New York State Department of Environmental Conservation
Draft SGEIS 9/30/2009, Page 4-9



Geologic Cross Section of New York

FIGURE 3.4

4 Conceptual Model for Risk Analysis

As described in Section 2, the process of hydraulic fracturing typically requires the handling of large volumes of HF fluid during the pumping and recovery phases. Although many controls and best management practices are established to reduce the likelihood and minimize the potential impacts of spills of HF fluids, some surface spills and/or HF fluid leaks may occur. For example, there could be leaks in pipe fittings or pump failures during HF fluid handling or pumping, or while flowback water is being recovered and stored for disposal. In addition, questions have been raised as to whether HF constituents could migrate upward from the Marcellus formation and contaminate shallow groundwater aquifers. We outline below the conceptual model for our risk analysis of the possible human health impacts of surface spills and the potential for upward migration of constituents from the Marcellus.

Our exposure and risk analysis examines the potential human health consequences associated with HF constituents possibly impacting drinking water resources from the following spill and/or migration scenarios:

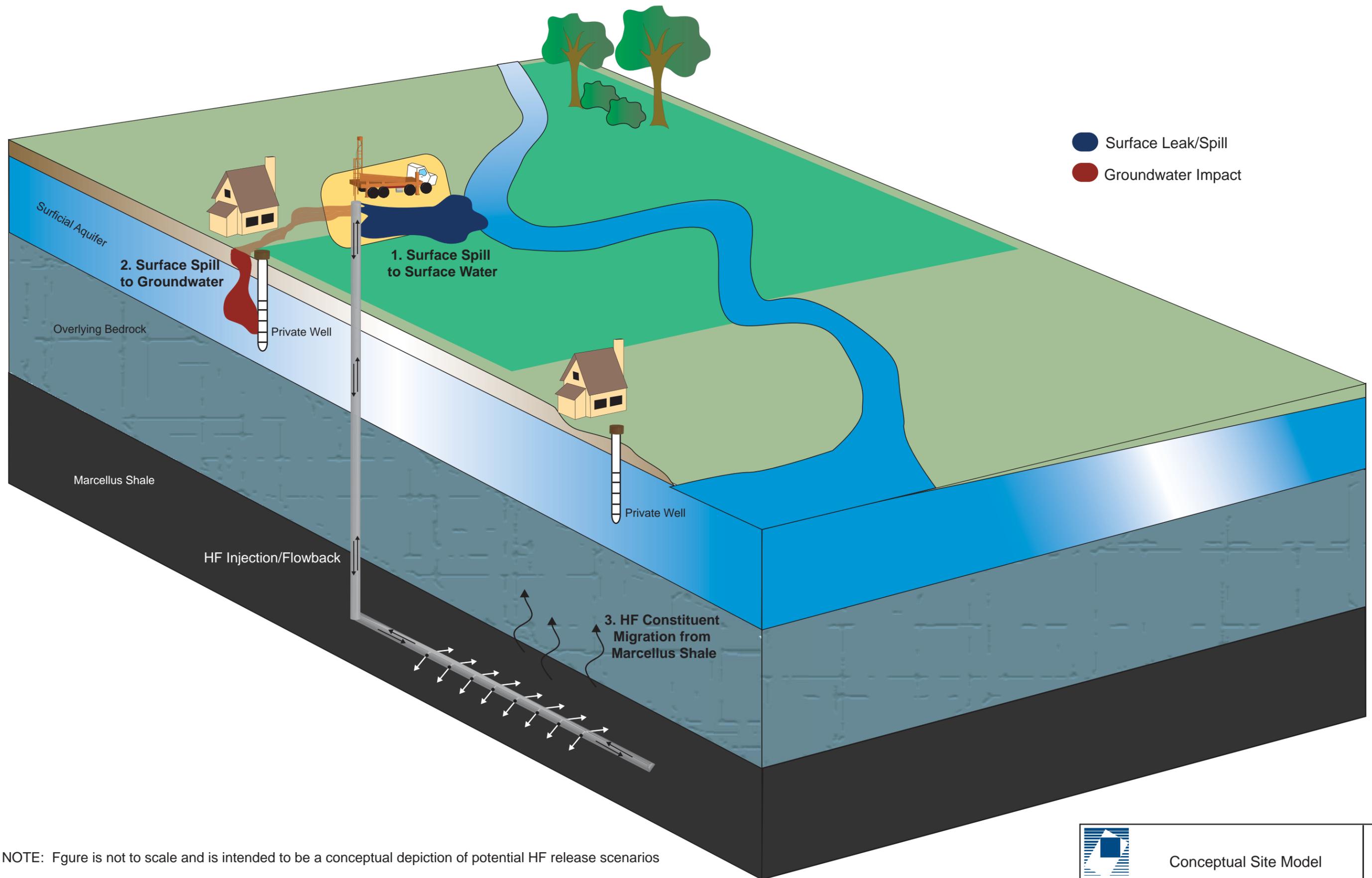
1. Surface spills during HF fluid pumping or flowback fluid recovery which potentially allow HF constituents to runoff the well pad and impact surface water used for drinking water;
2. Surface spills during HF fluid pumping or flowback fluid recovery that possibly lead to HF constituents migrating downward through soil and impacting shallow aquifers and nearby drinking water wells; and,
3. Potential upward migration of HF constituents from the Marcellus Shale into overlying shallow drinking water aquifers during the fracturing and post-fracturing periods.

Each of the migration/exposure pathways outlined above is numbered on Figure 4.1 which depicts the conceptual model for the drinking water exposure pathways in our risk analysis. As described in Section 5, for the surface spill analysis, we considered two different scenarios. One scenario examined the impacts of hypothetical "routine" small spills (we term this the "diffuse" spill scenario), and another scenario examined the potential impacts of a short-term ("sudden") spill. In order to be conservative (*i.e.*, health-protective) in our analysis, we have not taken into account any best management practices, institutional controls, or mitigation measures proposed by NYSDEC in the revised dSGEIS (discussed briefly in Section 2). For this reason, our analysis addresses "uncontrolled," or "unmitigated" surface spills of HF fluids.

If HF constituents in hypothetically uncontrolled surface spills migrate overland *via* surface runoff/erosion, 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, to impose conservative estimates for purposes of our analysis, assessing the hypothetical implications if: (i) 100% of the surface spill leaches to groundwater; and (ii) 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.

In addition to these surface spill exposure scenarios, we also examined the possibility that HF constituents might migrate upward from the Marcellus formation either during the HF process (the fracturing stage), or after the well has been completed (the production stage). Questions have been raised concerning this hypothetical migration potential, and NYSDEC also addressed this issue in its dSGEIS and revised dSGEIS; NYSDEC concluded that due to a variety of factors, this migration pathway is not a plausible mechanism for contaminating shallow groundwater resources. Our analysis in this report (Section 5.3) is an extension of the analysis in our earlier study (Gradient, 2009), and in both this analysis and our prior study, we similarly conclude this migration pathway is not plausible.

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 designed and installed, 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 5.2, based on an API study, NYSDEC's consultants estimated the risk of a properly constructed underground injection well contaminating a potable groundwater supply to be less than one in 50 million (revised dSGEIS, 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*.



NOTE: Figure is not to scale and is intended to be a conceptual depiction of potential HF release scenarios



Conceptual Site Model

FIGURE
4.1

Date: 12/05/2011

5 Exposure Analysis

This section describes the methods we used to evaluate the fate of potential spills of HF fluid during well development and fluid handling operations. As a central component of the exposure analysis, we develop dilution factors for each exposure pathway to assess the degree to which the HF constituent concentrations will be diluted from the point of the spill (*e.g.*, either to the surface for spills, or from the Marcellus formation for our upward migration analysis) to the point at which a potential drinking water exposure might occur.

5.1 Surface Spills

As described in Section 2, HF activities will commonly involve drilling multiple wells at a single pad. For example, the revised dSGEIS indicates that NYSDEC proposes to allow four wells to be developed on a single pad per year. Depending on the specific HF fluid systems used, the total fluid volumes used in hydraulically fracturing a well could range from as little as approximately 30,000 gallons to over 4,000,000 gallons (see Table 2.3). The volume of fluid that is recovered as flowback fluid is expected to be on the order of 20% of HF fluid used. This expected recovery rate is within the range reported for the Marcellus formation in northern Pennsylvania (9% to 35%). In addition, the Susquehanna River Basin Commission (SRBC) has reported the average flowback recovery to be 18% (SRBC, 2009).

5.1.1 Spill Volumes

We assess two different types of hypothetical surface spill scenarios. For one scenario, which we term a "diffuse" spill, we conservatively assume that small leaks/spills occur as much as daily throughout the year. Our second scenario examines the possible impacts of a "sudden" spill that occurs on a single day.

"Diffuse" Spills

For the diffuse spill scenario, we have assumed that leaks/spills occur during fluid handling that are relatively small at any one time, but that could hypothetically occur repeatedly throughout the year during HF activities. Furthermore, the leaks are assumed to occur potentially from multiple fluid handling

locations, such that the leaks/spills could cause contamination over a larger "footprint" than a single spill. For the diffuse spill scenario, we have assessed the possible impacts of releasing 10 gallons of fluid per day throughout the year (approximately 3,500 gallons per year), covering a surface area of 2 acres of the well pad. This is considered an upper-bound estimate of the total volume of small leaks/spills during a year that might go undetected. We emphasize that this hypothetical spill scenario was evaluated for the purposes of this study as a "what if" type scenario. Given the many controls and best management practices employed during HF operations (described in Section 2), it is not expected that multiple spills/leaks of this nature would occur at a well pad during a given year.

During the course of time, if uncontrolled, surface spills of this nature could migrate overland *via* surface runoff/erosion and contaminate adjacent surface water resources. In addition, surface spills are susceptible to leaching through the unsaturated zone (soil above the groundwater table) and potentially contaminating shallow aquifers. For our exposure and risk analysis we have evaluated two sets of extreme conditions, assessing the implications if, (i) 100% of the surface spill leaches to groundwater, and (ii) 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).

Sudden Spills

The second scenario, which we term a sudden spill, is one possibly resulting from an equipment malfunction during HF fluid pumping that results in a short-term localized spill of HF fluids to the surface. As noted earlier, the HF fracturing process is highly controlled. Given the automated monitoring that is utilized during HF, if malfunctions were to occur, it is anticipated that the HF pumping would be shut down quickly after detection of abnormal pressure drops or other signs of abnormal operating conditions.

For the sudden spill scenario, we have evaluated a range of potential fluid spill volumes, evaluating the potential impacts of individual spills of 1,000 gallons to as large as 10,000 gallons over a short time period.¹⁰ We chose a range of spill volumes for several reasons. First, the range of spill volumes provides perspective on how exposure and potential health risk could vary as a function of spill volume. In addition, because different HF fluid systems use different overall fluid volumes, with some using approximately 30,000 gallons overall, whereas others use over 4,000,000 gallons, it is not unreasonable to

¹⁰ A 10,000 gallon spill would represent several minutes of pumping under high pressure during hydraulic fracturing.

consider that those HF systems employing larger volumes have the potential for larger sudden spills than do the systems using smaller volumes. We consider 10,000 gallons to be a reasonable upper bound for purposes of this analysis. Given the automated monitoring that is utilized during HF, if malfunctions were to occur, it is anticipated that the HF pumping would be shut down quickly after detection of abnormal pressure drops or other signs of abnormal operating conditions. These automated detection procedures should limit the duration and magnitude of potential sudden spills. In fact, available data confirm that 10,000 gallons is a conservative upper bound for spill volumes. For example, based on incident report data maintained by the West Virginia Department of Environmental Protection relating to oil and gas exploration and productions activities, for the period 1990 to 2011, of the 323 spill incidents logged (with quantified spill volumes) the median spill volume was 55 gallons, and the 95th percentile was 2,750 gallons.¹¹ For these reasons, the sudden spill volumes we have assessed are considered reasonable ranges. A summary of the surface spill scenarios is given below.

As with the diffuse spill scenario, we evaluate the two sets of bounding conditions for this sudden spill scenario, assuming (i) 100% of each spill leaches to groundwater, and (ii) 100% of the spill impacts surface water. Those bounding assumptions add an extra level of conservatism to our analysis, as is the case for the diffuse spill scenario.

<i>Spill Scenario</i>	<i>Spill Volume</i>	<i>Notes</i>	<i>Impacted Area</i>
<i>Sudden Spill</i>	1,000 gal	HF Volumes ≤ 250,000 gal	0.1 acre
	10,000 gal	HF Volumes > 250,000 gal	1 acre
<i>Diffuse Spill</i>	3,500 gal	~10 gal/day x 350 days/yr	2 acres

Sudden spill impacted area assumes spill "thickness" of 1 cm (~0.4 inch). Diffuse spill impacted area assumes 0.2 cm spill thickness (<0.1 inch)

Comparison to 2009 Approach

We note that the spill scenarios evaluated here have evolved somewhat relative to the prior Gradient risk analysis in 2009. In that study, we evaluated potential impacts of a sudden spill where 8,500 gallons of HF fluid potentially impacted groundwater, and 8,500 gallons of HF fluid potentially impacted surface

¹¹ These spills include spills from surface impoundments as well as releases from pumps, pipes, tanks, etc. For spill volumes given in "barrels" we assumed these were 55 gallon barrels/drums. Source: https://apps.dep.wv.gov/oog/svsearch_new.cfm.

water. We modified the spill volumes in our current analysis because of the wide range of HF fluid volumes evaluated in this study, whereas we evaluated only a single HF fluid volume in our 2009 study. Given that some of the typical HESI HF fluid systems involve on the order of 30,000 gallons, it would be unreasonable to assume the volume of spills we had assessed in our 2009 study for such HF systems, and hence we adopted a range of spill volumes.¹² The range of sudden spill scenarios we evaluate here bracket the spill volume impacting either surface water or groundwater in our earlier analysis. Moreover, for HF fluid volumes less than 250,000 gallons, the sudden spill scenario (1,000 gallons) represents up to 4.5% of the volumes shown earlier in Table 2.3. For HF fluid volumes greater than 250,000 gallons, the sudden spill scenario (10,000 gallons) represents up to 2.5% of the HESI HF fluid volumes in Table 2.3. By comparison, the sudden spill volume potentially reaching a surface water or groundwater that was evaluated in our 2009 study represented 0.2% of the total HF fluid volume (approximately 4,000,000 gallons) for the spill scenario evaluated in 2009.

The diffuse spill volume we evaluate here, 10 gallons/day throughout the year, differs from our 2009 hypothetical scenario. In our 2009 study, the diffuse spill scenario equated to spills of approximately 175 gallons/day throughout the year, with 50% impacting surface water (32,240 gallons), and 50% impacting groundwater (32,240 gallons). Spills of such a large magnitude happening on a routine/daily basis are considered so implausible as to be unrealistic. Therefore, in this analysis we modified the diffuse spill scenario to one that is less unreasonable, although still quite conservative.

For comparison, we have calculated the exposure and potential health risks of HF spills for the 2009 spill scenarios in Appendix E. That analysis indicates that even if such large spill volumes are assumed, none of the exposure scenarios result in chemical concentrations that exceed human health based drinking water benchmarks.

5.1.2 Surface Spill Impacts to Groundwater

In this section, we examine the potential impacts to shallow aquifers for both the diffuse and sudden HF spill scenarios presented above. 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).

¹² For such HF systems, 8,500 gallons would represent a spill of over 25% of the entire volume used during the fracturing process, an amount considered to be an unrealistically large percentage given the automated monitoring systems employed during HF operations.

The migration of HF chemicals 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 5.1). During both steps in this process, the concentrations of chemicals in the spill fluids are diluted.

Conceptually, 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:

$$C_{WT} = \frac{C_{HF}}{DAF_L} \quad (5-1)$$

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

$$C_{well} = \frac{C_{WT}}{DAF_{gw}} \quad (5-2)$$

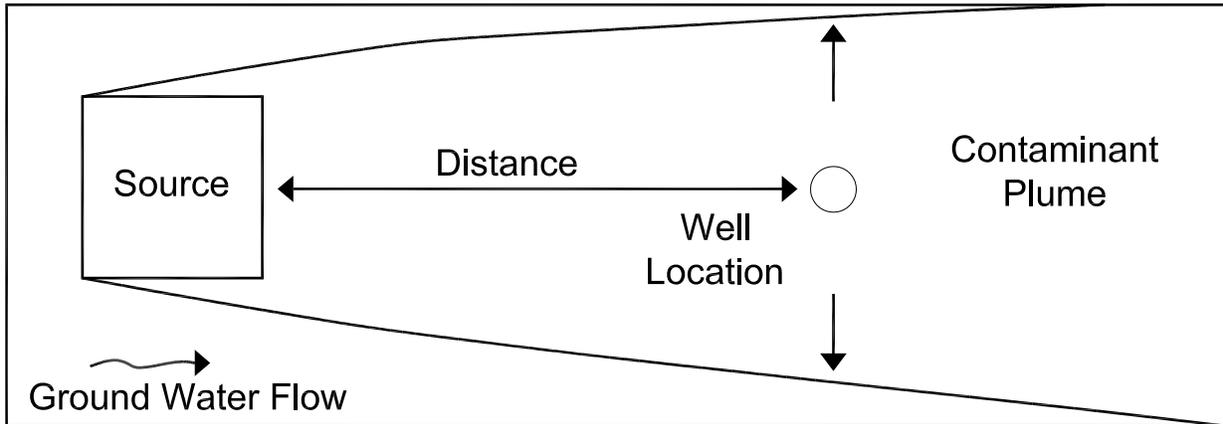
Step 1 and Step 2 Combined:

$$C_{well} = \frac{C_{HF}}{DAF_L \times DAF_{gw}} \quad (5-3)$$

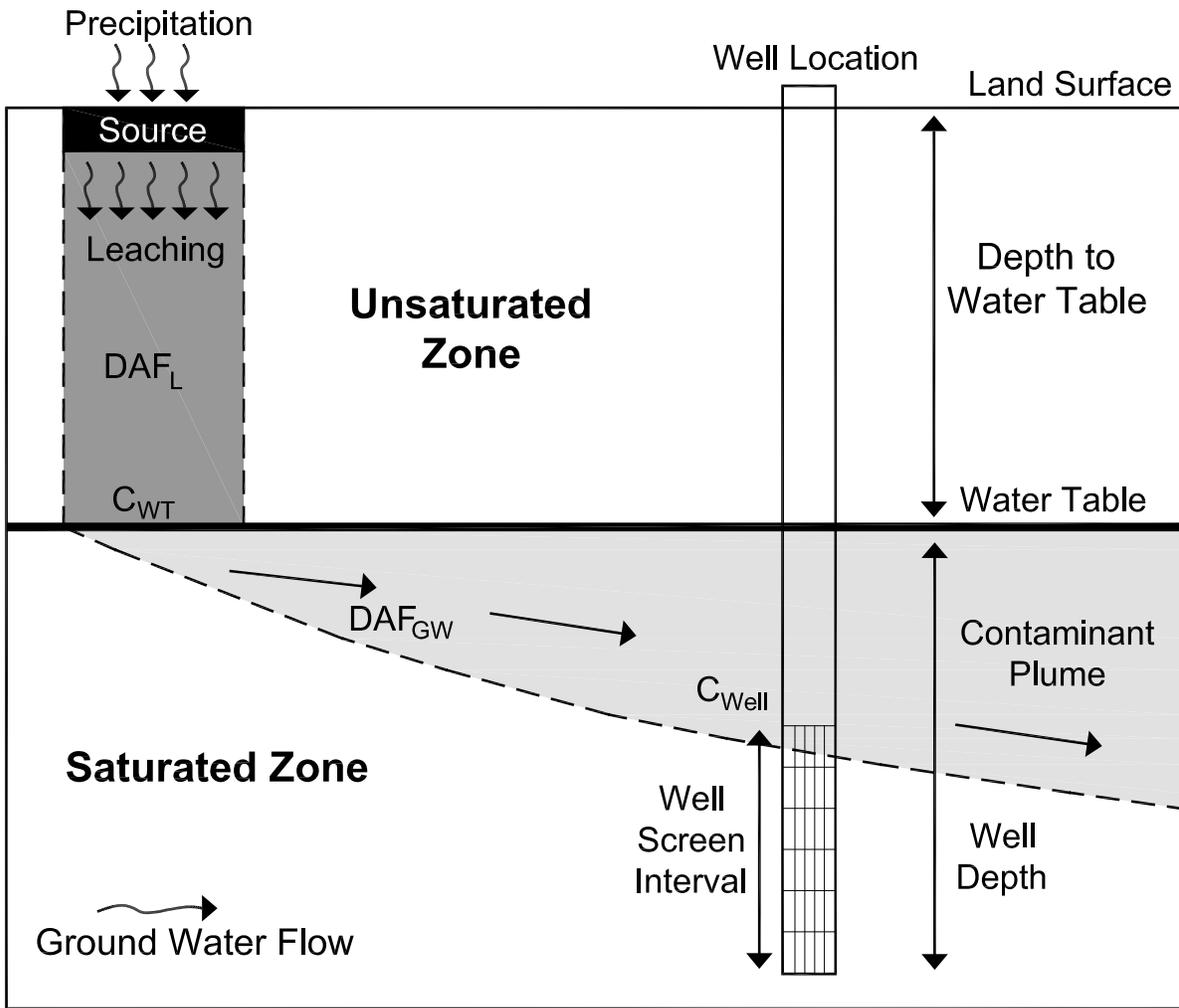
where:

- C_{well} = Concentration of HF constituent at well ($\mu\text{g/L}$)
- C_{HF} = Concentration of HF constituent in HF fluid spilled at the surface ($\mu\text{g/L}$)
- C_{WT} = Concentration of HF constituent entering water table at the bottom of the unsaturated zone ($\mu\text{g/L}$)
- DAF_L = Dilution attenuation factor due to leaching from the soil surface to the water table (unsaturated zone)
- DAF_{gw} = Dilution attenuation factor of leachate into groundwater (saturated zone)

Plan View



Cross Section View



File Path: G:\Projects\210116 HESI\Graphics\CADGIS\100210116_100-04_schematic.dwg



Leaching of Surface Spill to Groundwater

FIGURE 5.1

Date: 11/18/2011

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 attenuation factors ("DAFs") for both the unsaturated zone and the saturated zone.

Determining these DAFs – and therefore the ultimate concentration of chemicals leaching from a surface spill into an underlying aquifer, and subsequently contaminating a downgradient well – depends on a variety of parameters, including:

- Net infiltration rate;
- Depth to groundwater;
- Groundwater flow rates;
- Drinking water well depth; and
- Distance to well.

In our analysis of surface spill impacts to groundwater (soil-to-groundwater pathway), we have used values for these parameters and model-related assumptions that we consider reasonable, if not conservative (more likely to overestimate rather than underestimate chemical migration and exposure concentrations). Examples of our model assumptions that are conservative include:

- We considered two relatively shallow depths to the top of the water table when calculating the leaching DAFs, ranging from 5 to 10 meters (~15 and ~30 ft). Because dilution increases with increasing depth to the water table, evaluating shallow water tables in our analysis yields smaller DAFs than would be the case for aquifers beginning at greater depths. The shallow water table depths we evaluated are considered quite conservative. Drinking water wells more often than not draw water from deeper aquifers (on the order of several hundred feet beneath the surface) in order to avoid contaminants from septic leach-fields and agricultural chemical applications.
- We have assumed no chemical adsorption in the unsaturated zone in deriving the soil DAF values,¹³ and have modeled no degradation of HF constituents in the soil. This is a very conservative assumption, as many chemicals adsorb to soil and many chemicals biodegrade, both of which reduce their mobility and transport in the soil and groundwater.
- Similarly, no chemical adsorption or decay is included in the groundwater model used by US EPA to derive DAF values for the saturated zone (which we used here).

¹³ In our earlier 2009 study, we included chemical adsorption as a dilution/attenuation mechanism. In our current analysis we have dropped that component of the earlier analysis with the exception of three chemicals that are discussed in Appendix D. We chose to eliminate the consideration of chemical adsorption to simplify the analysis. Not only does this simplify the analysis, but it also is a more conservative (health protective) analysis which tends to overstate the potential for chemical migration (leading to lower DAF values).

- We used a range of relatively low chemical dispersion parameter values for the unsaturated zone model that yield only a moderate degree of chemical dilution in the unsaturated zone.¹⁴
- For the saturated zone, we have adopted "low-end" dilution factors (DAF_{gw}) developed by the US EPA for a wide range of hydrologic conditions (*i.e.*, 90 percent of the DAF values modeled by US EPA exceeded the DAF we used). The use of low-end dilution factors yields "high-end" estimates of constituent concentrations in groundwater.

The derivation of the respective unsaturated zone (DAF_L) and saturated zone (DAF_{gw}) dilution-attenuation factors is described below.

Leachate Migration to Groundwater (Unsaturated Zone)

Assuming that no spill mitigation measures are implemented, both surface spill scenarios (diffuse and sudden spills) would lead to a zone of surface soil contamination in the vicinity of the spill. The chemicals initially retained in the surface soil zone could subsequently leach to groundwater. The diffuse and sudden spill scenarios considered in this evaluation only differ in the amount of the spill, and the area over which the spill occurs.

The zone of surface soil contamination resulting from a surface spill (the "source area") can be characterized by its spatial dimensions – length, width, and initial depth of contamination. This is shown conceptually in plan view in Figure 5.1. The source areas for the spill scenarios evaluated in this report are summarized below. For the sudden spill, we have assumed that the spill would initially spread out over an area with an equivalent spill thickness of 1 centimeter (a little less than a half an inch). For the diffuse spill, we have assumed that it could impact an area as much as 2 acres, which is a significant percentage of the surface area of the well pad.

¹⁴ Dispersion in the advection dispersion equation is modeled with the dispersivity parameter " α " that models the spreading or dispersing of a chemical as it migrates through porous media.

<i>Spill Scenario</i>	<i>Spill Volume</i>	<i>Impacted Area</i>	<i>Spill Thickness</i>	<i>Initial Soil Depth Impacted</i> ^[a]
<i>Sudden Spill</i>	1,000 gal	0.1 acre	1	3 cm
	10,000 gal	1 acre	1	3 cm
<i>Diffuse Spill</i>	3,500 gal	2 acres	0.2	1 cm

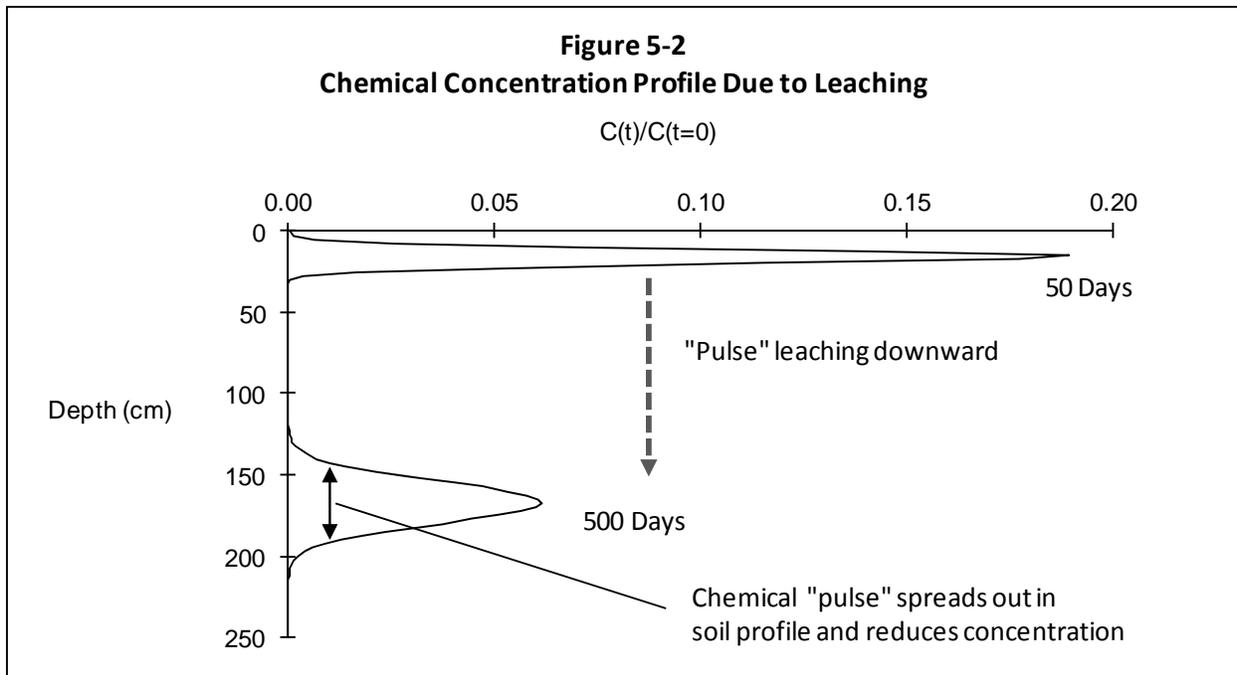
^[a] Initial contamination depth is x_0 in Appendix A.

Chemical migration in soil *via* leaching (*e.g.*, leaching in the unsaturated zone) is commonly modeled using a so-called "advection-dispersion equation" (ADE). The ADE is a mathematical equation describing the movement of chemicals in soil as a function of the flow of water, chemical adsorption to soil,¹⁵ and chemical dispersion. We present a mathematical description of the one dimensional ADE used in our analysis to derive the dilution factor for the unsaturated zone (DAF_L) in Appendix A.

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 the chemicals move downward, chemical dispersion occurs within the soil profile due to variability in the rate of water movement through pores of different sizes 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 5.2. This figure shows the chemical 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 concentration at time "t," or C(t), relative to the initial concentration of the chemical immediately following a spill, C(t=0), before any leaching occurs.¹⁶

¹⁵ As discussed above and in Appendix A, we have effectively eliminated adsorption from the equation for most chemicals, which would result in an underestimation of the amount of attenuation that would occur.

¹⁶ Immediately following a spill, before any leaching has occurred, the ratio C(t)/C(t=0) equals 1 (no dilution).



The unsaturated zone leaching dilution factor (DAF_L), can be expressed by rearranging Equation (5-1) presented earlier:

$$DAF_L = \frac{C_{HF}}{C_{WT}} \quad (5-4)$$

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 $C(t)$ in the ADE). The derivation of the leaching dilution factor is presented in Appendix A. The range of DAF values calculated, which vary as a function of dispersion within the soil zone and the depth to the water table (which, as discussed above, is assumed to be 5 to 10 meters), are summarized below.

Table 5.1 Summary of Unsaturated Zone DAF Values

Initial Chemical Spill Thickness In Soil	Range of DAF _L Values	DAF _L Used
1 cm (Diffuse spill)	105 to 195	150
3 cm (Sudden spills)	40 to 70	50

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 water table (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 (5-2) presented earlier:

$$C_{gw} = \frac{C_{WT}}{DAF_{gw}}$$

where:

- C_{gw} = Chemical concentration in groundwater mixing zone (µg/L)
- C_{WT} = Chemical concentration in leachate at the water table entering groundwater (µg/L)
- DAF_{gw} = Groundwater dilution attenuation factor (unitless)

We used the groundwater (saturated zone) DAF values derived by US EPA (1996) in their Soil Screening Guidance.¹⁷ We chose this approach because the US EPA conducted an extensive groundwater modeling effort, developing probability distributions of groundwater (saturated zone) DAF 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 DAF values:

¹⁷ In Gradient's 2009 study, the groundwater DAF was derived using the "EPA Groundwater Forum" mixing model also presented in the US EPA (1996) Soil Screening Guidance. The groundwater DAFs derived using that method are comparable to the probabilistic values US EPA derived which are used in this current analysis (see Appendix D for comparison to Gradient's 2009 study DAF values).

- The Agency assumed an infinite chemical source, with no chemical adsorption to soil, and no chemical degradation. In fact, many of the HF and flowback constituents adsorb strongly and/or biodegrade. Excluding these processes significantly underestimates dilution and attenuation of these chemicals.
- Drinking water wells were assumed to be on 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).
- 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, for a chemical plume to impact a more typical scenario involving a drinking water well drawing water from a greater depth requires the plume to migrate deeper within the aquifer, resulting in greater chemical dilution.¹⁸

The US EPA derived probability distributions of DAF values, varying as a function of source area and net precipitation/infiltration rates, unsaturated zone parameters (*e.g.*, depth to water table, hydraulic conductivity), and saturated zone parameters (*e.g.*, groundwater flow rate, thickness of aquifer). The DAF values derived by US EPA are summarized in Table 5.2 for chemical source areas ranging from 0.1 acres up to approximately 2 acres. As an example, the 90th percentile DAF value of 60 for a 1 acre source area indicates that the groundwater dilution will be 60 *or higher* in at least 90 percent of cases.¹⁹ We chose the US EPA 90th percentile DAF values for our groundwater (saturated zone) dilution factor (DAF_{gw}), because it represents a "high-end," conservative dilution factor without being overly conservative. Percentiles further out on the upper "tail" of the probability distribution are increasingly less likely, and represent extreme or rare events, that are not considered as meaningful for this analysis.

¹⁸ Because the US EPA adopted an infinite source and no chemical adsorption to soil, the groundwater DAFs the Agency derived implicitly exclude any dispersion/dilution within the unsaturated zone. Thus, the DAF values represent solely the effects of mixing and dilution within the saturated aquifer, and do not account for dilution within the unsaturated (soil) zone. 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 amount of attenuation that would actually occur in the unsaturated zone because it ignores adsorption and degradation.

¹⁹ Note that while US EPA reports the DAF values as "high end" percentiles of the probability distribution (*e.g.*, 85th, 90th and 95th percentiles), these statistics actually represent conservative DAF values whereby the majority of values modeled by US EPA exceed these values. This is self evident from the fact that the 85th percentile DAF values are larger than the 90th and 95th percentile values. Thus, the reported "90th percentile" values in fact represent the lowest 10th percentile DAF value within the cumulative probability distribution function derived by US EPA—90 percent of the DAFs are larger than the reported 90th percentile.

Table 5.2 Summary of Saturated Zone DAF Values

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

Source: US EPA (1996) Table 5.

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:

$$\text{Overall DAF} = \text{DAF}_L \times \text{DAF}_{\text{gw}}$$

The resulting dilution factors for the spill scenarios analyzed are summarized in Table 5.3. As noted earlier, a comparison of these dilution factors with those derived in Gradient's 2009 study is presented in Appendix D.

Table 5.3 Dilution Factors For Groundwater Pathway

Spill Volume		Saturated Zone DAF (US EPA 90 th Percentile DAF)	Unsaturated Zone DAF (Gradient Derived)	Overall DAF
<i>Sudden Spills</i>				
1,000 gal	(0.1 acre)	2,740	50	137,000
10,000 gal	(1 acre)	60	50	3,000
<i>Diffuse Spill</i>				
3,500 gal	(2 acres)	33	150	5,000

Groundwater HF Chemical Exposure Concentrations

Using the overall DAF values presented above, Tables 5.4 and 5.5 summarize the groundwater exposure concentrations for the sudden and diffuse HF fluid spill scenarios, respectively. Table 5.6 presents exposure concentrations based on these same spill scenarios assuming the spill consists of flowback water. These concentration estimates were utilized to quantify human health risks associated with the ingestion of drinking water, as discussed in Section 7.

5.1.3 Surface Water Exposure Pathway Scenario

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

If a surface spill occurs and HF fluid migrates to a nearby river/stream, it is necessary to estimate the concentration of the HF 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:

$$C_{sw} = C_{HF} \frac{Q_{HF}}{(Q_{HF} + Q_{sw})} \quad (5-5)$$

where:

C_{sw}	=	Chemical concentration in surface water ($\mu\text{g/L}$)
C_{HF}	=	Chemical concentration in HF fluid spilled ($\mu\text{g/L}$)
Q_{HF}	=	Discharge of HF fluid to surface water (m^3/day)
Q_{sw}	=	Flow of surface water in the mixing zone (m^3/day)

Table 5.4 Exposure Point Concentrations (EPC) -- Sudden HF Fluid Spill Scenario

Chemical	CAS No	Wellhead Concentration		Surface Water (1-yr DAF)		Surface Water (10-day DAF)		Groundwater	
		Min (ug/L)	Max (ug/L)	Min (ug/L)	Max (ug/L)	Min (ug/L)	Max (ug/L)	Min (ug/L)	Max (ug/L)
1,2,4 Trimethylbenzene	95-63-6	1,796	1,811	0.001	0.01	0.03	0.35	0.01	0.60
2-Bromo-2-nitro-1,3-propanediol	52-51-7	17,986	18,009	0.009	0.09	0.35	3.46	0.13	6.00
Acetic acid	64-19-7	40,307	4,303,895	0.021	2.27	0.78	82.77	0.29	31.42
Acetic anhydride	108-24-7	3,227,921	6,455,842	1.699	3.40	62.08	124.15	23.56	47.12
Alcohols, C12-16, ethoxylated	68551-12-2	7,944	1,045,385	0.042	0.55	1.53	20.10	1.15	7.95
Alcohols, C14-C15, ethoxylated	68951-67-7	133,446	133,446	0.070	0.07	2.57	2.57	0.97	0.97
Aldehyde	CBI	316,979	3,169,750	0.167	1.67	6.10	60.96	2.31	23.14
Alkyl (C14-C16) olefin sulfonate, sodium salt	68439-57-6	975,504	2,359,022	0.513	1.24	18.76	45.37	7.12	17.22
Amines, coco alkyl, ethoxylated	61791-14-8	98,809	616,560	0.052	0.32	1.90	11.86	0.72	4.50
Ammonium acetate	631-61-8	138,584	660,754	0.073	0.89	2.67	32.41	1.01	56.19
Ammonium chloride	12125-02-9	9,548	952,935	0.015	1.05	0.55	38.50	0.21	66.73
Ammonium persulfate	7727-54-0	80,264	153,676	0.422	0.81	15.44	29.55	26.75	51.23
Ammonium phosphate	7722-76-1	59,285	59,285	0.031	0.03	1.14	1.14	0.43	0.43
Attapulgite	12174-11-7	14,680	24,822	0.077	0.13	2.82	4.77	4.89	8.27
Bentonite, benzyl(hydrogenated tallow alkyl) dimethylammonium stearate complex	121888-68-4	40,987	74,557	0.028	0.39	1.02	14.34	0.39	24.85
Borate salt	CBI	324,146	548,110	1.706	2.88	62.34	105.41	108.05	182.70
C.I. Pigment Orange 5	3468-63-1	291	291	0.002	0.002	0.06	0.06	0.10	0.10
Calcium chloride	10043-52-4	6,853	24,491	0.005	0.13	0.19	4.71	0.07	8.16
Carbohydrate	CBI	27,045	27,045	0.014	0.01	0.52	0.52	0.20	0.20
Chloromethylnaphthalene quinoline quaternary amine	15619-48-4	5,929	1,590,803	0.003	0.84	0.11	30.59	0.04	11.61
Chlorous acid, sodium salt	7758-19-2	48,044	480,277	[a]	[a]	[a]	[a]	[a]	[a]
Citrus, extract	94266-47-4	136,812	136,812	0.720	0.72	26.31	26.31	45.60	45.60
Cobalt acetate	71-48-7	104,400	104,400	0.055	0.05	2.01	2.01	0.76	0.76
Crystalline silica, quartz	14808-60-7	310	36,258	0.001	0.19	0.02	6.97	0.01	12.09
Cured acrylic resin	CBI	32,622	32,622	0.017	0.02	0.63	0.63	0.24	0.24
Diethylene glycol	111-46-6	128,356	310,398	0.068	0.16	2.47	5.97	0.94	2.27
Diethylenetriamine	111-40-0	208,521	208,521	0.110	0.11	4.01	4.01	1.52	1.52
EDTA/Copper chelate	CBI	5,820	884,509	0.031	0.47	1.12	17.01	1.94	6.46
Ethanol	64-17-5	430,927	729,702	0.227	2.29	8.29	83.51	3.15	144.76
Ethoxylate fatty acid	CBI	63,777	112,693	0.034	0.59	1.23	21.67	0.47	37.56
Ethoxylate fatty acid	CBI	102,304	168,970	0.054	0.89	1.97	32.49	0.75	56.32
Ethoxylated branched C13 alcohol	78330-21-9	54,982	71,445	0.038	0.29	1.37	10.57	0.52	18.33
Ethoxylated fatty acid	CBI	99,125	168,970	0.052	0.89	1.91	32.49	0.72	56.32
Ethylene glycol monobutyl ether	111-76-2	385,067	931,193	0.203	0.49	7.41	17.91	2.81	6.80
Fatty acid ester	CBI	1,589	4,769	0.008	0.03	0.31	0.92	0.53	1.59
Fatty acid tall oil	CBI	132,404	988,077	0.070	0.52	2.55	19.00	0.97	7.21
Fatty acid tall oil amide	CBI	7,944	23,843	0.042	0.13	1.53	4.59	2.65	7.95
Fatty alcohol polyglycol ether surfactant	9043-30-5	20,981	21,265	0.011	0.11	0.40	4.04	0.15	7.00

Table 5.4 Exposure Point Concentrations (EPC) -- Sudden HF Fluid Spill Scenario

Chemical	CAS No	Wellhead Concentration		Surface Water (1-yr DAF)		Surface Water (10-day DAF)		Groundwater	
		Min (ug/L)	Max (ug/L)	Min (ug/L)	Max (ug/L)	Min (ug/L)	Max (ug/L)	Min (ug/L)	Max (ug/L)
Fatty acid ester ethoxylate	CBI	1,059	3,179	0.006	0.02	0.20	0.61	0.35	1.06
Formaldehyde	50-00-0	294	11,765	0.0002	0.01	0.01	0.45	0.00	0.78
Glycerine	56-81-5	30,567	30,567	0.016	0.02	0.59	0.59	0.22	0.22
Guar gum	9000-30-0	2,340,833	3,490,851	1.232	18.37	45.02	671.32	17.09	1163.62
Guar gum derivative	CBI	2,340,921	5,267,613	1.232	14.33	45.02	523.68	17.09	907.70
Heavy aromatic petroleum naphtha	64742-94-5	95,253	96,094	0.050	0.51	1.83	18.46	0.70	32.00
Hemicellulase enzyme	9012-54-8	3,005	3,005	0.002	0.00	0.06	0.06	0.02	0.02
Hydrochloric acid	7647-01-0	147,321	160,547,973	[a]	[a]	[a]	[a]	[a]	[a]
Hydrotreated light petroleum distillate	64742-47-8	79,436	238,433	0.418	1.25	15.28	45.85	26.48	79.48
Inorganic salt	CBI	29,973	107,111	0.023	0.56	0.83	20.60	0.31	35.70
Isopropanol	67-63-0	257,299	2,774,519	0.135	1.73	4.95	63.04	1.88	109.27
Magnesium chloride hexahydrate	7791-18-6	13,955	49,867	0.011	0.26	0.38	9.59	0.15	16.62
Methanol	67-56-1	57,960	3,063,037	0.158	1.61	5.78	58.90	2.19	22.36
Naphtha, hydrotreated heavy	64742-48-9	2,179,292	2,831,831	1.231	12.31	44.96	449.73	17.07	779.54
Naphthalene	91-20-3	10,683	10,778	0.006	0.06	0.21	2.07	0.08	3.59
Naphthenic acid ethoxylate	68410-62-8	104,540	2,572,951	0.055	1.35	2.01	49.48	0.76	18.78
Nonylphenol ethoxylated	127087-87-0	35,911	36,228	0.019	0.19	0.69	6.96	0.26	12.06
Olefin	CBI	890	890	0.0005	0.0005	0.02	0.02	0.01	0.01
Olefin	CBI	21,351	21,351	0.011	0.01	0.41	0.41	0.16	0.16
Olefin	CBI	13,345	13,345	0.007	0.01	0.26	0.26	0.10	0.10
Olefin	CBI	890	890	0.000	0.00	0.02	0.02	0.01	0.01
Organic acid salt	Mixture	128,857	128,857	0.068	0.07	2.48	2.48	0.94	0.94
Organic phosphonate	CBI	97,389	3,894,092	0.061	4.10	2.25	149.83	0.85	259.71
Oxylated phenolic resin	CBI	71,821	72,456	0.038	0.38	1.38	13.92	0.52	24.13
Oxylated phenolic resin	CBI	251,374	253,595	0.132	1.33	4.83	48.72	1.83	84.44
Polyacrylamide copolymer	CBI	147,752	443,486	0.778	2.33	28.41	85.29	49.25	147.83
Polyoxylated fatty amine salt	61791-26-2	423,891	1,185,692	0.223	0.62	8.15	22.80	3.09	8.65
Potassium carbonate	584-08-7	562,906	1,117,790	0.296	3.94	10.83	143.84	4.11	249.32
Potassium formate	590-29-4	258,454	437,030	1.360	2.30	49.70	84.04	86.15	145.68
Potassium hydroxide	1310-58-3	7,697	47,170	0.004	0.25	0.15	9.07	0.06	15.72
Potassium metaborate	13709-94-9	98,266	602,200	0.052	3.17	1.89	115.81	0.72	200.73
Propanol	71-23-8	38,802	38,802	0.020	0.02	0.75	0.75	0.28	0.28
Propargyl alcohol	107-19-7	53,378	53,378	0.028	0.03	1.03	1.03	0.39	0.39
Proprietary	CBI	18,792	18,792	0.099	0.10	3.61	3.61	6.26	6.26
Quaternary ammonium compound	CBI	118,653	118,653	0.624	0.62	22.82	22.82	39.55	39.55
Quaternary ammonium compounds, bis(hydrogenated tallow alkyl) dimethyl, salts with bentonite	68953-58-2	67,712	68,627	0.036	0.36	1.30	13.03	0.49	22.58
Quaternary ammonium salt	CBI	177,856	1,193,596	0.094	0.63	3.42	22.95	1.30	8.71

Table 5.4 Exposure Point Concentrations (EPC) -- Sudden HF Fluid Spill Scenario

Chemical	CAS No	Wellhead Concentration		Surface Water (1-yr DAF)		Surface Water (10-day DAF)		Groundwater	
		Min (ug/L)	Max (ug/L)	Min (ug/L)	Max (ug/L)	Min (ug/L)	Max (ug/L)	Min (ug/L)	Max (ug/L)
Reaction product of acetophenone, formaldehyde, thiourea and oleic acid in dimethyl formamide	68527-49-1	112,984	112,984	0.059	0.06	2.17	2.17	0.82	0.82
Silica gel	112926-00-8	3,003	3,602	0.016	0.02	0.58	0.69	1.00	1.20
Silica, amorphous -- fumed	7631-86-9	12,005	27,013	0.006	0.01	0.23	0.52	0.09	0.20
Sodium bicarbonate	144-55-8	48,019	108,054	0.025	0.06	0.92	2.08	0.35	0.79
Sodium carboxymethyl cellulose	9004-32-4	5,321	8,998	0.028	0.05	1.02	1.73	1.77	3.00
Sodium chloride	7647-14-5	3,095	1,279,579	0.016	6.06	0.60	221.46	1.03	383.87
Sodium glycolate	2836-32-0	92	155	0.0005	0.001	0.02	0.03	0.03	0.05
Sodium hydroxide	1310-73-2	6,003	573,737	0.003	3.02	0.12	110.33	0.04	191.25
Sodium hypochlorite	7681-52-9	28,526	37,653	0.020	0.20	0.72	7.24	0.27	12.55
Sodium iodide	7681-82-5	148,211	148,211	0.078	0.08	2.85	2.85	1.08	1.08
Sodium perborate tetrahydrate	10486-00-7	59,975	120,060	0.316	0.63	11.53	23.09	19.99	40.02
Sodium persulfate	7775-27-1	1,030	377,141	0.005	0.29	0.20	10.48	0.22	18.17
Sodium sulfate	7757-82-6	1	241,392	0.000003	0.13	0.00	4.64	0.00	1.76
Sodium sulfite	7757-83-7	30,174	30,174	0.016	0.02	0.58	0.58	0.22	0.22
Sodium thiosulfate	7772-98-7	3,620,876	3,620,876	1.906	1.91	69.63	69.63	26.43	26.43
Surfactant mixture	CBI	16,517	19,810	0.087	0.10	3.18	3.81	5.51	6.60
Surfactant mixture	CBI	9,009	10,805	0.047	0.06	1.73	2.08	3.00	3.60
Terpenoid	CBI	21,882	136,812	0.012	0.72	0.42	26.31	0.16	45.60
Terpenoid	CBI	40,398	41,764	0.021	0.02	0.78	0.80	0.29	0.30
Tributyl tetradecyl phosphonium chloride	81741-28-8	12,189	24,367	0.008	0.13	0.28	4.69	0.11	8.12
Triethanolamine zirconate	101033-44-7	176,136	176,136	0.093	0.09	3.39	3.39	1.29	1.29
Ulexite (B5H3O9.Ca.8H2O.Na)	1319-33-1	533,203	533,203	2.806	2.81	102.54	102.54	177.73	177.73
Zirconium, acetate lactate oxo ammonium complexes	68909-34-2	856,536	856,536	0.451	0.45	16.47	16.47	6.25	6.25

Notes:

Range of EPCs are calculated from the range of constituent concentrations in typical HESI HF systems over the range of DAF values based on spill volumes.

CBI - Confidential Business Information.

[a] Hydrochloric acid and chlorus acid are expected to be readily neutralized in the environment

Table 5.5 Exposure Point Concentrations (EPC) -- Diffuse HF Fluid Spill Scenario

Chemical	CAS No	Vol. Weighted Concentration*		Surface Water (1-yr DAF)		Groundwater	
		Min (ug/L)	Max (ug/L)	Min (ug/L)	Max (ug/L)	Min (ug/L)	Max (ug/L)
1,2,4 Trimethylbenzene	95-63-6	1	1,809	0.000002	0.003	0.0002	0.36
2-Bromo-2-nitro-1,3-propanediol	52-51-7	4,914	18,009	0.009	0.03	0.98	3.60
Acetic acid	64-19-7	1,758	1,232,727	0.003	2.28	0.35	246.55
Acetic anhydride	108-24-7	4,413	1,786,808	0.008	3.31	0.88	357.36
Alcohols, C12-16, ethoxylated	68551-12-2	412	759,924	0.001	1.41	0.08	151.98
Alcohols, C14-C15, ethoxylated	68951-67-7	618	73,869	0.001	0.14	0.12	14.77
Aldehyde	CBI	217	2,304,194	0.0004	4.27	0.04	460.84
Alkyl (C14-C16) olefin sulfonate, sodium salt	68439-57-6	570,603	2,089,604	1.057	3.87	114.12	417.92
Amines, coco alkyl, ethoxylated	61791-14-8	68	448,197	0.000	0.83	0.01	89.64
Ammonium acetate	631-61-8	6,044	532,083	0.011	0.99	1.21	106.42
Ammonium chloride	12125-02-9	1,219	586,392	0.002	1.09	0.24	117.28
Ammonium persulfate	7727-54-0	77,317	109,991	0.143	0.20	15.46	22.00
Ammonium phosphate	7722-76-1	586	43,096	0.001	0.08	0.12	8.62
Attapulgate	12174-11-7	12,064	24,822	0.022	0.05	2.41	4.96
Bentonite, benzyl(hydrogenated tallow alkyl) dimethylammonium stearate complex	121888-68-4	11,711	62,163	0.022	0.12	2.34	12.43
Borate salt	CBI	266,392	548,110	0.493	1.02	53.28	109.62
C.I. Pigment Orange 5	3468-63-1	281	291	0.001	0.001	0.06	0.06
Calcium chloride	10043-52-4	6,625	24,491	0.012	0.05	1.32	4.90
Carbohydrate	CBI	969	985	0.002	0.002	0.19	0.20
Chloromethylnaphthalene quinoline quaternary amine	15619-48-4	4	1,156,406	0.000	2.14	0.001	231.28
Chlorous acid, sodium salt	7758-19-2	34,764	346,755	[a]	[a]	[a]	[a]
Citrus, extract	94266-47-4	88,108	97,208	0.163	0.18	17.62	19.44
Cobalt acetate	71-48-7	22,957	84,069	0.043	0.16	4.59	16.81
Crystalline silica, quartz	14808-60-7	35	26,651	0.000	0.05	0.01	5.33
Cured acrylic resin	CBI	7,173	26,269	0.013	0.05	1.43	5.25
Diethylene glycol	111-46-6	75,079	274,948	0.139	0.51	15.02	54.99
Diethylenetriamine	111-40-0	1,017	1,072	0.002	0.002	0.20	0.21
EDTA/Copper chelate	CBI	4,315	5,820	0.008	0.01	0.86	1.16
Ethanol	64-17-5	297	710,490	0.001	1.32	0.06	142.10
Ethoxylate fatty acid	CBI	17,530	80,071	0.032	0.15	3.51	16.01
Ethoxylate fatty acid	CBI	28,120	120,058	0.052	0.22	5.62	24.01
Ethoxylated branched C13 alcohol	78330-21-9	15,710	57,532	0.029	0.11	3.14	11.51
Ethoxylated fatty acid	CBI	27,246	120,058	0.050	0.22	5.45	24.01
Ethylene glycol monobutyl ether	111-76-2	225,238	824,844	0.417	1.53	45.05	164.97
Fatty acid ester	CBI	203	3,388	0.0004	0.01	0.04	0.68
Fatty acid tall oil	CBI	91	718,265	0.0002	1.33	0.02	143.65
Fatty acid tall oil amide	CBI	1,016	16,941	0.002	0.03	0.20	3.39
Fatty alcohol polyglycol ether surfactant	9043-30-5	762	20,878	0.001	0.04	0.15	4.18
Fatty acid ester ethoxylate	CBI	135	2,259	0.0003	0.004	0.03	0.45

Table 5.5 Exposure Point Concentrations (EPC) -- Diffuse HF Fluid Spill Scenario

Chemical	CAS No	Vol. Weighted Concentration*		Surface Water (1-yr DAF)		Groundwater	
		Min (ug/L)	Max (ug/L)	Min (ug/L)	Max (ug/L)	Min (ug/L)	Max (ug/L)
Formaldehyde	50-00-0	291	2,722	0.001	0.01	0.06	0.54
Glycerine	56-81-5	14,884	23,494	0.028	0.04	2.98	4.70
Guar gum	9000-30-0	85,034	2,910,562	0.157	5.39	17.01	582.11
Guar gum derivative	CBI	778,086	4,590,385	1.441	8.50	155.62	918.08
HCl in 22 Baume Acid	7647-01-0	757	116,707,515	[a]	[a]	[a]	[a]
Heavy aromatic petroleum naphtha	64742-94-5	66	95,945	0.0001	0.18	0.01	19.19
Hemicellulase enzyme	9012-54-8	108	109	0.0002	0.0002	0.02	0.02
Hydrotreated light petroleum distillate	64742-47-8	10,160	169,413	0.019	0.31	2.03	33.88
Inorganic salt	CBI	28,974	107,110	0.054	0.20	5.79	21.42
Isopropanol	67-63-0	176	2,016,888	0.0003	3.73	0.04	403.38
Magnesium chloride hexahydrate	7791-18-6	13,489	49,867	0.025	0.09	2.70	9.97
Methanol	67-56-1	205	2,226,621	0.0004	4.12	0.04	445.32
Naphtha, hydrotreated heavy	64742-48-9	84,930	2,326,482	0.157	4.31	16.99	465.30
Naphthalene	91-20-3	7	10,761	0.00001	0.02	0.001	2.15
Naphthenic acid ethoxylate	68410-62-8	71	1,870,362	0.0001	3.46	0.01	374.07
Nonylphenol ethoxylated	127087-87-0	25	36,172	0.00005	0.07	0.00	7.23
Olefin	CBI	4	492	0.00001	0.001	0.001	0.10
Olefin	CBI	99	11,819	0.0002	0.02	0.02	2.36
Olefin	CBI	62	7,387	0.0001	0.01	0.01	1.48
Olefin	CBI	4	492	0.00001	0.00	0.001	0.10
Organic acid salt	Mixture	28,335	103,764	0.052	0.19	5.67	20.75
Organic phosphonate	CBI	96,426	901,081	0.179	1.67	19.29	180.22
Oxylated phenolic resin	CBI	49	72,343	0.0001	0.13	0.01	14.47
Oxylated phenolic resin	CBI	173	253,201	0.0003	0.47	0.03	50.64
Polyacrylamide copolymer	CBI	18,898	315,108	0.035	0.58	3.78	63.02
Polyoxylated fatty amine salt	61791-26-2	290	861,918	0.001	1.60	0.06	172.38
Potassium carbonate	584-08-7	245,793	900,118	0.455	1.67	49.16	180.02
Potassium formate	590-29-4	212,404	437,030	0.393	0.81	42.48	87.41
Potassium hydroxide	1310-58-3	3,748	28,064	0.007	0.05	0.75	5.61
Potassium metaborate	13709-94-9	47,850	358,286	0.089	0.66	9.57	71.66
Propanol	71-23-8	18,894	29,824	0.035	0.06	3.78	5.96
Propargyl alcohol	107-19-7	247	29,548	0.0005	0.05	0.05	5.91
Proprietary	CBI	13,598	13,913	0.025	0.03	2.72	2.78
Quaternary ammonium compound	CBI	76,414	84,306	0.142	0.16	15.28	16.86
Quaternary ammonium compounds, bis(hydrogenated tallow alkyl) dimethyl, salts with bentonite	68953-58-2	2,460	67,379	0.005	0.12	0.49	13.48
Quaternary ammonium salt	CBI	122	867,664	0.0002	1.61	0.02	173.53
Reaction product of acetophenone, formaldehyde, thiourea and oleic acid in dimethyl formamide	68527-49-1	523	62,542	0.001	0.12	0.10	12.51

Table 5.5 Exposure Point Concentrations (EPC) -- Diffuse HF Fluid Spill Scenario

Chemical	CAS No	Vol. Weighted Concentration*		Surface Water (1-yr DAF)		Groundwater	
		Min (ug/L)	Max (ug/L)	Min (ug/L)	Max (ug/L)	Min (ug/L)	Max (ug/L)
Silica gel	112926-00-8	2,606	3,003	0.005	0.01	0.52	0.60
Silica, amorphous -- fumed	7631-86-9	14,914	23,540	0.028	0.04	2.98	4.71
Sodium bicarbonate	144-55-8	59,655	94,162	0.110	0.17	11.93	18.83
Sodium carboxymethyl cellulose	9004-32-4	4,373	8,998	0.008	0.02	0.87	1.80
Sodium chloride	7647-14-5	5,414	1,201,010	0.010	2.22	1.08	240.20
Sodium glycolate	2836-32-0	75	155	0.0001	0.0003	0.02	0.03
Sodium hydroxide	1310-73-2	5,455	482,785	0.010	0.89	1.09	96.56
Sodium hypochlorite	7681-52-9	27,478	37,614	0.051	0.07	5.50	7.52
Sodium iodide	7681-82-5	1,465	107,740	0.003	0.20	0.29	21.55
Sodium perborate tetrahydrate	10486-00-7	7,671	120,060	0.014	0.22	1.53	24.01
Sodium persulfate	7775-27-1	746	54,517	0.001	0.10	0.15	10.90
Sodium sulfate	7757-82-6	0.4	185,534	0.000001	0.34	0.00	37.11
Sodium sulfite	7757-83-7	14,693	23,192	0.027	0.04	2.94	4.64
Sodium thiosulfate	7772-98-7	1,763,151	2,783,016	3.265	5.15	352.63	556.60
Surfactant mixture	CBI	14,334	16,517	0.027	0.03	2.87	3.30
Surfactant mixture	CBI	7,818	9,009	0.014	0.02	1.56	1.80
Terpenoid	CBI	6,015	97,208	0.011	0.18	1.20	19.44
Terpenoid	CBI	11,104	40,664	0.021	0.08	2.22	8.13
Tributyl tetradecyl phosphonium chloride	81741-28-8	12,069	19,509	0.022	0.04	2.41	3.90
Triethanolamine zirconate	101033-44-7	85,768	135,378	0.159	0.25	17.15	27.08
Ulexite (B5H3O9.Ca.8H2O.Na)	1319-33-1	385,811	394,764	0.714	0.73	77.16	78.95
Zirconium, acetate lactate oxo ammonium complexes	68909-34-2	188,346	689,739	0.349	1.28	37.67	137.95

Notes:

* Volume weighted HF concentration is the range of concentrations for the overall frac job (weighted by concentration and volume of individual stages).

Surface water 10-day DAF is not applicable to the diffuse spill scenario which is for small hypothetical releases throughout the year.

Range of EPCs are calculated from the range of constituent concentrations in typical HESI HF systems over the range of DAF values which vary based on spill volumes.

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[a] Hydrochloric acid and chlorus acid are expected to be readily neutralized in the environment

Table 5.6 Exposure Point Concentrations (EPCs) -- Flowback Spill Scenarios

CAS No.	Parameter ^[a]		Median Flowback Concentration (ug/L)	EPC (ug/L)	
				Surface Water	Ground Water
			Lowest DAF^[b]	5,200	3000
7439-90-5	Aluminum	Total	70	0.01	0.02
7664-41-7	Aqueous ammonia	Total	44,800	8.6	14.9
7440-38-2	Arsenic	Total	90	0.0	0.0
7440-39-3	Barium	Dissolved	212,000	40.8	70.7
7440-39-3	Barium	Total	1,450,000	278.8	483.3
7440-42-8	Boron	Total	2,060	0.4	0.7
24959-67-9	Bromide	Total	607,000	116.7	202.3
7440-43-9	Cadmium	Total	25	0.00	0.01
7440-70-2	Calcium	Total	4,241,000	815.6	1413.7
7440-47-3	Chromium	Dissolved	539	0.1	0.2
7440-47-3	Chromium	Total	82	0.02	0.03
7440-48-4	Cobalt	Total	398	0.1	0.1
7440-50-8	Copper	Total	25	0.0	0.0
7439-89-6	Iron	Dissolved	63,250	12.2	21.1
7439-89-6	Iron	Total	29,200	5.6	9.7
7439-92-1	Lead	Total	35	0.01	0.01
7439-93-2	Lithium	Dissolved	61,350	11.8	20.5
7439-93-2	Lithium	Total	90,400	17.4	30.1
7439-95-4	Magnesium	Total	177,000	34.0	59.0
7439-96-5	Manganese	Dissolved	2,975	0.6	1.0
7439-96-5	Manganese	Total	1,890	0.4	0.6
7439-98-7	Molybdenum	Total	440	0.1	0.1
7440-02-0	Nickel	Total	30	0.01	0.01
64743-03-9	Phenols	Total	191	0.0	0.1
7440-09-7	Potassium	Total	125,000	24.0	41.7
7440-23-5	Sodium	Total	23,500,000	4519.2	7833.3
7440-24-6	Strontium	Dissolved	629,000	121.0	209.7
7440-24-6	Strontium	Total	1,115,000	214.4	371.7
14808-79-8	Sulfate	Total	1,000	0.2	0.3
7440-66-6	Zinc	Total	36	0.01	0.01
71-43-2	Benzene		479.5	0.1	0.2
100-41-4	Ethyl Benzene		53.6	0.01	0.02
108-88-3	Toluene		833	0.2	0.3
1330-20-7	xylenes		444	0.1	0.1
NORM ^[c]			Max (pCi/L)	pCi/L	pCi/L
	Ra-228		18.4	0.004	0.006
	Ra-226		33	0.006	0.011
	Cs-137		10.5	0.002	0.004

Notes:

- [a] Chemicals measured in Marcellus flowback samples reported in rdSGEIS detected in more than 3 samples.
- [b] The scenario with the minimum DAF was chosen to show the upper-bound EPCs.
- [c] Naturally occurring radioactive material. No constituents detected in over 3 samples. We have included at max detected concentration.

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

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

Where DAF_{sw} is the surface water dilution attenuation factor:

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

Thus, the concentration of HF constituents in surface water (C_{sw}) resulting from a spill can be calculated using a DAF 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 very 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, in fact, unrealistic and significantly overstates the amount of spilled fluid that would reach a surface water body.

As discussed in Section 5.1.1, our analysis is based on upper-bound spill volumes of 1,000 gallons and 10,000 gallons for sudden spills, and 3,500 gallons for a diffuse spill. Each of these spill volumes represent the variable Q_{HF} in Equation (5-5). 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.

Representative Surface Water Flow

Given the wide range of stream sizes overlying the Marcellus Shale, as well as the inherent temporal variability of stream flow, the exact flow conditions that will be present in the event of an HF fluid spill are unpredictable. However, with the wealth of available long-term stream gauge monitoring data throughout the region overlying the Marcellus Shale, we have developed a distribution of possible stream flows that might receive an HF fluid spill.

As detailed in Appendix B, USGS maintains an extensive network of stream monitoring stations in this region of New York (Figure B.1 in Appendix B shows the spatial coverage of these gauging stations). We evaluated the available data for 147 USGS gauging stations, representing stations with sufficient data to reliably estimate stream discharge (*i.e.*, flow rate) during representative flow conditions (a robust data

set). These 147 stations have monitoring periods ranging from two to 104 complete years (*i.e.*, years with at least 365 daily mean discharge values), with a typical monitoring record containing about 37 complete years of data. The number of complete years of data is reported for each station in Appendix B, Table B.1.2. Annual high, average, and low flows were calculated for each year of record for a given stream gauge and then used to analyze the distribution of these stream flow classes across all gauges. Having more years of data always improves the reliability of such analyses, however, analyzing the collection of data from numerous (147) stream gauges also lends a high degree of reliability to our analysis as a whole. A characterization of the range of flows (high to low) is given below.

High Flows	<p>Maximum mean daily discharge is the maximum daily discharge value measured for a given stream during its entire period of record, and represents an infrequent high flow condition.</p> <p>Average Annual Maximum Mean Daily Discharge is the average of all of the yearly maximum mean daily flows for all the years of record for a given gauging station. This provides an indication of high daily flows that occur on average in any particular year.</p>
Average Flows	<p>Average annual mean daily discharge is the average of the annual mean daily discharge values for all complete years for a given station, and represents the typical flow for that stream/river.</p>
Low Flows	<p>Lowest annual mean daily discharge is the minimum daily mean flow measured in an entire year of daily flow measurements for a given stream, and represents a typical low daily flow condition for that stream. Note that the Lowest Annual Mean Daily Discharge is essentially the "mirror image" of the Average Annual Maximum Mean Daily Discharge, where one is the subset of "low flows" and the other "high flows."</p>

Detailed statistics for each of the 147 USGS gauging stations for each stream flow parameter described above are provided in Table B.1.1, with summaries of the overall data set provided in Table 5.7. The 90th percentile of the data set represents a relatively large stream or river; the 50th percentile represents a median sized stream or river; and the 10th percentile represents a relatively small stream for the Marcellus Shale region. The flow variation across these percentiles illustrates the variability in stream sizes throughout the region.

**Table 5.7 USGS Surface Water Flow Statistics
Overlying the Marcellus Shale in New York^[a]**

Daily Flow Value	Million Gallons Per Day (MGD) ¹
<i>Maximum Mean Daily Discharge</i>	
90 th Percentile	25,363
50 th Percentile	2,476
10 th Percentile	257
<i>Average Annual Maximum Mean Daily Discharge</i>	
90 th Percentile	9,822
50 th Percentile	1,353
10 th Percentile	129
<i>Average Annual Mean Daily Discharge</i>	
90 th Percentile	852
50 th Percentile	82
10 th Percentile	12
<i>Lowest Annual Mean Daily Discharge</i>	
90 th Percentile	431
50 th Percentile	53
10 th Percentile	5.2

[a] Analysis of USGS data for 147 gauging stations is summarized in Appendix B.

As a conservative (health protective) assumption, we based our analysis on the Lowest Annual Mean Daily Discharge (LAMDD) values and within this data set we selected the 10th percentile value of 5.2 MGD to estimate surface water dilution factors for the surface spill scenarios. This is a conservative approach because the low flow values represent "worst case" conditions, and among these low flow values the vast majority (90%) of low flow values exceed this value.

The surface water dilution estimation also requires specifying the period of time in which the spilled fluid mixes with the stream flow (the low flow value of 5.2 MGD) . For diffuse HF fluid spill scenarios, we have assumed that during the course of the year in which this type of spill occurs, 100% of the constituents migrate to a stream or river *via* runoff and erosion (ignoring any added dilution contributed by rainfall). For this scenario, the HF spill is mixed into a surface runoff flow representing the annual stream flow over the course of one year. For the sudden spill scenario, we calculated a range of surface

water DAF values. One DAF value assumes that the entire contents of the spill are washed off the pad during the course of the year. For the second DAF value calculated, we evaluate a scenario where 100% of the spill constituents are washed into a stream over a shorter time period of 10 days. The resulting surface water DAF values for the surface spill scenarios are summarized in Table 5.8.

Table 5.8 Summary of Surface Water DAFs

Surface Water Dilution Factors	Sudden Spills		Diffuse Spills
	1,000 gal	10,000 gal	3,500 gal
DAF – annual dilution	1,900,000	190,000	540,000
DAF – 10 day dilution	52,000	5,200	N/A

DAF values using 10th Percentile Low Annual Mean Daily Discharge (5.2 MGD). N/A = not applicable for this scenario.

Using these DAFs, Tables 5.4 and 5.5 present the modeled concentrations of HF fluid constituents for the diffuse and sudden spill scenarios, respectively. Table 5.6 presents modeled concentrations of flowback constituents for both of these spill scenarios. These concentration estimates were utilized to quantify human health risks *via* drinking water, as discussed in Section 7.

5.2 Subsurface Casing Failure Evaluation

This section examines the likelihood of HF constituents entering a potable aquifer as a result of a rupture or leakage from the gas well's casing. As discussed in Section 2, gas wells are carefully designed, with a number of key design and monitoring elements to protect drinking water aquifers and to fully isolate the natural gas producing zone of the well. 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 HF elements, such as gas well design, fracturing pressure required, and duration of fracturing, are determined by highly specialized professionals using site setting information and sophisticated computer models.
- Gas wells are constructed with up to four protective casings, carefully designed to ensure that the gas well is only in communication with the natural gas bearing zone (*i.e.*, the Marcellus Shale in New York) and to isolate the well from other hydrogeologic units that

overlie the gas producing zone – referred to as "zonal isolation" (Figure 2.1). Each of these casings is secured by placing a cement seal, thereby completely vertically isolating 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).
- Prior to initiation of HF, the well is again pressure tested to ensure that the well can withstand the fracking pressure 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 a 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 is extremely low. As noted in the revised dSGEIS (p. 6-41), based on an API study, NYSDEC 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 gas wells are subjected to positive pressures for an extremely short duration (one to two days of HF) 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" (revised dSGEIS, p. 6-41). Given the extremely low probability of casing leakage affecting potable aquifers, exposures and risks for this scenario were not quantified in the risk evaluation.

5.3 Marcellus Shale Migration Pathway

As described earlier, it is anticipated that on average approximately 20% of the HF fluids will be recovered after fracturing as "flowback" fluids. Consequently, approximately 80% of the HF fluids will remain in the Marcellus Shale formation. While the majority of the fluid is water, HF constituents will also remain in the formation. The possibility that residual HF constituents in the fractured gas-containing formation will migrate upward and potentially contaminate overlying potable aquifers depends on the

manner in which fluids are sequestered in the target formation, the ability of the overlying formations to transmit water, and the tendency for water (and chemicals) to migrate upward from the target formation. We examine these conditions in this section.

We examine the potential for upward HF constituent migration from the Marcellus Shale formation into an overlying potable aquifer for two phases of the HF process:

1. The "Fracturing Phase" when high fracturing pressures are applied, but for a short duration; and
2. The well operation phase when pumping and long-term gas production occurs ("Production Phase").

For both the fracturing and production phases, we evaluate the plausibility that HF constituents could migrate from the Marcellus Shale formation to overlying potable aquifers either through pore spaces (primary porosity) or fractures (secondary porosity) within the bedrock. It is critical, however, to understand the baseline conditions (*i.e.*, pre-HF) in the area of the proposed natural gas exploration to place the effect of the HF process in proper context. Therefore, we first discuss the physical setting of the Marcellus Shale formation in New York and the state of the *in-situ* fluids (methane and water) under ambient conditions prior to fracturing activities.

5.3.1 Baseline Conditions

Geologic studies show that the Marcellus Shale deposits have been hydraulically isolated from overlying formations for long periods, on the order of hundreds of millions of years (Laughrey *et al.*, 2004; Harper, 2008; USGS, 2009). In the southern portion of New York where HF stimulations would occur, the Marcellus Shale formation is present at depths of 4,000-8,500 ft (Figure 3.1). At these great depths, the Marcellus Shale lies beneath numerous layers of low permeability rocks, including shale, siltstone, and limestone (Figure 3.4).²⁰ In contrast, typical potable aquifers are less than 850 ft deep (revised dSGEIS, p. 2-23). Thus, the top of the Marcellus Shale formation and the nearest potable aquifer are often separated by several thousand feet of effectively impermeable bedrock.

²⁰ Figure 2.4 shows the relative position of the Marcellus Shale to other rock layers in New York. However, the Marcellus Shale is significantly deeper (4,000 to 8,500 feet bgs) in the areas targeted for natural gas production than what is shown in this drawing.

Because many of these intervening layers are impermeable, they have blocked fluid migration (Lash, 2006) and trapped pressurized natural gas and saline water within the Marcellus Shale for hundreds of millions of years (Laughrey *et al.*, 2004; Harper, 2008; USGS, 2009). These inherent characteristics of the Marcellus Shale and overlying formations have effectively isolated it from potable aquifers, as is clearly demonstrated by the following observations:

- High total dissolved solids/salts (on the order of 100,000 ppm) are present in the Marcellus Shale – an artifact of ancient seawater trapped by overlying impermeable layers (Russell, 1972). Sea salts are some of the most mobile solutes and would be expected to migrate faster than any other constituent. However, the presence of saline water in the Marcellus Shale clearly indicates that the formation is hydrologically isolated and that fluids are not migrating upward to potable aquifers.
- Hydraulic isolation has resulted in methane being trapped in the Marcellus Shale under high pressure for hundreds of millions of years – another clear indication of the effectiveness of the hydraulic isolation.
- The intrinsic permeability of shales ranges from 0.1 to 0.00001 millidarcy (md) (revised dSGEIS, p. 4-3). This range of permeability values corresponds to saturated hydraulic conductivities (for water) of approximately 10^{-7} to 10^{-11} cm/s – extremely low values, consistent with properties for a "confining layer" that effectively blocks water migration (Fetter, 2001).
- Black shales (such as the Marcellus) that contain methane in their pores have historically served as nearly impermeable seals for underlying fluids (Lash, 2006). Methane gas has a very low solubility in water, hence methane and water do not mix (they are referred to as immiscible). As a result, gas-filled pores block the flow of water. This phenomenon results in sharp decreases in hydraulic conductivity in areas where gas has accumulated in pore spaces (Brooks and Corey, 1964; van Genuchten, 1980; Morel-Seytous *et al.*, 1996, Figure C.1). Thus, the presence of gas black shales above the Marcellus formation will further reduce the already low hydraulic conductivities and increase the effectiveness of these natural hydraulic barriers.

To summarize, the low intrinsic permeability of the Marcellus Shale formation and the presence of multiple layers of low permeability rock formations above the Marcellus Shale have hydraulically isolated the Marcellus Shale deposits. The presence of concentrated brine and significant reserves of trapped natural gas in the Marcellus Shale formation are a testament to the effectiveness of the hydraulic isolation of the Marcellus Shale from other overlying formations.

5.3.2 Fracturing Phase

The HF process, discussed in Section 2, is undertaken in stages and completed in a relatively short time period (one to two days per well). HF fluids (water and additives) and proppants are pumped into a well

at high pressures (*i.e.*, 1.5 to two times ambient reservoir pressure)²¹ in multiple stages *via* a horizontal well. Each stage lasts on the order of hours, with the entire process being completed within one to two days. After the HF treatment has been completed, pumps begin pulling material out of the production well, first to remove HF fluid and naturally-occurring fluids from the formation, and then to commence gas production. During the gas production phase, pressure in the gas well is lower than ambient pressure in the formation, causing gas and liquid to migrate toward the well. Therefore, high fracturing pressures are only applied for a short duration, whereas subsequent gas production is conducted over the long-term.

The upward growth of fractures is constrained by a number of natural characteristics of the rocks overlying the Marcellus, as well as the inherent design of the HF stimulation. For example, *in-situ* stress contrasts between the overlying rock strata, as well as other endemic properties of the Marcellus and overlying formations, has been shown to limit fracture growth (see Appendix C for details). In addition, the inherent design of the HF stimulation seeks to create a fracture network in the target formation, but not beyond it; any fluids and fractures that extend beyond the target formation represent a waste of resources because they will not contribute to increased oil or gas production. Recent studies have shown a strong correlation between the volume of fluid pumped down the well (akin to the amount of energy put into the HF stimulation) and the size of the fracture network (Mayerhofer *et al.*, 2010). Thus, the fluid volumes used in HF operations inherently limit fracture growth potential, such that it is not plausible for fractures to reach an overlying aquifer. Indeed, a comprehensive study by Fisher (2010) that mapped fracture propagation in the Marcellus Shale (and the Barnett Shale) has clearly shown that hydraulic fractures stay well below the bases of overlying potable aquifers (Figure 5.3). Thus, it is not plausible for HF fluid to reach an overlying potable aquifer *via* a continuous fracture network.

For a number of reasons, it is also not plausible for HF fluid to migrate to an overlying potable aquifer *via* rock pore spaces. In order for fluid to migrate away from the fracture zone, there must be a pressure gradient driving the fluid flow. Pressure propagation through the types of layered rock formations overlying the Marcellus occurs very slowly. For example, a step change in pressure would require thousands to millions of years to travel through several thousand feet of rock with the permeability range expected for shales overlying the Marcellus (Toth and Millar, 1983). The pressures imposed by the HF process, however, are not sustained over such a long period, but are rather a short pulse. Not only is the travel time of a pressure pulse from the Marcellus to an overlying aquifer extremely long, the magnitude of the pressure pulse dissipates rapidly with distance from the fracture zone (Mathias and van Reeuwijk,

²¹ The reservoir pressure gradient was reported as 0.55 to 0.6 psi/ft (dSGEIS, 2009), and the fracturing pressure gradient was previously calculated by ICF (2009, equation 12). The ratio of fracturing pressure to reservoir pressure from these two sources ranges from 1.5 to 2, indicating that fracturing pressure is only marginally higher than ambient reservoir pressure.

2009). Thus, it is not realistic to assume that the pressures applied during the relatively short HF stimulations would be able to drive fluid flow upward through thousands of feet of relatively impermeable rock to an overlying drinking water aquifer.

5.3.3 Production Phase

During the HF stimulation, some fluid will be pushed into the rock pore spaces, a process known as leak-off. Other fluid may also be pushed outward ahead of the proppant, such that the fractures close back on themselves once the HF pressure is relaxed, causing fluid to get trapped in these pinched-off fractures. In aggregate, these two processes trap the majority of HF fluid pumped into the Marcellus formation (*circa* 80%). When production (*i.e.*, pumping) begins at the well, fluids will flow into it under the influence of active pumping. Fluids, including HF fluid that leaked-off, but that are within the continuous fracture network, may slowly diffuse back out of the rock pore spaces and gradually be collected at the well as flowback.

HF fluid that migrated beyond the continuous fracture network, such as that contained in pinched-off fractures, will be subject to the ambient flow conditions that were present before the HF stimulation occurred. Although measurements of the ambient flow direction are not available, anecdotal information suggests that upward flow towards a potable aquifer does not occur. For example, the entrapment of natural gas and concentrated brine in the Marcellus and other proximate strata is an indication that upward flow does not occur under ambient conditions (see Appendix C for more discussion).

Despite the lack of a mechanism to drive upward flow from the Marcellus to an overlying drinking water aquifer, we nonetheless evaluated this pathway. In order to create a hypothetical scenario of upward flow from the Marcellus, we applied the highest reported reservoir pressure gradient (0.6 psi/ft; revised dSGEIS, p. 5-142) to the entire column of rocks and overburden overlying the Marcellus. Under this assumption and by taking into consideration the permeability of rocks overlying the Marcellus, we estimated the DAF for this hypothetical pathway. 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 the Marcellus is given by the following equation:

$$C_{gw} = \frac{C_M}{DAF_M}$$

Where DAF_M is the overall dilution attenuation factor for upward migration from the Marcellus and C_M is the concentration of HF constituents in the Marcellus. The dilution factor (DAF_M) is comprised of two components, one to account for dilution of constituents into the bedrock pore space between the Marcellus and the bottom of a shallow aquifer, and another to account for mixing based on the hypothetical rate of upward flow (from the shale formation) relative to the groundwater flow rate in the shallow aquifer.²²

As described in Appendix C, the value of DAF_M thus derived is 1,650,000 for a 100 ft thick aquifer and 8,700,000 for a 1,000 ft thick aquifer. In comparison to the surface spill scenarios, dilution for upward migration from the Marcellus is significantly greater (if upward migration occurs at all). Because greater dilution connotes lower risk, the risks for the hypothetical upward migration scenario would be less than the shallow spill scenario, and were not explicitly quantified in our risk analysis.

5.3.4 Marcellus Migration Conclusions

We have analyzed the potential for HF additive migration from the Marcellus Shale to an overlying drinking water aquifer and reviewed previous studies on the subject. Based on this analysis, we have concluded:

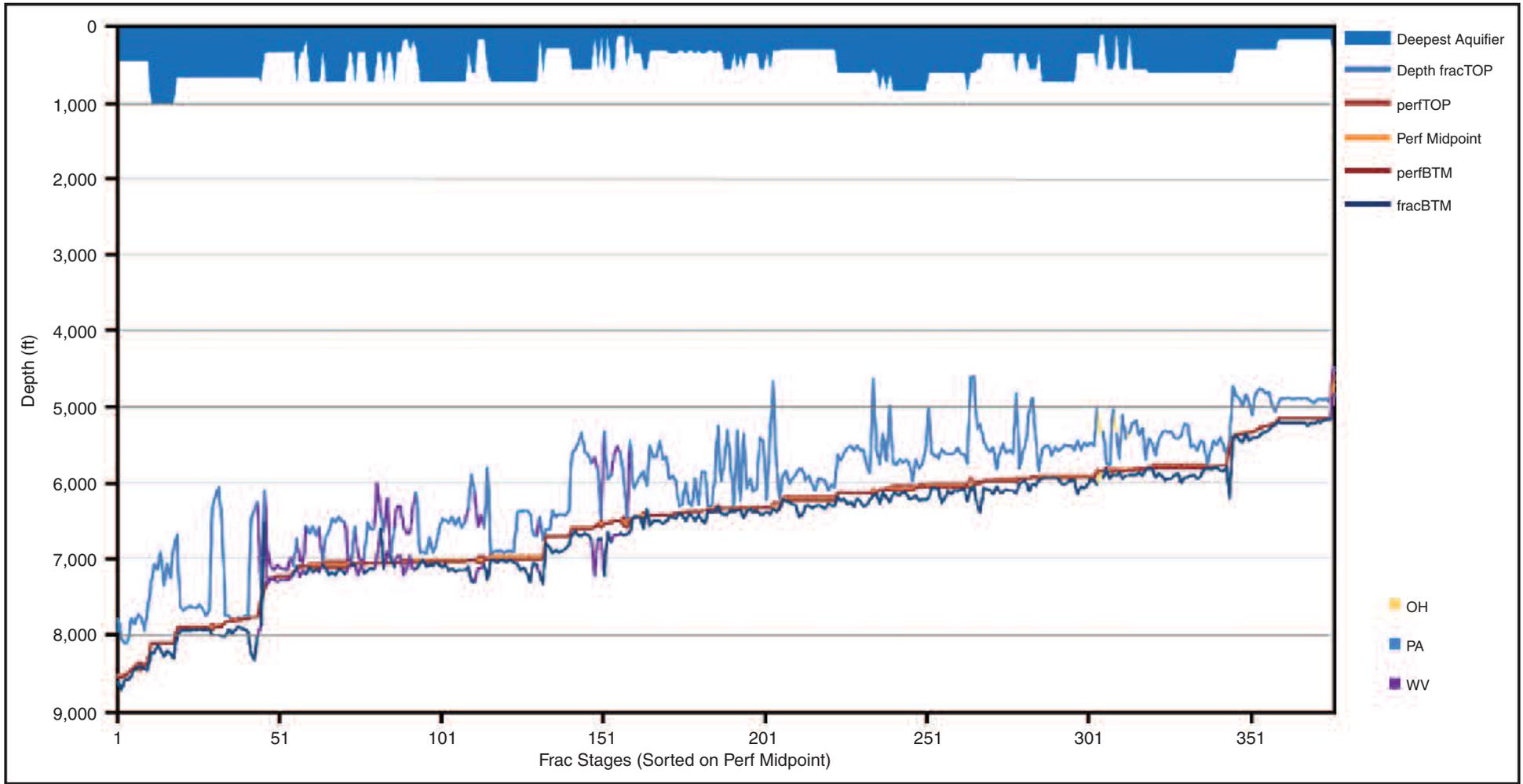
- Under ambient conditions, fluids in the Marcellus Shale (saline water and methane) are hydraulically isolated from overlying formations by thousands of feet of overlying rock, containing numerous natural confining layers. Consequently, these deeply isolated fluids are trapped and do not migrate to potable aquifers.
- During the HF stimulation, elevated pressures are applied for a short duration that is inadequate for mobilizing HF constituents to potable aquifers. In addition, application of HF pressure is not expected to result in interconnected fractures to overlying potable aquifers, given the significant thickness of rocks (thousands of feet) overlying the Marcellus Shale and the natural mechanisms that inhibit fracture propagation (*e.g.*, *in-situ* stress contrasts and embedded concretions). As a result, neither flow through the primary or secondary porosity to drinking water aquifers appears feasible.
- Development of the gas well, after stimulation, causes fluid in the well's capture zone to migrate toward the well, rather than upward. 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 the Marcellus Shale to a potable aquifer were plausible, the rate of migration would be such that the dilution/attenuation of groundwater in the overlying aquifer would be significant, and would reduce the HF fluid

²² 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 Marcellus formation and the shallow drinking water zone.

constituent concentrations in drinking water (from the overlying aquifer) to concentrations well below health-based standards/benchmarks.

Based on our analysis, it is extremely implausible that HF constituents pumped into the Marcellus Shale could reach an overlying potable aquifer. The results of our analysis are consistent with and augment the conclusions reached in the revised dSGEIS that HF is not expected to adversely affect drinking water aquifers. These conclusions are consistent with the findings of a prior US EPA (2004a) study, which had examined the potential migration of HF constituents into drinking water aquifers in coalbed formations. That US EPA study concluded that HF and gas production from coalbed formations posed little threat of HF constituents contaminating overlying drinking water aquifers. The setting and physical characteristics of the Marcellus Shale are such that migration of HF constituents from the Marcellus formation is even less likely than migration from coalbed formations and would also not pose human health concerns.

DRAFT



Source: Fisher, 2010.

File Path: G:\Projects\210116 HESI\Graphics\NonCAD\Figure5.xai



Marcellus Shale Mapped Fracture Treatments

FIGURE 5.3

Date: 11/02/2011

6 Human Health Chemical Toxicity Analysis

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 from Marcellus operations 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 RBCs used in this risk analysis. More detailed information is presented in Appendix E.

6.1 Overview

As presented in the revised dSGEIS, and reflected in the HESI HF fluid systems, a wide variety of additives and their associated chemical constituents could be used in hydraulic fracturing. In Section 6.2, we provide information noting the common uses of many of the HF constituents. 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 chemicals without quantitative toxicity information, we used a qualitative approach to identify compounds with low human hazard potential that could reasonably be eliminated from the quantitative risk evaluation.

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, 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 that do not require tolerance limits when used in accordance with good agricultural and manufacturing practices.²³ Some of the HF chemicals falling into this inert category include: glycerine, sodium benzoate, sodium acetate, and sodium sulfate (US EPA, 2009a).
- *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 fragrances found in food or personal care products (NLM, 2009; US EPA, 2007b).
- *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, 2009b; 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).

²³ In some cases, some restrictions are specified.

6.3 Hierarchy for Determining RBCs

We used a tiered approach to identify or develop health-protective RBCs for the HF constituents. in typical HESI HF fluid systems Use of tiered hierarchies for defining constituent toxicity is a standard risk assessment practice (US EPA, 2003;; US EPA, 20011a,b). 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, 2009x), 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" Regional Screening Levels (RSLs) published by the US EPA (2011a) as the RBC, where they were available. RSLs are based on long-term drinking water consumption (2 liters per day for 30 years) and are US EPA-recommended benchmarks for screening level risk assessments.
- If MCLs and RSLs were not available, we used quantitative oral toxicity factors published by US 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.*, 70-kg individual ingesting 2 L/day of water over a 30-year period). The specific hierarchy of Agency sources from which the published toxicity factors were obtained is described in Appendix E.
- 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 a safety factor of 3,000, which is the maximum uncertainty factor recommended by US EPA guidance (US EPA, 2002). The choice of the maximum US EPA-recommended uncertainty factor is health-protective since it results in the lowest possible RBC for a given constituent.
- For chemicals lacking repeat dose oral toxicity data, but having an established inhalation standard (*e.g.*, in m³/day), a drinking water RBC was determined using route-to-route extrapolation (*i.e.*, inhalation to oral) using standard exposure assumptions that form the basis of the inhalation guideline (*i.e.*, a 70 kg individual breathing 20 m³/day of air).
- For compounds that did not have quantitative toxicity information, we used the following procedure:
 - ▶ HF constituents were cross-referenced against chemicals classified as GRAS (US FDA), inert (US EPA), or compounds characterized by Health Canada as being a low potential human health concern. Additionally, compounds were evaluated against US EPA's criteria for low risk polymers. Chemicals appearing on these lists or meeting the low risk polymer criteria were considered to have a low

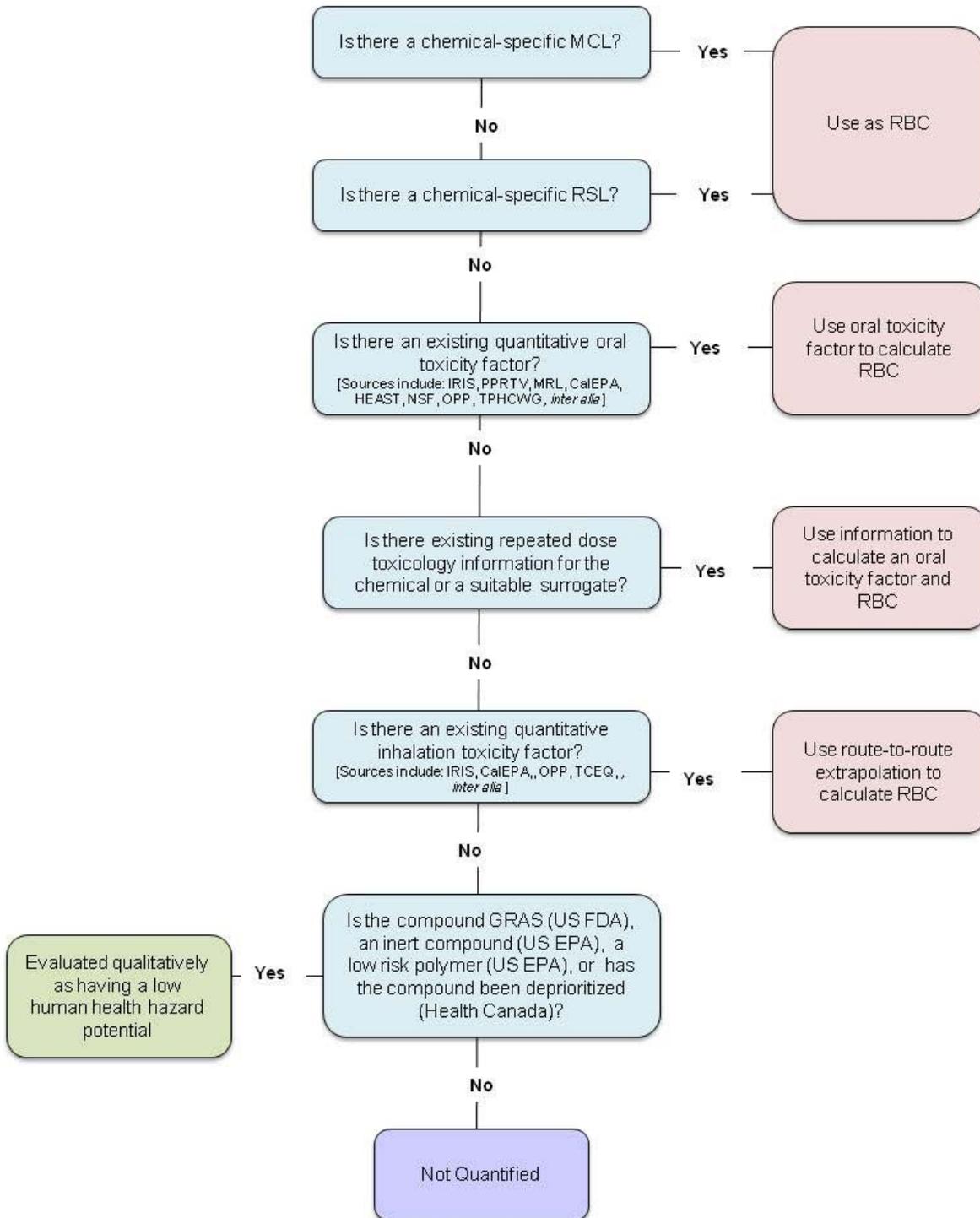
human hazard potential and no RBC was assigned as the chemicals could reasonably be excluded from the quantitative risk analysis.

- ▶ For compounds that were not included on the above lists, due to the lack of both quantitative and qualitative hazard information, it was not possible to evaluate these compounds in this risk evaluation. Only five percent of the constituents evaluated fell into this category.²⁴

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

²⁴ Five of the HESI HF constituents fall into this category as shown in Table E.2.

Figure 6.1
Flowchart of 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 accidental spills of HF constituents. In the risk characterization step, the chemical risk based concentrations (RBCs) 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, or hazard quotient, relating the estimated HF additive concentration in drinking water (based on dilution for each respective pathway as described in Section 5), to the chemical's risk-based concentration:

$$HQ = \frac{C_{HF}/DAF}{RBC}$$

The numerator of this equation gives the concentration in the drinking water (where the DAF 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.

The risk analysis results, *i.e.*, the calculated HQ values, are presented in Tables 7.1 through 7.5 and discussed in the following sub-sections.

7.1 HESI HF Constituents

The calculated HQ values for all constituents in the typical HESI HF fluids, for both the diffuse and sudden spill scenarios, are well below 1. Table 7.1 shows the range of potential HQs for each of the chemicals in the typical HESI HF systems under our sudden spill scenario. Our analysis resulted in ranges for several reasons. First, several of the different HF systems may contain some of the same chemicals listed in Table 7.1, but at different concentrations. Additionally, under our sudden spill scenario, there is the possibility of two spill volumes—a spill of 1,000 gal for HF system fluid volumes

less than 250,000 gallons and a spill of 10,000 for HF system fluid volumes greater than or equal to 250,000 gallons. As a result of both different HF constituent concentrations in different fluid systems, and varying spill volumes evaluated (yielding varying DAF values), the chemical HQs vary for individual constituents. The minimum and maximum chemical HQs that reflect these differences for the sudden spill scenario are summarized in Table 7.1. We note also that for the sudden spill scenario we examined two surface water dilution conditions: mixing over the course of a year, or mixing over a short-time period (10 days). Even under this short-term mixing (minimal dilution) case, the HQs are less than 1 (Table 7.1).

The HQs for the diffuse spill scenario are presented in Table 7.2. Because a single spill volume was used for the diffuse spill scenario, Table 7.2 provides the minimum and maximum chemical HQs reflecting the range of HF constituent concentrations among the different HESI HF fluid systems.

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 sudden spills of individual HF stages are summarized in Table 7.4; the HQs for diffuse spills were summed over all HF fluid systems (Table 7.5). The Hazard Indices for all scenarios evaluated are less than 1, indicating that there is no evidence of potential human health concerns.

We did not quantify human health risks associated with migration of HF constituents from the Marcellus Shale to overlying potable aquifers. As discussed in Section 5, the DAFs for this hypothetical migration pathway are much greater than the DAFs 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 the Marcellus Shale 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 conservative assumptions, the calculated HQs were generally orders of magnitude less than 1, the US EPA guideline value, and the Hazard Indices were also less than 1.

7.2 Flowback Constituents

HQs were quantified for the diffuse spill scenario using the measured flowback data reported in the revised dSGEIS (based on flowback data from the Marcellus formation in Pennsylvania and West Virginia). The calculated HQ values for all flowback constituents are below 1, ranging from 2×10^{-7} to 0.6 (Table 7.3). Similar to the case for HF systems, we also computed a Hazard Index (HI) by summing the HQs for all the individual flowback constituents. As shown in Table 7.3, the HI for flowback is also less than 1 for all scenarios evaluated.

These results indicate that the potential human health risks posed by constituents measured in Marcellus HF flowback *via* drinking water exposures are insignificant, as defined by Agency-based guidelines. Because these flowback data were taken from Marcellus Shale development in two neighboring states, it is expected that flowback composition in New York's Marcellus shale will be similar, and thus human health risks would be similarly insignificant.

Table 7.1 HESI HF Additive Hazard Quotients (HQ) -- Sudden Spill Scenario

Chemical	CAS No.	RBC ^[a]	Surface Water HQ ^[a]				Groundwater HQ ^[a]	
		(ug/L)	1-year Flow DAF		10-day Flow DAF		Min	Max
			Min	Max	Min	Max		
1,2,4 Trimethylbenzene	95-63-6	70	1.4E-05	1.4E-04	4.9E-04	5.0E-03	1.9E-04	8.6E-03
2-Bromo-2-nitro-1,3-propanediol	52-51-7	3,500	2.7E-06	2.7E-05	9.9E-05	9.9E-04	3.8E-05	1.7E-03
Acetic acid	64-19-7	499,800	4.2E-08	4.5E-06	1.6E-06	1.7E-04	5.9E-07	6.3E-05
Acetic anhydride	108-24-7	499,800	3.4E-06	6.8E-06	1.2E-04	2.5E-04	4.7E-05	9.4E-05
Alcohols, C12-16, ethoxylated	68551-12-2	13,125	3.2E-06	4.2E-05	1.2E-04	1.5E-03	8.8E-05	6.1E-04
Alcohols, C14-C15, ethoxylated	68951-67-7	13,125	5.4E-06	5.4E-06	2.0E-04	2.0E-04	7.4E-05	7.4E-05
Aldehyde	CBI	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]
Alkyl (C14-C16) olefin sulfonate, sodium salt	68439-57-6	1,155	4.4E-04	1.1E-03	1.6E-02	3.9E-02	9.6E-05	2.3E-04
Amines, coco alkyl, ethoxylated	61791-14-8	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]
Ammonium acetate	631-61-8	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]
Ammonium chloride	12125-02-9	7,980	1.9E-06	1.3E-04	6.9E-05	4.8E-03	2.6E-05	8.4E-03
Ammonium persulfate	7727-54-0	490	8.6E-04	1.7E-03	3.2E-02	6.0E-02	5.5E-02	1.0E-01
Ammonium phosphate	7722-76-1	30,000	1.0E-06	1.0E-06	3.8E-05	3.8E-05	1.4E-05	1.4E-05
Attapulgite	12174-11-7	4,480,000	1.7E-08	2.9E-08	6.3E-07	1.1E-06	1.1E-06	1.8E-06
Bentonite, benzyl(hydrogenated tallow alkyl) dimethylammonium stearate complex	121888-68-4	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]
Borate salt	CBI	3,100	5.5E-04	9.3E-04	2.0E-02	3.4E-02	3.5E-02	5.9E-02
C.I. Pigment Orange 5	3468-63-1	280	5.5E-06	5.5E-06	2.0E-04	2.0E-04	3.5E-04	3.5E-04
Calcium chloride	10043-52-4	11,655	4.4E-07	1.1E-05	1.6E-05	4.0E-04	6.1E-06	7.0E-04
Carbohydrate	CBI	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]
Chloromethylnaphthalene quinoline quaternary amine	15619-48-4	[a2]	[a2]	[a2]	[a2]	[a2]	[a2]	[a2]
Chlorous acid, sodium salt	7758-19-2	1,000	[c]	[c]	[c]	[c]	[c]	[c]
Citrus, extract	94266-47-4	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]
Cobalt acetate	71-48-7	5	1.1E-02	1.1E-02	4.0E-01	4.0E-01	2.4E-04	2.4E-04
Crystalline silica, quartz	14808-60-7	29,155	1.7E-08	6.5E-06	6.3E-07	2.4E-04	2.4E-07	4.1E-04
Cured acrylic resin	CBI	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]
Diethylene glycol	111-46-6	3,500	1.9E-05	4.7E-05	7.1E-04	1.7E-03	2.7E-04	6.5E-04
Diethylenetriamine	111-40-0	805	1.4E-04	1.4E-04	5.0E-03	5.0E-03	1.9E-03	1.9E-03
EDTA/Copper chelate	CBI	630	4.9E-05	7.4E-04	1.8E-03	2.7E-02	3.1E-03	1.0E-02
Ethanol	64-17-5	28,000	8.1E-06	8.2E-05	3.0E-04	3.0E-03	1.1E-04	5.2E-03
Ethoxylate fatty acid	CBI	66,792	5.0E-07	8.9E-06	1.8E-05	3.2E-04	7.0E-06	5.6E-04
Ethoxylate fatty acid	CBI	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]
Ethoxylated branched C13 alcohol	78330-21-9	13,125	2.9E-06	2.2E-05	1.0E-04	8.1E-04	4.0E-05	1.4E-03
Ethoxylated fatty acid	CBI	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]
Ethylene glycol monobutyl ether	111-76-2	1,600	1.3E-04	3.1E-04	4.6E-03	1.1E-02	1.8E-03	4.2E-03
Fatty acid ester	CBI	1,000	8.4E-06	2.5E-05	3.1E-04	9.2E-04	5.3E-04	1.6E-03
Fatty acid tall oil	CBI	29,155	2.4E-06	1.8E-05	8.7E-05	6.5E-04	3.3E-05	2.5E-04
Fatty acid tall oil amide	CBI	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]

Table 7.1 HESI HF Additive Hazard Quotients (HQ) -- Sudden Spill Scenario

Chemical	CAS No.	RBC ^[a]	Surface Water HQ ^[a]				Groundwater HQ ^[a]	
		(ug/L)	1-year Flow DAF		10-day Flow DAF		Min	Max
			Min	Max	Min	Max		
Fatty alcohol polyglycol ether surfactant	9043-30-5	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]
Fatty acid ester ethoxylate	CBI	350,000	1.6E-08	4.8E-08	5.8E-07	1.7E-06	1.0E-06	3.0E-06
Formaldehyde	50-00-0	3,100	6.0E-08	4.0E-06	2.2E-06	1.5E-04	8.3E-07	2.5E-04
Glycerine	56-81-5	93,333	1.7E-07	1.7E-07	6.3E-06	6.3E-06	2.4E-06	2.4E-06
Guar gum	9000-30-0	[a1]						
Guar gum derivative	CBI	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]
HCl in 22 Baume Acid	7647-01-0	200	[c]	[c]	[c]	[c]	[c]	[c]
Heavy aromatic petroleum naphtha	64742-94-5	1,400	3.6E-05	3.6E-04	1.3E-03	1.3E-02	5.0E-04	2.3E-02
Hemicellulase enzyme	9012-54-8	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]
Hydrotreated light petroleum distillate	64742-47-8	3,500	1.2E-04	3.6E-04	4.4E-03	1.3E-02	7.6E-03	2.3E-02
Inorganic salt	CBI	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]
Isopropanol	67-63-0	350,000	3.9E-07	4.9E-06	1.4E-05	1.8E-04	5.4E-06	3.1E-04
Magnesium chloride hexahydrate	7791-18-6	175,000	6.0E-08	1.5E-06	2.2E-06	5.5E-05	8.3E-07	9.5E-05
Methanol	67-56-1	7,800	2.0E-05	2.1E-04	7.4E-04	7.6E-03	2.8E-04	2.9E-03
Naphtha, hydrotreated heavy	64742-48-9	3,500	3.5E-04	3.5E-03	1.3E-02	1.3E-01	4.9E-03	2.2E-01
Naphthalene	91-20-3	310	1.8E-05	1.8E-04	6.6E-04	6.7E-03	2.5E-04	1.2E-02
Naphthenic acid ethoxylate	68410-62-8	210	2.6E-04	6.4E-03	9.6E-03	2.4E-01	5.0E-05	1.2E-03
Nonylphenol ethoxylated	127087-87-0	2,345	8.1E-06	8.1E-05	2.9E-04	3.0E-03	1.1E-04	5.1E-03
Olefin	CBI	100	4.7E-06	4.7E-06	1.7E-04	1.7E-04	6.5E-05	6.5E-05
Olefin	CBI	1,000	1.1E-05	1.1E-05	4.1E-04	4.1E-04	1.6E-04	1.6E-04
Olefin	CBI	1,000	7.0E-06	7.0E-06	2.6E-04	2.6E-04	9.7E-05	9.7E-05
Olefin	CBI	1,000	4.7E-07	4.7E-07	1.7E-05	1.7E-05	6.5E-06	6.5E-06
Organic phosphonate	CBI	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]
Oxylated phenolic resin	CBI	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]
Oxylated phenolic resin	CBI	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]
Polyacrylamide copolymer	CBI	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]
Polyoxylated fatty amine salt	61791-26-2	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]
Potassium carbonate	584-08-7	2,345,000	1.3E-07	1.7E-06	4.6E-06	6.1E-05	1.8E-06	1.1E-04
Potassium formate	590-29-4	3,500	3.9E-04	6.6E-04	1.4E-02	2.4E-02	2.5E-02	4.2E-02
Potassium hydroxide	1310-58-3	2,345,000	1.7E-09	1.1E-07	6.3E-08	3.9E-06	2.4E-08	6.7E-06
Potassium metaborate	13709-94-9	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]
Propanol	71-23-8	101,675	2.0E-07	2.0E-07	7.3E-06	7.3E-06	2.8E-06	2.8E-06
Propargyl alcohol	107-19-7	31	9.1E-04	9.1E-04	3.3E-02	3.3E-02	1.3E-02	1.3E-02
Proprietary	CBI	[a2]	[a2]	[a2]	[a2]	[a2]	[a2]	[a2]
Quaternary ammonium compound	CBI	[a2]	[a2]	[a2]	[a2]	[a2]	[a2]	[a2]
Quaternary ammonium compounds, bis(hydrogenated tallow alkyl) dimethyl, salts with bentonite	68953-58-2	145,845	2.4E-07	2.4E-06	8.9E-06	8.9E-05	3.4E-06	1.5E-04
Quaternary ammonium salt	CBI	[a2]	[a2]	[a2]	[a2]	[a2]	[a2]	[a2]

Table 7.1 HESI HF Additive Hazard Quotients (HQ) -- Sudden Spill Scenario

Chemical	CAS No.	RBC ^[a]	Surface Water HQ ^[a]				Groundwater HQ ^[a]	
		(ug/L)	1-year Flow DAF		10-day Flow DAF		Min	Max
			Min	Max	Min	Max		
Reaction product of acetophenone, formaldehyde, thiourea and oleic acid in dimethyl formamide	68527-49-1	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]
Silica gel	112926-00-8	29,155	5.4E-07	6.5E-07	2.0E-05	2.4E-05	3.4E-05	4.1E-05
Silica, amorphous -- fumed	7631-86-9	29,155	2.2E-07	4.9E-07	7.9E-06	1.8E-05	3.0E-06	6.8E-06
Sodium bicarbonate	144-55-8	1,998,500	1.3E-08	2.8E-08	4.6E-07	1.0E-06	1.8E-07	3.9E-07
Sodium carboxymethyl cellulose	9004-32-4	45,500	6.2E-07	1.0E-06	2.2E-05	3.8E-05	3.9E-05	6.6E-05
Sodium chloride	7647-14-5	2,901,500	5.6E-09	2.1E-06	2.1E-07	7.6E-05	3.6E-07	1.3E-04
Sodium glycolate	2836-32-0	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]
Sodium hydroxide	1310-73-2	1,150,000	2.7E-09	2.6E-06	1.0E-07	9.6E-05	3.8E-08	1.7E-04
Sodium hypochlorite	7681-52-9	1,120	1.8E-05	1.8E-04	6.4E-04	6.5E-03	2.4E-04	1.1E-02
Sodium iodide	7681-82-5	160	4.9E-04	4.9E-04	1.8E-02	1.8E-02	6.8E-03	6.8E-03
Sodium perborate tetrahydrate	10486-00-7	11,667	2.7E-05	5.4E-05	9.9E-04	2.0E-03	1.7E-03	3.4E-03
Sodium persulfate	7775-27-1	2,345	2.3E-06	1.2E-04	8.5E-05	4.5E-03	9.3E-05	7.7E-03
Sodium sulfate	7757-82-6	500,000	5.4E-12	2.5E-07	2.0E-10	9.3E-06	2.2E-10	3.5E-06
Sodium sulfite	7757-83-7	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]
Sodium thiosulfate	7772-98-7	500,000	3.8E-06	3.8E-06	1.4E-04	1.4E-04	5.3E-05	5.3E-05
Surfactant mixture	CBI	13,125	6.6E-06	7.9E-06	2.4E-04	2.9E-04	4.2E-04	5.0E-04
Surfactant mixture	CBI	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]	[a1]
Terpenoid	CBI	2,917	3.9E-06	2.5E-04	1.4E-04	9.0E-03	5.5E-05	1.6E-02
Terpenoid	CBI	2,917	7.3E-06	7.5E-06	2.7E-04	2.8E-04	1.0E-04	1.0E-04
Tributyl tetradecyl phosphonium chloride	81741-28-8	105	7.3E-05	1.2E-03	2.7E-03	4.5E-02	1.0E-03	7.7E-02
Triethanolamine zirconate	101033-44-7	[a2]	[a2]	[a2]	[a2]	[a2]	[a2]	[a2]
Ulexite (B5H3O9.Ca.8H2O.Na)	1319-33-1	3,100	9.1E-04	9.1E-04	3.3E-02	3.3E-02	5.7E-02	5.7E-02
Zirconium, acetate lactate oxo ammonium complexes	68909-34-2	[a2]	[a2]	[a2]	[a2]	[a2]	[a2]	[a2]

Notes

CBI - Confidential Business Information. Gradient was provided chemical-specific CAS and chemical names and used this information to evaluate chemical-specific toxicity.

[a] Chemicals with no RBC and no HQ are either classified as having low human health hazard potential or have no available human health toxicity information (see Appendix E).

[a1]: chemical listed as inert, GRAS, low priority, etc. [a2]: No toxicity information available

[b] Groundwater pathway DAF applied chemical adsorption in soil for three chemicals (see Appendix A).

[c] Hydrochloric acid and chlorous acid are expected to be readily neutralized in the environment.

Table 7.2 HESI HF Additive Hazard Quotients (HQ) -- Diffuse Spill Scenario

Chemical	CAS No.	RBC ^[a] (ug/L)	Surface Water HQ ^[a]		Groundwater HQ ^[a]	
			Min	Max	Min	Max
1,2,4 Trimethylbenzene	95-63-6	70	3.3E-08	4.8E-05	3.5E-06	5.2E-03
2-Bromo-2-nitro-1,3-propanediol	52-51-7	3,500	2.6E-06	9.5E-06	2.8E-04	1.0E-03
Acetic acid	64-19-7	499,800	6.5E-09	4.6E-06	7.0E-07	4.9E-04
Acetic anhydride	108-24-7	499,800	1.6E-08	6.6E-06	1.8E-06	7.2E-04
Alcohols, C12-16, ethoxylated	68551-12-2	13,125	5.8E-08	1.1E-04	6.3E-06	1.2E-02
Alcohols, C14-C15, ethoxylated	68951-67-7	13,125	8.7E-08	1.0E-05	9.4E-06	1.1E-03
Aldehyde	CBI	[a1]	[a1]	[a1]	[a1]	[a1]
Alkyl (C14-C16) olefin sulfonate, sodium salt	68439-57-6	1,155	9.1E-04	3.4E-03	1.5E-03	5.6E-03
Amines, coco alkyl, ethoxylated	61791-14-8	[a1]	[a1]	[a1]	[a1]	[a1]
Ammonium acetate	631-61-8	[a1]	[a1]	[a1]	[a1]	[a1]
Ammonium chloride	12125-02-9	7,980	2.8E-07	1.4E-04	3.1E-05	1.5E-02
Ammonium persulfate	7727-54-0	490	2.9E-04	4.2E-04	3.2E-02	4.5E-02
Ammonium phosphate	7722-76-1	30,000	3.6E-08	2.7E-06	3.9E-06	2.9E-04
Attapulgite	12174-11-7	4,480,000	5.0E-09	1.0E-08	5.4E-07	1.1E-06
Bentonite, benzyl(hydrogenated tallow alkyl) dimethylammonium stearate complex	121888-68-4	[a1]	[a1]	[a1]	[a1]	[a1]
Borate salt	CBI	3,100	1.6E-04	3.3E-04	1.7E-02	3.5E-02
C.I. Pigment Orange 5	3468-63-1	280	1.9E-06	1.9E-06	2.0E-04	2.1E-04
Calcium chloride	10043-52-4	11,655	1.1E-06	3.9E-06	1.1E-04	4.2E-04
Carbohydrate	CBI	[a1]	[a1]	[a1]	[a1]	[a1]
Chloromethylnaphthalene quinoline quaternary amine	15619-48-4	[a2]	[a2]	[a2]	[a2]	[a2]
Chlorous acid, sodium salt	7758-19-2	1,000	[c]	[c]	[c]	[c]
Citrus, extract	94266-47-4	[a1]	[a1]	[a1]	[a1]	[a1]
Cobalt acetate	71-48-7	5	8.5E-03	3.1E-02	1.5E-03	5.3E-03
Crystalline silica, quartz	14808-60-7	29,155	2.2E-09	1.7E-06	2.4E-07	1.8E-04
Cured acrylic resin	CBI	[a1]	[a1]	[a1]	[a1]	[a1]
Diethylene glycol	111-46-6	3,500	4.0E-05	1.5E-04	4.3E-03	1.6E-02
Diethylenetriamine	111-40-0	805	2.3E-06	2.5E-06	2.5E-04	2.7E-04
EDTA/Copper chelate	CBI	630	1.3E-05	1.7E-05	1.4E-03	1.8E-03
Ethanol	64-17-5	28,000	2.0E-08	4.7E-05	2.1E-06	5.1E-03
Ethoxylate fatty acid	CBI	66,792	4.9E-07	2.2E-06	5.2E-05	2.4E-04
Ethoxylate fatty acid	CBI	[a1]	[a1]	[a1]	[a1]	[a1]
Ethoxylated branched C13 alcohol	78330-21-9	13,125	2.2E-06	8.1E-06	2.4E-04	8.8E-04
Ethoxylated fatty acid	CBI	[a1]	[a1]	[a1]	[a1]	[a1]
Ethylene glycol monobutyl ether	111-76-2	1,600	2.6E-04	9.5E-04	2.8E-02	1.0E-01
Fatty acid ester	CBI	1,000	3.8E-07	6.3E-06	4.1E-05	6.8E-04
Fatty acid tall oil	CBI	29,155	5.7E-09	4.6E-05	6.2E-07	4.9E-03
Fatty acid tall oil amide	CBI	[a1]	[a1]	[a1]	[a1]	[a1]
Fatty alcohol polyglycol ether surfactant	9043-30-5	[a1]	[a1]	[a1]	[a1]	[a1]
Fatty acid ester ethoxylate	CBI	350,000	7.2E-10	1.2E-08	7.7E-08	1.3E-06

Table 7.2 HESI HF Additive Hazard Quotients (HQ) -- Diffuse Spill Scenario

Chemical	CAS No.	RBC ^[a] (ug/L)	Surface Water HQ ^[a]		Groundwater HQ ^[a]	
			Min	Max	Min	Max
Formaldehyde	50-00-0	3,100	1.7E-07	1.6E-06	1.9E-05	1.8E-04
Glycerine	56-81-5	93,333	3.0E-07	4.7E-07	3.2E-05	5.0E-05
Guar gum	9000-30-0	[a1]	[a1]	[a1]	[a1]	[a1]
Guar gum derivative	CBI	[a1]	[a1]	[a1]	[a1]	[a1]
HCl in 22 Baume Acid	7647-01-0	200	[c]	[c]	[c]	[c]
Heavy aromatic petroleum naphtha	64742-94-5	1,400	8.7E-08	1.3E-04	9.4E-06	1.4E-02
Hemicellulase enzyme	9012-54-8	[a1]	[a1]	[a1]	[a1]	[a1]
Hydrotreated light petroleum distillate	64742-47-8	3,500	5.4E-06	9.0E-05	5.8E-04	9.7E-03
Inorganic salt	CBI	[a1]	[a1]	[a1]	[a1]	[a1]
Isopropanol	67-63-0	350,000	9.3E-10	1.1E-05	1.0E-07	1.2E-03
Magnesium chloride hexahydrate	7791-18-6	175,000	1.4E-07	5.3E-07	1.5E-05	5.7E-05
Methanol	67-56-1	7,800	4.9E-08	5.3E-04	5.3E-06	5.7E-02
Naphtha, hydrotreated heavy	64742-48-9	3,500	4.5E-05	1.2E-03	4.9E-03	1.3E-01
Naphthalene	91-20-3	310	4.4E-08	6.4E-05	4.7E-06	6.9E-03
Naphthenic acid ethoxylate	68410-62-8	210	6.3E-07	1.6E-02	9.3E-07	2.4E-02
Nonylphenol ethoxylated	127087-87-0	2,345	2.0E-08	2.9E-05	2.1E-06	3.1E-03
Olefin	CBI	100	7.6E-08	9.1E-06	8.2E-06	9.8E-04
Olefin	CBI	1,000	1.8E-07	2.2E-05	2.0E-05	2.4E-03
Olefin	CBI	1,000	1.1E-07	1.4E-05	1.2E-05	1.5E-03
Olefin	CBI	1,000	7.6E-09	9.1E-07	8.2E-07	9.8E-05
Organic phosphonate	CBI	[a1]	[a1]	[a1]	[a1]	[a1]
Oxylated phenolic resin	CBI	[a1]	[a1]	[a1]	[a1]	[a1]
Oxylated phenolic resin	CBI	[a1]	[a1]	[a1]	[a1]	[a1]
Polyacrylamide copolymer	CBI	[a1]	[a1]	[a1]	[a1]	[a1]
Polyoxylated fatty amine salt	61791-26-2	[a1]	[a1]	[a1]	[a1]	[a1]
Potassium carbonate	584-08-7	2,345,000	1.9E-07	7.1E-07	2.1E-05	7.7E-05
Potassium formate	590-29-4	3,500	1.1E-04	2.3E-04	1.2E-02	2.5E-02
Potassium hydroxide	1310-58-3	2,345,000	3.0E-09	2.2E-08	3.2E-07	2.4E-06
Potassium metaborate	13709-94-9	[a1]	[a1]	[a1]	[a1]	[a1]
Propanol	71-23-8	101,675	3.4E-07	5.4E-07	3.7E-05	5.9E-05
Propargyl alcohol	107-19-7	31	1.5E-05	1.8E-03	1.6E-03	1.9E-01
Proprietary	CBI	[a2]	[a2]	[a2]	[a2]	[a2]
Quaternary ammonium compound	CBI	[a2]	[a2]	[a2]	[a2]	[a2]
Quaternary ammonium compounds, bis(hydrogenated tallow alkyl) dimethyl, salts with bentonite	68953-58-2	145,845	3.1E-08	8.6E-07	3.4E-06	9.2E-05
Quaternary ammonium salt	CBI	[a2]	[a2]	[a2]	[a2]	[a2]
Reaction product of acetophenone, formaldehyde, thiourea and oleic acid in dimethyl formamide	68527-49-1	[a1]	[a1]	[a1]	[a1]	[a1]
Silica gel	112926-00-8	29,155	1.7E-07	1.9E-07	1.8E-05	2.1E-05
Silica, amorphous -- fumed	7631-86-9	29,155	9.5E-07	1.5E-06	1.0E-04	1.6E-04

Table 7.2 HESI HF Additive Hazard Quotients (HQ) -- Diffuse Spill Scenario

Chemical	CAS No.	RBC ^[a] (ug/L)	Surface Water HQ ^[a]		Groundwater HQ ^[a]	
			Min	Max	Min	Max
Sodium bicarbonate	144-55-8	1,998,500	5.5E-08	8.7E-08	6.0E-06	9.4E-06
Sodium carboxymethyl cellulose	9004-32-4	45,500	1.8E-07	3.7E-07	1.9E-05	4.0E-05
Sodium chloride	7647-14-5	2,901,500	3.5E-09	7.7E-07	3.7E-07	8.3E-05
Sodium glycolate	2836-32-0	[a1]	[a1]	[a1]	[a1]	[a1]
Sodium hydroxide	1310-73-2	1,150,000	8.8E-09	7.8E-07	9.5E-07	8.4E-05
Sodium hypochlorite	7681-52-9	1,120	4.5E-05	6.2E-05	4.9E-03	6.7E-03
Sodium iodide	7681-82-5	160	1.7E-05	1.2E-03	1.8E-03	1.3E-01
Sodium perborate tetrahydrate	10486-00-7	11,667	1.2E-06	1.9E-05	1.3E-04	2.1E-03
Sodium persulfate	7775-27-1	2,345	5.9E-07	4.3E-05	6.4E-05	4.6E-03
Sodium sulfate	7757-82-6	500,000	1.4E-12	6.9E-07	1.5E-10	7.4E-05
Sodium sulfite	7757-83-7	[a1]	[a1]	[a1]	[a1]	[a1]
Sodium thiosulfate	7772-98-7	500,000	6.5E-06	1.0E-05	7.1E-04	1.1E-03
Surfactant mixture	CBI	13,125	2.0E-06	2.3E-06	2.2E-04	2.5E-04
Surfactant mixture	CBI	[a1]	[a1]	[a1]	[a1]	[a1]
Terpenoid	CBI	2,917	3.8E-06	6.2E-05	4.1E-04	6.7E-03
Terpenoid	CBI	2,917	7.0E-06	2.6E-05	7.6E-04	2.8E-03
Tributyl tetradecyl phosphonium chloride	81741-28-8	105	2.1E-04	3.4E-04	2.3E-02	3.7E-02
Triethanolamine zirconate	101033-44-7	[a2]	[a2]	[a2]	[a2]	[a2]
Ulexite (B5H3O9.Ca.8H2O.Na)	1319-33-1	3,100	2.3E-04	2.4E-04	2.5E-02	2.5E-02
Zirconium, acetate lactate oxo ammonium complexes	68909-34-2	[a2]	[a2]	[a2]	[a2]	[a2]

Notes

CBI - Confidential Business Information. Gradient was provided chemical-specific CAS and chemical names and used this information to evaluate chemical-specific toxicity.

[a] Chemicals with no RBC and no HQ are either classified as having low human health hazard potential or have no available human health toxicity information (see Appendix E).

[a1]: chemical listed as inert, GRAS, low priority, etc. [a2]: No toxicity information available

[b] Groundwater pathway DAF applied chemical adsorption in soil for three chemicals (see Appendix A).

[c] Hydrochloric acid and chlorous acid are expected to be readily neutralized in the environment.

Table. 7.3 Flowback Constituent Hazard Quotients (HQ)

CAS No.	Parameter ^[a]		Surface Water	Ground Water	RBC (ug/L)	Upper Bound HQs	
			EPC ^[b] (ug/L)	EPC ^[b] (ug/L)		Surface Water	Groundwater
7439-90-5	Aluminum	Total	0.01	0.02	16,000	8.4E-07	1.5E-06
7664-41-7	Aqueous ammonia	Total	8.6	14.9	30,000	2.9E-04	5.0E-04
7440-38-2	Arsenic	Total	0.02	0.03	10	1.7E-03	3.0E-03
7440-39-3	Barium	Dissolved	40.8	70.7	2,000	2.0E-02	3.5E-02
7440-39-3	Barium	Total	278.8	483.3	2,000	1.4E-01	2.4E-01
7440-42-8	Boron	Total	0.4	0.7	3,100	1.3E-04	2.2E-04
24959-67-9	Bromide	Total	116.7	202.3	6,000	1.9E-02	3.4E-02
7440-43-9	Cadmium	Total	0.005	0.008	5	9.6E-04	1.7E-03
7440-70-2	Calcium	Total	815.6	1,413.7	1,249,500	6.5E-04	1.1E-03
7440-47-3	Chromium	Dissolved	0.1	0.2	100	1.0E-03	1.8E-03
7440-47-3	Chromium	Total	0.0	0.0	100	1.6E-04	2.7E-04
7440-48-4	Cobalt	Total	0.1	0.1	5	1.6E-02	2.8E-02
7440-50-8	Copper	Total	0.005	0.008	1,300	3.6E-06	6.3E-06
7439-89-6	Iron	Dissolved	12.2	21.1	11,000	1.1E-03	1.9E-03
7439-89-6	Iron	Total	5.6	9.7	11,000	5.1E-04	8.8E-04
7439-92-1	Lead	Total	0.007	0.012	15	4.5E-04	7.8E-04
7439-93-2	Lithium	Dissolved	11.8	20.5	70	1.7E-01	2.9E-01
7439-93-2	Lithium	Total	17.4	30.1	70	2.5E-01	4.3E-01
7439-95-4	Magnesium	Total	34.0	59.0	175,000	1.9E-04	3.4E-04
7439-96-5	Manganese	Dissolved	0.6	1.0	320	1.8E-03	3.1E-03
7439-96-5	Manganese	Total	0.4	0.6	320	1.1E-03	2.0E-03
7439-98-7	Molybdenum	Total	0.1	0.1	78	1.1E-03	1.9E-03
7440-02-0	Nickel	Total	0.006	0.010	300	1.9E-05	3.3E-05
64743-03-9	Phenols	Total	0.04	0.1	4,500	8.2E-06	1.4E-05
7440-09-7	Potassium	Total	24.0	41.7	2,345,000	1.0E-05	1.8E-05
7440-23-5	Sodium	Total	4,519.2	7,833.3	1,151,500	3.9E-03	6.8E-03
7440-24-6	Strontium	Dissolved	121.0	209.7	9,300	1.3E-02	2.3E-02
7440-24-6	Strontium	Total	214.4	371.7	9,300	2.3E-02	4.0E-02
14808-79-8	Sulfate	Total	0.2	0.3	500,000	3.8E-07	6.7E-07
7440-66-6	Zinc	Total	0.007	0.012	4,700	1.5E-06	2.6E-06
<i>Organic Constituents</i>							
71-43-2	Benzene		0.1	0.2	5	1.8E-02	3.2E-02
100-41-4	Ethyl Benzene		0.01	0.02	700	1.5E-05	2.6E-05
108-88-3	Toluene		0.2	0.3	1,000	1.6E-04	2.8E-04
1330-20-7	xylenes		0.09	0.15	10,000	8.5E-06	1.5E-05
<i>NORM</i> ^[d]			pCi/L	pCi/L	pCi/L		
	Ra-228		0.004	0.006	5	7.1E-04	1.2E-03
	Ra-226		0.006	0.011	5	1.3E-03	2.2E-03
	Cs-137		0.002	0.004	1.74	1.2E-03	2.0E-03
Sum of HQs:						3 E-01	5 E-01

Notes:

- [a] Chemicals measured in Marcellus flowback samples reported in rdSGEIS detected in more than 3 samples.
- [b] Exposure point concentrations (EPC) using lowest DAF to evaluate upper bound HQs (see Table 5.6).
- [c] The sum of HQs used the dissolved species HQ, when available. Using total concentration results, the sum of HQs does not exceed 1.
- [d] Naturally occurring radioactive material. No constituents detected in over 3 samples. We have included in HQ calculations at the maximum detected concentrations.

Table 7.4 HESI HF Fluid System Hazard Indices (HI)—Sudden Spill Scenario

Formulation Name	HF Stage	HF Volume (gal)	Spill Volume (gal)	Sum of HQs Surface Water		Sum of HQs Groundwater
				1-yr flow DAF	10-day DAF	
Pre-frac Acid 01	Pre-frac	34,000	1,000	0.0010	0.04	0.01
Pre-frac Acid 02	Pre-frac	73,000	1,000	0.0073	0.27	0.01
Pre-frac Acid 03	Pre-frac	5,000	1,000	0.0004	0.01	0.00
Foam frac 01	TW	5,340	1,000	0.0006	0.02	0.00
Foam frac 01	XLF	22,082	1,000	0.0129	0.47	0.01
Gel frac 01	XLF	1,915,000	10,000	0.0028	0.10	0.18
Hybrid frac 01	LF	170,000	1,000	0.0004	0.02	0.01
Hybrid frac 01	WF	4,500,000	10,000	0.0010	0.04	0.07
Hybrid frac 02	TW	816,750	10,000	0.0023	0.08	0.15
Hybrid frac 02	XLF	2,329,000	10,000	0.0030	0.11	0.19
Hybrid frac 03	LF	29,203	1,000	0.0002	0.01	0.00
Hybrid frac 03	XLF	97,000	1,000	0.0001	0.00	0.00
Hybrid frac 04	TW	393,700	10,000	0.0012	0.04	0.08
Hybrid frac 04	Flush	461,993	10,000	0.0010	0.04	0.06
Hybrid frac 04	XLF	2,154,500	10,000	0.0086	0.31	0.54
Hybrid frac 05	TW	849,000	10,000	0.0013	0.05	0.08
Hybrid frac 05	XLF	1,247,100	10,000	0.0043	0.16	0.27
Hybrid frac 06	TW	7,000	1,000	0.0010	0.04	0.01
Hybrid frac 06	LF	175,680	1,000	0.0005	0.02	0.01
Hybrid frac 06	XLF	1,179,324	10,000	0.0055	0.20	0.35
Water frac 01	WF	4,500,000	10,000	0.0010	0.04	0.07
Water frac 02	WF	4,500,000	10,000	0.0011	0.04	0.07
Water frac 03	WF	7,310,000	10,000	0.0008	0.03	0.05
Water frac 04	Flush	204,600	1,000	0.00002	0.00	0.00
Water frac 04	LF	502,200	10,000	0.0009	0.03	0.06

Table 7.5 HESI HF Fluid System Hazard Indices (HI)—Diffuse Spill Scenario

Formulation Name	HF_Stage	Total Volume (gal)	Spill Volume (gal)	Sum of HQs	
				Surface Water	Groundwater
Foam frac 01	TW + XLF	27,422	3,500	0.037	0.29
Foam frac 01	TW + XLF+Pre03	32,422	3,500	0.032	0.25
Foam frac 01	TW + XLF+Pre01	61,422	3,500	0.018	0.33
Foam frac 01	TW + XLF+Pre02	100,422	3,500	0.029	0.34
Gel frac 01	XLF	1,915,000	3,500	0.001	0.11
Gel frac 01	XLF+Pre03	1,920,000	3,500	0.001	0.11
Gel frac 01	XLF+Pre01	1,949,000	3,500	0.001	0.11
Gel frac 01	XLF+Pre02	1,988,000	3,500	0.002	0.11
Hybrid frac 01	LF + WF	4,670,000	3,500	0.0004	0.04
Hybrid frac 01	LF + WF+Pre03	4,675,000	3,500	0.0004	0.04
Hybrid frac 01	LF + WF+Pre01	4,704,000	3,500	0.0004	0.05
Hybrid frac 01	LF + WF+Pre02	4,743,000	3,500	0.001	0.05
Hybrid frac 02	TW + XLF	3,145,750	3,500	0.001	0.11
Hybrid frac 02	TW + XLF+Pre03	3,150,750	3,500	0.001	0.11
Hybrid frac 02	TW + XLF+Pre01	3,179,750	3,500	0.001	0.11
Hybrid frac 02	TW + XLF+Pre02	3,218,750	3,500	0.002	0.11
Hybrid frac 03	LF+XLF	126,203	3,500	0.0005	0.05
Hybrid frac 03	LF+XLF+Pre03	131,203	3,500	0.0005	0.05
Hybrid frac 03	LF+XLF+Pre01	160,203	3,500	0.001	0.12
Hybrid frac 03	LF+XLF+Pre02	199,203	3,500	0.010	0.16
Hybrid frac 04	TW+XLF+Flush	3,010,193	3,500	0.002	0.25
Hybrid frac 04	TW+XLF+Flush+Pre03	3,015,193	3,500	0.002	0.24
Hybrid frac 04	TW+XLF+Flush+Pre01	3,044,193	3,500	0.002	0.25
Hybrid frac 04	TW+XLF+Flush+Pre02	3,083,193	3,500	0.003	0.25
Hybrid frac 05	TW+XLF	2,096,100	3,500	0.001	0.12
Hybrid frac 05	TW+XLF+Pre03	2,101,100	3,500	0.001	0.12
Hybrid frac 05	TW+XLF+Pre01	2,130,100	3,500	0.001	0.12
Hybrid frac 05	TW+XLF+Pre02	2,169,100	3,500	0.002	0.13
Hybrid frac 06	LF+XLF+TW	1,362,004	3,500	0.002	0.21
Hybrid frac 06	LF+XLF+TW+Pre03	1,367,004	3,500	0.002	0.21
Hybrid frac 06	LF+XLF+TW+Pre01	1,396,004	3,500	0.002	0.21
Hybrid frac 06	LF+XLF+TW+Pre02	1,435,004	3,500	0.003	0.21
Water frac 01	WF	4,500,000	3,500	0.0004	0.04
Water frac 01	WF+Pre03	4,505,000	3,500	0.0004	0.04
Water frac 01	WF+Pre01	4,534,000	3,500	0.0004	0.04
Water frac 01	WF+Pre02	4,573,000	3,500	0.001	0.04
Water frac 02	WF	4,500,000	3,500	0.0004	0.04
Water frac 02	WF+Pre03	4,505,000	3,500	0.0004	0.04
Water frac 02	WF+Pre01	4,534,000	3,500	0.0004	0.05
Water frac 02	WF+Pre02	4,573,000	3,500	0.001	0.05
Water frac 03	WF	7,310,000	3,500	0.0003	0.03
Water frac 03	WF+Pre03	7,315,000	3,500	0.0003	0.03
Water frac 03	WF+Pre01	7,344,000	3,500	0.0003	0.03
Water frac 03	WF+Pre02	7,383,000	3,500	0.001	0.03
Water frac 04	LF+Flush	706,800	3,500	0.0002	0.03
Water frac 04	LF+Flush+Pre03	711,800	3,500	0.0003	0.03
Water frac 04	LF+Flush+Pre01	740,800	3,500	0.0004	0.04
Water frac 04	LF+Flush+Pre02	779,800	3,500	0.003	0.06

Notes:

HF systems could potentially use any of the three Pre-Frac Acids (Pre01, Pre02, Pre03).

8 Conclusions

This study, which elaborates on our earlier analysis (Gradient, 2009), addresses health risk concerns associated with HF fluid and flowback constituents in the event of spills during HF operations. We have examined several types of possible spill scenarios, both hypothetical leaks/spills occurring essentially continuously during HF operations, as well as sudden spills that might result from a temporary equipment malfunction. We adopted conservative (health protective) approaches in our analysis that more likely than not over predict the possible impacts of such spills (*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, along with conservative parameters for these models, we estimated dilution attenuation factors for each exposure pathway to assess the possible concentrations of HF and flowback 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 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) 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. 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 attenuation mechanisms which are expected to reduce concentrations in potable aquifers and surface waters to levels well below health-based drinking water concentrations. We note that the NYSDEC-proposed setback requirements and mitigation measures in the revised dSGEIS, were not considered in our analysis. Our findings indicate that the need for these proposed setbacks has not been established on the basis of a formal exposure and risk analysis and should be reconsidered. The NYSDEC proposed setbacks and restrictions are subject to public comment prior to issuing a final SGEIS.

Conservative Assumptions

- 100% of spill assumed to impact both surface water and groundwater
- Surface water dilution for as short as 10-day flow period
- 10th percentile lowest mean daily flow value used for dilution
- Selected US EPA's lowest 10th percentile groundwater dilution factor
- Adsorption of chemicals in soil largely ignored
- Degradation of chemicals in soil and groundwater ignored
- Assumed very shallow depth to groundwater (5 to 10 meters)

Our earlier analysis (Gradient, 2009), and our further analysis in this report, confirms that migration of HF fluid constituents from the Marcellus Shale up through overlying bedrock to a surface aquifer is an implausible chemical migration pathway. 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 to potable aquifers. In addition, given the significant thickness of bedrock (thousands of feet) overlying the Marcellus Shale and the natural mechanisms that inhibit fracture propagation, the fracturing pressures are not expected to result in interconnected fractures to overlying potable aquifers. 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. Finally, even if groundwater migration from the Marcellus Shale to a potable aquifer were hypothetically assumed, the rate of migration would be extremely slow and the resulting DAF would be greater than a million-fold. 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 DAF, this exposure pathway does not pose a threat to drinking water resources.

9 References

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Appendix A

Unsaturated Zone Dilution-Attenuation Factor Derivation

A.1 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 (Javandel *et al.*, 1984):

$$D_e \frac{\partial^2 C}{\partial x^2} - v_e \frac{\partial C}{\partial x} - \lambda C = \frac{\partial C}{\partial t} \quad (\text{A-1})$$

where:

$$D_e = \frac{D}{R} \quad (\text{A-2})$$

$$v_e = \frac{v}{R} \quad (\text{A-3})$$

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

C	=	aqueous phase contaminant concentration (mg/L)
x	=	distance along flow path (cm)
t	=	time (yr)
v	=	water infiltration velocity (cm/yr)
v_e	=	average chemical transport velocity in the x direction (cm/yr)
I	=	Net infiltration ($\text{cm}^3/\text{cm}^2\text{-yr}$, or equivalently cm/yr)
θ	=	soil water content ($\text{cm}^3\text{-water}/\text{cm}^3\text{-soil}$)
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:

$$R = \left(1 + \frac{K_d \rho}{\phi} \right) \quad (\text{A-4})$$

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.

$$K_d = f_{oc} K_{oc} \quad (\text{A-5})$$

Values for K_{oc} are available for certain organic chemicals in 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.

We emphasize here that with the two exceptions noted below, we have not included chemical adsorption in our leaching analysis, such that chemical "retardation" is not considered (*i.e.*, $R=1$ in all calculations except for two compounds).

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):

$$D = \alpha_L v \quad (\text{A-6})$$

where:

$$\begin{aligned} \alpha_L &= \text{longitudinal dispersivity (m)} \\ v &= \text{average pore water velocity in the x direction (m/yr)} \end{aligned}$$

The chemical concentration in leachate at a depth x in the soil column for a soil column initially contaminated with a uniform concentration C_o to a depth x_o with no biodegradation is given by (Enfield *et al.*, 1982):

$$C(x,t) = \frac{1}{2} C_o \left\{ \left[\operatorname{erf} \frac{x + x_o - v_e t}{2(D_e t)^{1/2}} \right] - \left[\operatorname{erf} \frac{x - v_e t}{2(D_e t)^{1/2}} \right] \right\} \quad (\text{A-7})$$

where:

$$\begin{aligned} C(x,t) &= \text{concentration in leachate at depth } x \text{ and time } t \text{ (mg/L)} \\ C_o &= \text{initial concentration in leachate (mg/L)} \\ x_o &= \text{initial depth of contamination (m)} \end{aligned}$$

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

$$\begin{array}{lll}
 \text{Initial Conditions:} & C = C_0 & 0 \leq x \leq x_0 \quad @ t = 0 \\
 & C = 0 & x > x_0 \quad @ t = 0 \\
 \text{Boundary Condition:} & \partial C / \partial x = 0 & x \rightarrow \infty @ t \geq 0
 \end{array}$$

It should be noted that the x-direction represents the vertical depth, measured from the ground surface (x=0).

A.2 Chemical Adsorption and Distribution in Pore Water

If a surface release of HF fluid occurs, the HF chemical can be redistributed into both the soil pore water and some portion can adsorb to the soil. The total chemical concentration per unit volume of soil is simply the sum of the concentration in the pore water (aqueous phase) plus the concentration adsorbed to soil:¹

$$C_T = \rho C_s + \theta C_w \quad (\text{A-8})$$

where:

$$\begin{array}{ll}
 C_T & = \text{total chemical concentration in pore water } (\mu\text{g}/\text{cm}^3) \\
 C_w & = \text{chemical concentration in pore water } (\text{mg}/\text{L} \equiv \mu\text{g}/\text{cm}^3) \\
 C_s & = \text{chemical concentration in soil } (\text{mg}/\text{kg} \equiv \mu\text{g}/\text{g}) \\
 \theta & = \text{soil water content } (\text{cm}^3\text{-water}/\text{cm}^3\text{-soil}) \\
 \rho & = \text{soil dry bulk density } (\text{g}/\text{cm}^3)
 \end{array}$$

Chemical adsorption to soil is commonly described by a first order (linear) isotherm (US EPA, 1996):

$$C_s = K_d C_w \left(10^{-3} \frac{\text{L}}{\text{g}} \right) \left(10^3 \frac{\text{g}}{\text{kg}} \right) \quad (\text{A-9})$$

where:

$$K_d = \text{soil-water distribution coefficient } (\text{mg}_{\text{chem}}/\text{kg}_{\text{soil}} \text{ per } \text{mg}_{\text{chem}}/\text{L}_{\text{water}}) \text{ (or when units are combined gives } \text{L}_{\text{water}}/\text{kg}_{\text{soil}})$$

¹ As a conservative measure, we have neglected possible partitioning of HF constituents in soil-vapor.

Substitution of (A-9) into (A-10) gives,

$$C_T = \rho K_d C_w + \theta C_w \quad (\text{A-10})$$

or

$$C_T = C_w (\rho K_d + \theta)$$

Immediately after a release, the total concentration of the HF constituent would be in the aqueous phase:

$$C_T = \theta C_{HF} \quad (\text{A-11})$$

Substituting the right side of Equation (A-12) into the left side of Equation (A-11), gives the initial pore water concentration of the HF constituent:

$$\theta C_{HF} = C_w (\rho K_d + \theta)$$

which upon rearranging gives,

$$C_w = C_{HF} \frac{\theta}{(\rho K_d + \theta)} \quad (\text{A-13})$$

For a chemical with little or no adsorption ($K_d \approx 0$), Equation (A-13) indicates the chemical concentration in pore water would equal the chemical concentration in the HF fluid (*e.g.*, the ratio on the right side of the equation reduces to $\theta/\theta = 1$).

Equation (A-13) can be rearranged in terms of a soil-pore water DAF as simply the ratio of the constituent concentration in the HF fluid, divided by the constituent concentration in pore water:

$$DAF_w = \frac{C_{HF}}{C_w}$$

or

$$DAF_w = \frac{(\rho K_d + \theta)}{\theta} \quad (\text{A-14})$$

A pore water DAF_w was quantified for the three compounds listed below, all of which adsorb readily to soil. These pore water DAF values are multiplied by the leaching DAF_L values (summarized below in Section A.3) for these compounds to account for chemical partitioning in the soil. In our 2009

study (Gradient, 2009) we had applied pore water DAFs to all chemicals. With the exception of these three chemicals listed below, as a conservative simplification in our current analysis we have not considered adsorption as an attenuation process.

Chemical	CAS	K_{oc}	K_d	Pore Water DAF
Cobalt acetate	71-48-7	-	125.9	630
Alkyl (C14-C16) olefin sulfonate, sodium salt	68439-57-6		2104	12.6
Naphthenic acid ethoxylate	68410-62-8		2,412	14.5

Soil $f_{oc} = 0.006$ g/g (USEPA, 1996 used in calculation of K_d for organic constituents).

A.3 Model Parameters and Calculated Unsaturated Zone DAFs

The required parameters, and the values used in our evaluation are provided below. Because our analysis must be generally applicable to a range of conditions, we have selected parameters based on typical defaults adopted by US EPA (1996) in its development of chemical "Soil Screening Levels" or SSLs. In general, these parameters are considered appropriate for a general screening level evaluation such as this one.

Parameter	Value	Source/Notes
Net infiltration (cm/yr)	36.8 cm/yr	See Appendix B
Water content (θ)	$0.3 \text{ cm}^3/\text{cm}^3$	US EPA (1996)
Porosity (ϕ)	$0.43 \text{ cm}^3/\text{cm}^3$	US EPA (1996)
Bulk density (ρ)	$1.5 \text{ g}/\text{cm}^3$	US EPA (1996)
Organic carbon (f_{oc})	0.006	US EPA (1996)
Chemical OC partition coefficient (K_{oc})	N/A	Not needed ($R=1$)
Disperivity (α_L)	0.25 cm to 0.5 cm	Freeze and Cherry (1979)
Initial soil contamination depth (x_o)	1 cm, 3 cm	See text Section 5

Using these model parameter values, we calculated the average chemical concentration within the leaching "plume," when the midpoint of the plume intersects the water table. We calculated this concentration profile using shallow water table depths of 5 and 10 meters. In the table below, we summarize the DAFs for the leachate as it enters the groundwater. As the results show, as the depth to the water table increases, the DAF values also increase due to the increased dilution and attenuation of the "plume."

Table A.1 Summary of Unsaturated Zone Dilution Attenuation Factors at Water Table

Depth to Water Table	Unsaturated Zone DAF _L	
	Dispersivity (α_L)	
	0.25 cm	0.5 cm
Initial Contamination Depth $x_0 = 1$ cm		
5 meters	105	150
10 meters	150	195
Initial Contamination Depth $x_0 = 3$ cm		
5 meters	40	55
10 meters	50	70

Note: DAF: Dilution Attenuation Factor = $1/(C/C_0)$. These values assume no biodegradation.

The DAF_L values are influenced not only by the depth to the water table, but also by the amount of chemical dispersion, the parameter "D" in the ADE, which is modeled as a function of the dispersivity (α_L). We have calculated the DAFs for a range of dispersivity, ranging from what is considered a low value of 0.25 cm (for soils typical of coarse grained materials), up to a value two-fold higher. As can be seen from the results above, the DAF_L values increase by approximately 30% to 40% when the dispersivity is doubled.

The range of dispersivity values we used (0.25 cm to 0.5 cm) is consistent with the range of experimental values determined in laboratory soil column studies (Toride *et al.*, 2003). Those column studies however used well graded sandy materials, that are unlikely to exhibit the large variability (heterogeneity) in particle size (and pore size) distribution found under field conditions. For example, 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 large variability of several orders of magnitude. In our derivation of the unsaturated zone DAF, we have examined flow length scales of 5 to 10 meters. Thus, the dispersivity values we used in the model range from 0.03% to 0.1% of these flow length scales, which would place these dispersivities at the very low end of the range observed by Gelhar *et al.* (1992). Based on the foregoing, the dispersivity values used in the ADE for determining the unsaturated zone DAFs are likely to be quite conservative, and under predict actual dilution under field conditions.

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Appendix B

Determination of Representative Surface Water Flow and Net Infiltration

An evaluation of the impacts associated with a potential surface release of HF additives, and their potential impacts *via* runoff to surface water or subsurface migration to groundwater, requires information on typical stream flows within the region, as well as net infiltration (groundwater recharge). This appendix presents the data sources and a summary of this information pertinent to the southern tier region of New York where the Marcellus Shale formation exists.

B.1 Stream Discharge Data

Representative stream flow rates (*e.g.*, daily discharge) of the receiving water are needed in order to estimate the dilution of chemicals, if discharged to a stream or river. The volume of surface water that will dilute a given inadvertent release of HF fluid is clearly variable within the southern tier of New York where development of natural gas from the Marcellus Shale formation is proposed. For example, 341 catchment basin areas in NYS range from 0.41 to 4,773 mi² and the median area is 57.9 mi² (USGS, 2006, Table 10).

Surface water that ends up in a stream proximate to HF operations may originate from surface runoff and/or from groundwater recharge. In order to evaluate the range of representative stream flow within the Marcellus region, we analyzed stream flow data available from the extensive network of US Geological Survey (USGS) gauging stations in this region of New York.

Representative stream flows in watershed basins overlying the Marcellus Shale were evaluated using daily stream discharge data from the USGS. The extensive network of USGS gauging stations covering this region of New York is shown in Figure B.1. In order to obtain characteristic surface water discharges over the entire Marcellus Shale formation, we used U.S. EPA's "Better Evaluation Science Integrating point & Non-point Sources" (BASINS), version 4.0.¹ BASINS 4.0 downloads data directly from the USGS National Water Information System (NWIS).² Using the GIS interface in BASINS 4.0 we selected all discharge gauges overlying the Marcellus Shale region in NYS as shown in Figure B.1, and then downloaded NWIS data for each stream including drainage area and mean daily discharge data.

Using the analysis tools in BASINS 4.0, we calculated the annual mean daily flows³ from the daily discharge data for each of the selected stream gauges with sufficient data to reliably estimate stream

¹ Downloaded from: http://water.epa.gov/scitech/datait/models/basins/BASINS4_index.cfm (US EPA, 2011)

² <http://waterdata.usgs.gov/nwis> (USGS, 2011)

³ For a given stream gauge, the average by year for the daily mean discharge values for only those years with a complete daily mean discharge dataset (at least 365 data points).

discharge during representative flow conditions. This resulted in a flow dataset comprised of 147 discharge gauges overlying the Marcellus Shale. The drainage areas for these gauges ranged from 0.11 to 4,773 mi² with a median area of 87 mi². Table B.1.1 presents summary statistics for the maximum daily flow,⁴ average annual maximum daily flow,⁵ average annual mean daily flow,⁶ and the lowest annual mean daily flow⁷ for the Marcellus Shale regional stream flow dataset. Stream flow analysis results for individual stations are presented in Table B.1.2.

**Table B.1.1
Marcellus Shale Regional Stream Flow Analysis Results**

	Drainage Area mi ²	Maximum Mean Daily Flow		Average Annual Maximum Daily Flow		Average Annual Mean Daily Flow		Lowest Annual Mean Daily Flow	
		cfs	MGD	cfs	MGD	cfs	MGD	cfs	MGD
Average	324	14,891	9,625	5,406	3,494	480	310	263	170
Minimum	0.11	0.50	0.32	0.31	0.20	0.068	0.044	0.053	0.034
Maximum	4,773	163,000	105,356	65,119	42,090	7,850	5,074	4,633	2,994
10th percentile	10	397	257	199	129	19	12	8.1	5.2
25th percentile	35	1,780	1,151	805	520	56	36	35	22
50th percentile	87	3,838	2,476	2,093	1,353	126	82	82	53
75th percentile	276	11,400	7,368	4,813	3,111	378	244	205	132
90th percentile	863	39,240	25,363	15,195	9,822	1,318	852	667	431

⁴ The maximum daily flow value for a given stream gauge.

⁵ The average of the annual maximum daily flow values for a given stream gauge.

⁶ The average of the annual mean daily flow values for a given stream gauge.

⁷ The minimum of the annual mean daily flow values for a given stream gauge.

Table B.1.2. Summary of USGS NWIS Discharge Data for Stream Gauges over Marcellus Shale Formation in New York State

USGS Discharge Station	Station Name	Drainage area [mi ²]	Years of Data ^[a]	Maximum daily discharge		Mean annual maximum daily discharge		Average Annual Mean Daily Flow		Lowest Annual Mean Daily Flow	
				[cfs]	[MGD]	[cfs]	[MGD]	[cfs]	[MGD]	[cfs]	[MGD]
1413088	EAST BRANCH DELAWARE RIVER AT ROXBURY NY	14	7	407	263	281	182	27	17	14	9.2
1413398	BUSH KILL NEAR ARKVILLE NY	47	10	2,370	1,532	1,325	856	99	64	58	37
1413408	DRY BROOK AT ARKVILLE	82	11	4,580	2,960	2,617	1,691	185	120	108	70
1413500	EAST BR DELAWARE R AT MARGARETVILLE NY	163	70	11,300	7,304	4,195	2,712	313	202	165	106
1414000	PLATTE KILL AT DUNRAVEN NY	35	31	1,740	1,125	847	547	69	44	38	25
1414500	MILL BROOK NEAR DUNRAVEN NY	25	70	2,080	1,344	786	508	56	36	36	23
1415000	TREMPER KILL NEAR ANDES NY	33	70	1,830	1,183	790	510	60	39	29	19
1415500	TERRY CLOVE KILL NEAR PEPACTON NY	14	24	1,070	692	404	261	27	17	14	9.2
1416500	COLES CLOVE KILL NEAR PEPACTON NY	28	8	1,230	795	754	487	57	37	39	25
1417000	EAST BRANCH DELAWARE RIVER AT DOWNSVILLE NY	372	66	17,700	11,441	4,723	3,053	319	206	29	19
1417500	EAST BR DELAWARE RIVER AT HARVARD NY	458	62	22,600	14,608	6,975	4,508	533	344	150	97
1418000	BEAVER KILL NEAR TURNWOOD NY	41	10	2,490	1,609	1,607	1,039	113	73	91	59
1418500	BEAVER KILL AT CRAIGIE CLAIR NY	82	32	5,140	3,322	2,638	1,705	191	123	118	77
1419000	WILLOWEMOC CREEK AT DEBRUCE NY	41	3	2,610	1,687	1,840	1,189	114	74	98	63
1419500	WILLOWEMOC CREEK NR LIVINGSTON MANOR NY	63	32	4,020	2,598	2,073	1,340	143	92	78	51
1420000	LITTLE BEAVER KILL NR LIVINGSTON MANOR NY	20	56	1,810	1,170	736	476	45	29	23	15
1420500	BEAVER KILL AT COOKS FALLS NY	241	93	23,500	15,189	7,865	5,084	568	367	307	198
1420980	E BR DELAWARE RIVER ABV READ CR AT FISHS EDDY NY	766	90	38,600	24,949	15,804	10,215	1,364	881	610	394
1421000	EAST BR DELAWARE R AT FISHS EDDY NY	784	94	55,700	36,002	16,790	10,853	1,373	888	610	394
1421610	WEST BRANCH DELAWARE RIVER AT HOBART NY	16	7	412	266	308	199	29	19	17	11
1421614	TOWN BROOK TRIBUTARY SOUTHEAST OF HOBART NY	0.76	9	69	45	32	21	1.8	1.2	0.90	0.58
1421618	TOWN BROOK SOUTHEAST OF HOBART NY	14	10	839	542	508	328	31	20	17	11
1421900	W BR DELAWARE RIVER UPSTREAM FROM DELHI NY	134	43	6,380	4,124	3,026	1,956	239	154	136	88
1422000	WEST BRANCH DELAWARE RIVER AT DELHI NY	142	32	5,320	3,439	2,859	1,848	230	148	136	88
1422389	COULTER BROOK NEAR BOVINA CENTER NY	0.76	10	26	17	16	10	1.7	1.1	0.82	0.53
1422500	LITTLE DELAWARE RIVER NEAR DELHI NY	50	42	2,150	1,390	1,155	747	93	60	51	33
1422700	W B DELAWARE R NR HAMDEN NY	256	7	8,720	5,636	5,944	3,842	340	220	264	171
1422738	WOLF CREEK AT MUNDAL NY	0.61	9	74	48	23	15	1.2	0.77	0.67	0.43
1422747	EAST BROOK EAST OF WALTON NY	25	9	3,540	2,288	957	619	49	32	27	17
1423000	WEST BRANCH DELAWARE RIVER AT WALTON NY	332	57	22,400	14,478	8,011	5,178	596	385	329	213
1423500	DRYDEN BROOK NEAR GRANTON NY	8.1	14	347	224	203	131	14	8.8	8.1	5.3
1424000	TROUT CREEK NEAR ROCKROYAL NY	20	14	715	462	510	329	30	19	19	12
142400103	TROUT CREEK NEAR TROUT CREEK NY	20	25	1,550	1,002	566	366	35	22	19	12
1424500	TROUT CREEK AT CANNONVILLE NY	50	22	2,450	1,584	1,195	772	85	55	60	39
1425000	WEST BR DELAWARE RIVER AT STILESVILLE NY	456	55	27,700	17,904	6,590	4,259	645	417	76	49
1425500	COLD SPRING BROOK AT CHINA NY	1.5	33	89	58	44	28	2.6	1.7	1.5	1.0
1425675	OQUAGA CREEK NEAR NORTH SANFORD NY	4.7	11	237	153	115	74	9.1	5.9	5.7	3.7
1426000	OQUAGA CREEK AT DEPOSIT NY	68	32	3,460	2,236	1,700	1,099	109	70	64	41
1426500	WEST BRANCH DELAWARE RIVER AT HALE EDDY NY	595	94	35,200	22,752	10,437	6,746	955	617	208	135
1427405	DELAWARE R NR CALLICOON NY	1708	7	40,200	25,984	21,429	13,851	2,860	1,849	2219	1434
1427500	CALLICOON CREEK AT CALLICOON NY	110	41	5,550	3,587	2,640	1,706	177	114	84	54
1427510	DELAWARE RIVER AT CALLICOON NY	1820	32	127,000	82,088	34,616	22,374	2,860	1,848	1679	1085
1428000	TENMILE RIVER AT TUSTEN NY	46	26	3,340	2,159	919	594	65	42	28	18
1428500	DELAWARE R ABOVE LACKAWAXEN R NR BARRYVILLE NY	2020	67	140,000	90,490	38,400	24,820	3,323	2,148	1384	894
1432900	MONGAUP RIVER AT MONGAUP VALLEY NY	77	5	3,830	2,476	2,976	1,924	179	116	139	90
1433500	MONGAUP RIVER NEAR MONGAUP NY	200	55	12,300	7,950	2,288	1,479	344	223	154	100
1434000	DELAWARE RIVER AT PORT JERVIS NY	3070	103	163,000	105,356	54,093	34,964	5,247	3,391	2140	1383
143400680	E BR NEVERSINK R NORTHEAST OF DENNING NY	8.9	17	1,000	646	541	350	32	21	20	13
1434017	EAST BR NEVERSINK RIVER NR CLARYVILLE NY	23	16	2,060	1,331	1,025	663	74	48	44	29
1434025	BISCUIT BK ABOVE PIGEON BK AT FROST VALLEY NY	3.7	24	500	323	182	117	11	7	6.5	4.2
1434092	SHELTER CREEK BELOW DRY CREEK NR FROST VALLEY NY	0.62	14	52	34	28	18	2	1	1.1	0.74
1434105	HIGH FALLS BROOK AT FROST VALLEY NY	2.7	4	67	43	55	36	7	4	5.5	3.5
1434498	WEST BRANCH NEVERSINK R AT CLARYVILLE	34	16	3,100	2,004	1,952	1,261	113	73	68	44
1435000	NEVERSINK RIVER NEAR CLARYVILLE NY	67	67	6,090	3,936	2,958	1,912	193	125	123	79
1435500	NEVERSINK RIVER AT HALLS MILLS NEAR CURRY NY	69	11	5,900	3,814	2,939	1,900	197	128	124	80
1436000	NEVERSINK RIVER AT NEVERSINK NY	93	66	6,920	4,473	1,737	1,123	94	61	11	7.3
1436500	NEVERSINK RIVER AT WOODBOURNE NY	113	50	7,700	4,977	2,160	1,396	154	99	49	32
1436690	NEVERSINK RIVER AT BRIDGEVILLE NY	171	15	15,400	9,954	4,381	2,832	240	155	152	98
1437000	NEVERSINK RIVER AT OAKLAND VALLEY NY	223	44	12,300	7,950	4,903	3,169	390	252	143	92
1437500	NEVERSINK RIVER AT GODEFFROY NY	307	70	21,000	13,574	5,157	3,333	483	312	204	132
1496500	OAKS CREEK AT INDEX NY	102	59	2,280	1,474	1,182	764	171	111	101	65
1497000	CHERRY VALLEY CREEK AT WESTVILLE NY	81	2	2,500	1,616	2,275	1,470	124	80	104	67
1497500	SUSQUEHANNA R AT COLLIERSVILLE NY	349	43	7,540	4,874	4,177	2,700	553	358	338	219
1498500	CHARLOTTE CREEK AT WEST DAVENPORT NY	167	36	5,910	3,820	3,033	1,960	250	162	140	91
1499000	OTEGO CREEK NEAR ONEONTA NY	108	27	3,600	2,327	2,201	1,423	166	107	100	65
1500000	OULEOUT CREEK AT EAST SIDNEY NY	103	67	3,820	2,469	1,732	1,119	176	114	97	63
1500500	SUSQUEHANNA RIVER AT UNADILLA NY	982	58	21,000	13,574	12,151	7,854	1,575	1,018	932	603
1501000	UNADILLA RIVER NEAR NEW BERLIN NY	199	43	5,980	3,865	3,444	2,226	317	205	209	135
1501500	SAGE BROOK NEAR SOUTH NEW BERLIN NY	0.61	34	44	28	17	11	1	1	0.63	0.41
1502000	BUTTERNUT CREEK AT MORRIS NY	60	56	3,700	2,392	1,426	922	100	64	60	39
1502500	UNADILLA RIVER AT ROCKDALE NY	520	67	19,000	12,281	8,761	5,663	864	558	524	339
1503000	SUSQUEHANNA RIVER AT CONKLIN NY	2232	95	72,100	46,602	30,587	19,770	3,628	2,345	2066	1335
1505000	CHENANGO RIVER AT SHERBURNE NY	263	59	9,840	6,360	4,031	2,605	407	263	257	166
1505500	CANASAWACTA CREEK NEAR SOUTH PLYMOUTH NY	58	29	2,900	1,874	1,415	914	98	63	72	46
1507000	CHENANGO RIVER AT GREENE NY	593	32	16,500	10,665	8,710	5,630	885	572	595	385
1507500	GENEGANTSLET CR AT SMITHVILLE FLATS NY	82	31	3,980	2,573	1,994	1,289	135	87	87	56
1508000	SHACKHAM BROOK NEAR TRUXTON NY	3.2	35	170	110	88	57	5.3	3.4	3.5	2.2
1508500	ALBRIGHT CREEK AT EAST HOMER NY	6.8	29	382	247	194	126	12	7.6	8.0	5.2
1508803	WEST BR TIOUGHNIOGA RIVER AT HOMER NY	72	14	1,990	1,286	1,078	697	126	82	82	53
1509000	TIOUGHNIOGA RIVER AT CORTLAND NY	292	67	12,600	8,144	5,644	3,648	505	326	307	198
1509150	GRIDLEY CREEK ABOVE EAST VIRGIL NY	10	6	1,500	970	731	472	23	15	13	8.5

Table B.1.2. Summary of USGS NWIS Discharge Data for Stream Gauges over Marcellus Shale Formation in New York State

USGS Discharge Station	Station Name	Drainage area [mi ²]	Years of Data ^[a]	Maximum daily discharge		Mean annual maximum daily discharge		Average Annual Mean Daily Flow		Lowest Annual Mean Daily Flow	
				[cfs]	[MGD]	[cfs]	[MGD]	[cfs]	[MGD]	[cfs]	[MGD]
1510000	OTSELIC RIVER AT CINCINNATUS NY	147	63	8,800	5,688	3,716	2,402	274	177	161	104
1510500	OTSELIC RIVER NEAR UPPER LISLE NY	217	31	8,200	5,300	5,163	3,337	377	244	257	166
1512500	CHENANGO RIVER NEAR CHENANGO FORKS NY	1483	94	55,400	35,808	21,518	13,908	2,457	1588	1548	1000
1514000	OWEGO CREEK NEAR OWEGO NY	185	47	9,540	6,166	4,580	2,961	281	181	167	108
1515000	SUSQUEHANNA RIVER NEAR WAVERLY NY	4773	64	124,000	80,148	65,119	42,090	7,850	5074	4633	2994
1520500	TIOGA RIVER AT LINDLEY NY	771	64	63,000	40,721	14,789	9,559	815	527	387	250
1521500	CANISTEO RIVER AT ARKPORT NY	31	70	1,300	840	634	410	36	23	18	12
1522000	CANISTEO RIVER AT HORNE LL NY	94	4	2,590	1,674	2,113	1,365	78	51	50	32
1522500	KARR VALLEY CREEK AT ALMOND NY	27	30	1,700	1,099	856	553	30	19	16	10
1523500	CANACADEA CREEK NEAR HORNE LL NY	58	65	3,970	2,566	1,139	736	68	44	37	24
1524500	CANISTEO R BELOW CANACADEA CR @ HORNE LL NY	158	65	7,440	4,809	2,153	1,392	162	105	96	62
1525000	BENNETTS CR AT CANISTEO NY	95	8	3,960	2,560	2,648	1,711	108	70	60	39
1525500	CANISTEO RIVER AT WEST CAMERON NY	340	32	11,500	7,433	6,389	4,130	342	221	206	133
1525981	TUSCARORA CREEK ABOVE SOUTH ADDISON NY	102	7	7,180	4,641	2,934	1,897	119	77	67	43
1526000	TUSCARORA CR NR SOUTH ADDISON NY	114	32	5,820	3,762	2,706	1,749	93	60	43	27
1526500	TIOGA RIVER NEAR ERWINS NY	1377	89	110,000	71,099	23,375	15,109	1,415	914	697	451
1527000	COHOCTON RIVER AT COHOCTON NY	52	30	2,120	1,370	487	315	56	36	32	21
1527500	COHOCTON RIVER AT AVOCA NY	152	12	3,450	2,230	2,274	1,470	197	128	115	74
1528000	FIVEMILE CREEK NEAR KANONA NY	67	57	4,180	2,702	1,278	826	76	49	38	24
1529000	MUD CREEK NEAR SAVONA NY	77	44	5,110	3,303	821	530	42	27	12	7.6
1529500	COHOCTON RIVER NEAR CAMPBELL NY	470	89	24,400	15,771	6,377	4,122	467	302	220	142
1529950	CHEMUNG RIVER AT CORNING NY	2006	33	87,100	56,298	26,536	17,152	2,210	1429	1104	714
1530500	NEWTOWN CREEK AT ELMIRA NY	78	69	3,030	1,958	1,534	991	87	56	39	26
1531000	CHEMUNG RIVER AT CHEMUNG NY	2506	97	159,000	102,771	40,892	26,431	2,615	1690	1212	783
3011000	GREAT VALLEY CREEK NEAR SALAMANCA NY	137	16	8,500	5,494	4,233	2,736	223	144	154	100
3011020	ALLEGHENY RIVER AT SALAMANCA NY	1608	104	67,900	43,888	23,315	15,070	2,792	1805	1620	1047
3013000	CONEWANGO CREEK AT WATERBORO NY	290	54	8,150	5,268	3,811	2,463	541	349	303	196
3014500	CHADAKOIN RIVER AT FALCONER NY	194	72	2,020	1,306	1,232	796	365	236	197	127
4213410	CATTARAUGUS CR NR ARCADE NY	79	4	3,030	1,958	2,340	1,512	122	79	104	67
4213450	BUTTERMILK CREEK NEAR SPRINGVILLE NY	30	5	1,560	1,008	949	614	48	31	41	26
4213500	CATTARAUGUS CREEK AT GOWANDA NY	436	64	22,900	14,802	9,698	6,268	754	487	459	297
4214000	CATTARAUGUS CREEK AT VERSAILLES NY	466	7	16,000	10,342	10,414	6,731	672	435	553	358
4220470	DYKE CREEK NEAR ANDOVER NY	38	3	735	475	653	422	48	31	39	25
4220500	DYKE CR AT WELLSVILLE NY	72	4	3,580	2,314	2,093	1,353	100	65	75	49
4221000	GENESEE RIVER AT WELLSVILLE NY	288	37	13,800	8,920	5,428	3,508	394	255	231	149
4221500	GENESEE RIVER AT SCIO NY	308	55	12,500	8,079	5,493	3,550	379	245	210	136
4221600	VAN CAMPEN CREEK AT FRIENDSHIP NY	46	3	3,020	1,952	1,548	1,001	67	43	52	34
4221720	ANGELICA CREEK AT TRANSIT BRIDGE NY	87	3	4,350	2,812	2,287	1,478	107	69	85	55
4221820	GENESEE R AT BELFAST NY	644	2	7,390	4,777	6,895	4,457	692	447	676	437
4222000	CANEADEA CREEK AT CANEADEA NY	62	18	3,690	2,385	1,261	815	84	55	40	26
4222900	EAST KOY CREEK AT EAST KOY NY	47	4	880	569	609	394	58	38	42	27
4223000	GENESEE RIVER AT PORTAGEVILLE NY	984	99	72,000	46,538	17,856	11,541	1,287	832	661	428
4223500	GENESEE RIVER AT ST. HELENA NY	1009	3	24,300	15,707	17,723	11,456	1,233	797	839	542
4224650	CANASERAGA CREEK AT CANASERAGA NY	58	3	815	527	627	405	54	35	40	26
4224775	CANASERAGA CREEK ABOVE DANVILLE NY	89	31	3,680	2,379	1,432	926	102	66	65	42
4225000	CANASERAGA CREEK NEAR DANVILLE NY	152	53	5,430	3,510	2,404	1,554	150	97	80	52
4225500	CANASERAGA CREEK AT GROVELAND NY	180	11	4,500	2,909	2,635	1,703	195	126	128	83
4226000	KESHEQUA CR @ CRAIG COLONY @ SONYEA NY	68	16	3,120	2,017	1,450	937	52	34	37	24
4227000	CANASERAGA CREEK AT SHAKERS CROSSING NY	335	44	5,150	3,329	3,196	2,066	308	199	150	97
4227500	GENESEE RIVER NEAR MOUNT MORRIS NY	1424	96	45,700	29,539	13,073	8,450	1,715	1109	906	586
4228900	SPRINGWATER CREEK AT SPRINGWATER NY	10	4	128	83	62	40	8.0	5.2	5.2	3.3
4232482	KEUKA LAKE OUTLET AT DRESDEN NY	207	42	2,200	1,422	930	601	196	127	85	55
4233000	CAYUGA INLET NEAR ITHACA NY	35	70	1,750	1,131	631	408	40	26	16	10
4233286	SIXMILE CREEK AT BROOKTONDALE NY	27	5	1,340	866	837	541	54	35	44	28
4233300	SIXMILE CREEK AT BETHEL GROVE, NY	39	12	2,700	1,745	1,066	689	65	42	41	27
4234000	FALL CREEK NEAR ITHACA NY	126	82	8,280	5,352	2,499	1,615	189	122	95	61
4234018	SALMON CREEK AT LUDLOWVILLE NY	82	3	1,280	827	842	544	79	51	43	28
4235150	FLINT CREEK AT POTTER NY	31	10	2,890	1,868	660	427	34	22	15	10.0
4235250	FLINT CREEK AT PHELPS NY	102	40	2,670	1,726	1,189	768	93	60	34	22
4235300	OWASCO INLET AT MORAVIA NY	106	8	6,400	4,137	3,075	1,988	152	98	92	60
4235440	OWASCO OUTLET AT GENESEE ST., AUBURN NY	207	9	2,560	1,655	1,586	1,025	317	205	194	125
4236500	SKANEATELES CREEK AT WILLOW GLEN NY	76	11	204	132	143	92	75	49	42	27
4237946	ONONDAGA CR TRIB 6 BLW MUDBOIL AREA AT TULLY NY	0.32	16	23	15	7	5	0.98	0.63	0.61	0.39
4237962	ONONDAGA CREEK NEAR CARDIFF NY	34	6	1,070	692	743	480	70	45	56	36
424014980	SPAFFORD CR TRIB NR SAWMILL RD NR SPAFFORD NY	0.11	5	0.50	0.32	0.31	0.20	0.068	0.044	0.053	0.034
4240180	NINEMILE CREEK NEAR MARIETTA NY	45	43	931	602	272	176	42	27	3.8	2.5
Average		324	37	14,891	9,625	5,406	3,494	480	310	263	170
Minimum		0.11	2	0.50	0.32	0.31	0.20	0.068	0.044	0.053	0.034
Maximum		4,773	104	163,000	105,356	65,119	42,090	7,850	5,074	4,633	2,994
10th percentile		10	5	397	257	199	129	19	12	8.1	5.2
25th percentile		35	10	1,780	1,151	805	520	56	36	35	22
50th percentile		87	32	3,830	2,476	2,093	1,353	126	82	82	53
75th percentile		276	59	11,400	7,368	4,813	3,111	378	244	205	132
90th percentile		863	71	39,240	25,363	15,195	9,822	1,318	852	667	431

Notes:
 1. Data from USGS NWIS Database, accessed by BASINS 4.0
 2. Stream gages are located above the Marcellus shale formation in New York State
 3. Individual discharge station flow statistics calculated using BASINS 4.0
 [a] Defined as years with 365 or more daily mean discharge values

B.2 Estimation of Net Infiltration of Precipitation to Groundwater

The downward leaching of chemicals from a shallow spill into an underlying aquifer is driven by the amount of water percolating through the unsaturated (vadose) zone. This percolation (*e.g.*, inches/year or cm/yr) is determined "net" infiltration of precipitation. Net infiltration (I) is that portion of total precipitation (P) that is not lost *via* runoff (R) or evapotranspiration (ET) or changes in water storage (ΔS) within the unsaturated zone:

$$I = P - ET - R - \Delta S$$

Using both water balance and stream baseflow estimation methods, the USGS (1998) estimated net infiltration for the Batavia Kill Basin in Southern New York (termed "effective recharge" in the USGS report). Baseflow, which is defined as the component of stream flow that originates from groundwater discharge rather than overland runoff, provides an estimate of net infiltration. Conceptually, baseflow is the net infiltration to groundwater minus losses⁸ that may occur in transport of infiltrated runoff from recharge zone to stream discharge point. Although the extent to which baseflow is less than net infiltration will vary based on local conditions, the Batavia Kill Basin overlying the Marcellus Shale has baseflow of nearly 98% of net infiltration (USGS, 1998). The USGS estimated that the effective recharge (baseflow) amounted to approximately 34% of total precipitation in this basin, or 36.8 cm/yr.

Another study by USGS (2007) provides estimates of the variation of the annual baseflow component of the surface flow for streams within the Delaware River Watershed in NYS.⁹ The baseflow estimates were developed using both hydrograph separation and spatial data (GIS) analysis of the streams. Since portions of this watershed are found atop the Marcellus Shale Formation, this information provides additional information from which to estimate net infiltration in the region. Of the total 147 sub-watersheds in the Delaware River Watershed, 28 of them fall partially or fully within NYS, with watershed areas ranging from 25.8 to 210 mi². Table B.2.1 summarizes the range of annual baseflow for the sub-watersheds within NYS for return periods of 2 years (*e.g.*, frequent values), up to 50 years (*e.g.*, infrequent values occurring once every 50 years). The overall minimum baseflow reported for the Delaware River Watershed in NYS is 14.5 cm/yr, and the maximum is 51.3 cm/yr.

⁸ Such as groundwater evapo-transpiration, aquifer withdrawals from wells, or groundwater that reappears as surface springs/wetlands, prior to discharge to a receiving water.

⁹ The paper includes sub-watersheds in Pennsylvania and New Jersey, however the discussion here is based only on those sub-watersheds of the Delaware River Watershed that are in New York.

As noted above, baseflow is a measure of net infiltration. The analysis of baseflow in subwatersheds of the Delaware River within NYS, indicates that the net infiltration of 36.8 cm/yr determined by the USGS for the Batavia Kill Basin (north of the Delaware River Watershed) is consistent with the range of baseflow values with return periods ranging from 2 to 10 years, or in other words values that occur with reasonable frequency. Therefore, we used a net infiltration value of 36.8 cm/yr in our leaching analysis.

Table B.2.1
Delaware River Basin Average Annual
Baseflow

Return Period	(MGD/mi ²)	(cm/yr)
2-yr (hi)	0.962	51.3
2-yr (lo)	0.517	27.6
5-yr (hi)	0.741	39.5
5-yr (lo)	0.401	21.4
10-yr (hi)	0.691	36.9
10-yr (lo)	0.336	17.9
25-yr (hi)	0.607	32.4
25-yr (lo)	0.272	14.5
50-yr (hi)	0.554	29.6
50-yr (lo)	0.305	16.3

Source: USGS (2007, Table 5)

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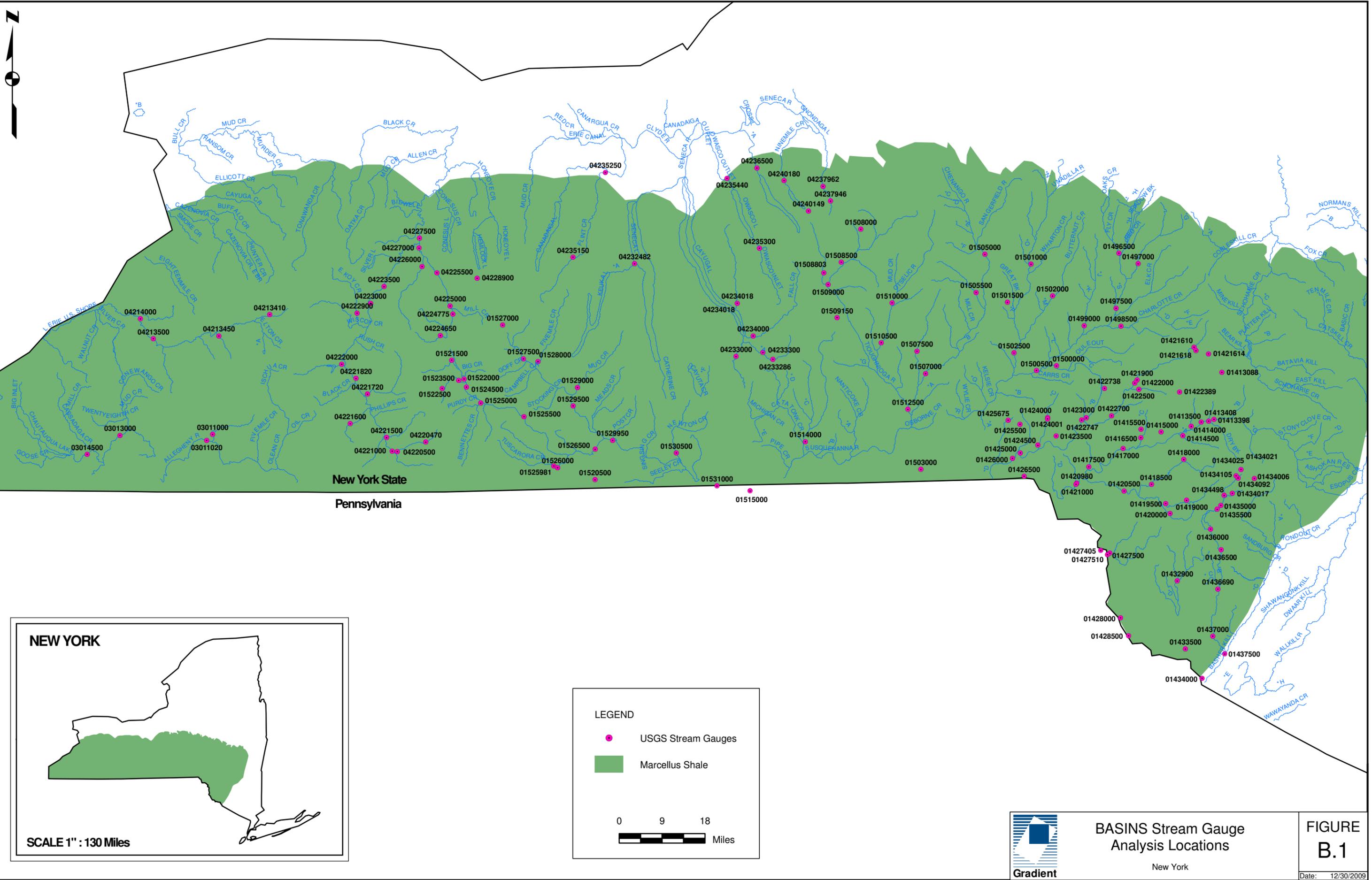
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**BASINS Stream Gauge
Analysis Locations**

New York

**FIGURE
B.1**

Date: 12/30/2009

Appendix C

Analysis of Hypothetical Upward Migration of HF Constituents From the Marcellus Shale Formation

C.1 Potential for Upward HF Constituent Migration via Rock Pores (Primary Porosity)

As part of the Draft Supplemental Generic Environmental Impact Statement (dSGEIS) prepared by the New York Department of Environmental Conservation (NYSDEC, 2009), ICF (2009) evaluated the potential for HF additives to migrate upward to an overlying potable aquifer *via* rock pores using extremely conservative and hypothetical worst-case assumptions. For example, one of the key simplifying assumptions of the ICF analysis was that the Marcellus Shale remains under fracturing pressure for an indefinitely long time period (*i.e.*, until pressure within the formation stops changing with time – mathematically referred to as steady state). Clearly, this is a hypothetical worst-case assumption because in reality the HF pressure is only applied for one to two days and "steady state" will not be achieved. Consequently, the application of the HF pressure is like a short-term pressure pulse and not the constant pressure application postulated in the ICF analysis. In addition, the ICF analysis utilized a number of other conservative assumptions:

- A range of shale hydraulic conductivity values from 10^{-4} to 10^{-9} cm/sec *vs.* more typical values of 10^{-7} to 10^{-11} cm/s (Hornberger *et al.*, 1998);
- Assumed complete drawdown in a 1,000-ft well (*i.e.*, well had been completely dewatered due to pumping);
- Minimum Marcellus Shale depth of 2,000 ft bgs compared to typical values of 4,000 to 8,500 ft bgs in the area targeted for gas exploration (CRS, 2009);
- Potable aquifer depths up to 1,000 ft – somewhat deeper than the maximum depth reported (850 ft) in southern NYS; and
- Ignored attenuation due to adsorption, dispersion, dilution, and biodegradation – mechanisms expected to reduce the migration rate of HF additives in the subsurface and also reduce constituent concentrations.

Despite using these conservative, hypothetical worst-case assumptions, the ICF analysis indicated that the duration of HF pressure application was several orders of magnitude shorter than the time required for migration of water to the nearest potable aquifer (*i.e.*, pressure application period of days *vs.* migration time of thousands of years). This analysis clearly demonstrates that even under unrealistic conditions the migration of HF additives *via* rock pores to overlying drinking water aquifers is implausible during the fracturing period.

Under realistic conditions, the HF process causes a much smaller perturbation in the system than the scenario modeled by ICF. The effective isolation of the Marcellus Shale by the large thickness of

overlying low permeability and impermeable rocks will keep the modest pressure increase (1.5 to 2 times ambient reservoir pressure) localized during the one- to two-day treatment period. Pressures will drop off rapidly with distance from the injection point and are not likely to propagate very far, if at all, above the Marcellus. Thus, it is anticipated that the short-term pressure pulse applied during the fracturing period will never reach an overlying potable aquifer.

Fluid Capture and Isolation

After HF stimulation, fluid extraction begins in the pumping well, recovering a portion of injected fluids (anticipated to be approximately 20% in New York state). During this production phase, the gas well has a capture zone that draws fluids (liquid and gas) from the adjoining fracture network and pore spaces. Any fluids within this capture zone migrate from the formation toward the well, rather than upward. Therefore, HF additives in the flowback water are removed from the formation and cannot migrate upward to a drinking water aquifer.

The injected fluid beyond the well's capture zone will reside in rock pore spaces or be trapped in pinched-off fractures. Entrapment of HF additives in pinched-off fractures – a phenomenon that results in isolated pockets of HF fluid – was previously described by US EPA (2004). Overall, the fate of the HF additives beyond the gas well's capture zone and the ability of such constituents to migrate upward toward a potable aquifer depends on two key factors:

1. *The direction of the vertical hydraulic gradient:* The hydraulic gradient is defined by the difference in hydraulic (or potentiometric) head between two water bearing units (*e.g.*, Marcellus Shale and the nearest potable aquifer). The direction of the hydraulic head gradient – upward or downwards – is defined by the relative magnitudes of the potentiometric heads. For HF additives to migrate upward to a potable aquifer, the hydraulic head in the Marcellus Shale has to be greater than the head in the potable aquifer. Currently, no hydraulic head measurements are available for the Marcellus Shale formation in New York so no conclusions regarding the feasibility of upward migration from the Marcellus Shale to overlying potable aquifers can be drawn from hydraulic gradient data alone.
2. *The magnitude of the hydraulic conductivity:* The hydraulic conductivity defines the ability of a geologic unit to transmit water and, by extension, dissolved constituents. The hydraulic conductivity of the Marcellus Shale unit is extremely small (on the order of 10^{-7} to 10^{-11} cm/sec), which greatly limits its ability to transmit water or HF additives, also acknowledged by ICF (2009).

The effects of partial saturation and buoyancy will further limit the potential for upward flow. Partial saturation, such as in gas rich strata where methane occupies part of the pore space in addition to water, can significantly reduce hydraulic conductivity—in some cases by several orders of magnitude (see Figure C.1). Furthermore, in order for dense brines (such as those present in the Marcellus) to flow upward through less dense (*i.e.*, less saline) groundwater, a larger hydraulic gradient must exist to counteract the tendency for brines to sink. The effects of partial saturation and buoyancy make it even less likely for upward flow to occur, however, we have ignored these processes in our subsequent quantitative analysis.

Overall, the low hydraulic conductivity of the Marcellus Shale formation, the thick sequence of rocks between the Marcellus and the nearest potable aquifer, and natural barriers to upward flow are expected to result in the HF additives beyond the well's capture zone remaining trapped within the Marcellus Shale – similar to the methane and saline water that have remained hydraulically isolated within the Marcellus Shale for hundreds of millions of years.

HF Additive Attenuation

In addition to the physical hydraulic isolation mechanisms that trap fluids in the Marcellus Shale, concentration of any of the constituents of HF additives that begin to move with groundwater will attenuate with distance from the injection location due to dilution, dispersion, retardation, and biodegradation. Retardation is expected to be a key mechanism that will further limit the mobility of HF constituents, given the high organic carbon content of the Marcellus Shale formation. Organic compounds (a majority of the HF additives) tend to adsorb (stick) to organic carbon, a phenomenon that further slows down their migration rate relative to water. This chemical-specific migration velocity is equal to V/R , where V is the water velocity, and R is the chemical retardation factor, given by:

$$R = 1 + K_d \left(\frac{\rho_b}{n} \right)$$

where:

- K_d = Soil-water distribution coefficient (m^3/kg);
- ρ_b = Bulk density (kg/m^3); and
- n = Porosity (m^3/m^3).

The soil-water distribution coefficient is commonly calculated based on the amount of organic carbon in the subsurface materials, and the chemical organic-carbon partition coefficient:

$$K_d = f_{oc}K_{oc}$$

f_{oc} = Fraction organic carbon content (kg-OC/kg-soil)

K_{oc} = Organic carbon partition coefficient (L-water/kg-soil)

Although some of the organic carbon within the Marcellus Shale deposits may not be available to serve as sorption sites (already consumed by hydrocarbons), retardation is anticipated to play a significant role in sequestering HF additives. Even using the lower-end of the range of organic carbon values for the Marcellus Shale (1%) indicates that migration of HF constituents will be significantly retarded, due to the high propensity of the vast majority of the HF constituents to adsorb to organic carbon. In addition to organic carbon, the clay particles that dominate the mineral composition of shale will also serve as adsorption sites for both organic and inorganic constituents.

Although some of the HF constituents, such as the alcohols, are not strongly bound and migrate readily in groundwater ($R \approx 1$), chemical retardation factors on the order of $R \approx 100$ to $R > 10,000$ would be expected for long chain hydrocarbon HF constituents. Chemical retardation factors for solvents evaluated in the flowback water (*e.g.*, benzene, ethylbenzene, xylene and toluene), would be on the order of $R \approx 5$ to 20, or more. Thus, chemical retardation alone (in the absence of other attenuation mechanisms) would increase travel times significantly for a number of HF constituents.

In addition to organic compounds, naturally occurring metals mobilized by certain HF constituents (*e.g.*, acids) during the fracturing process will also be retarded by sorption to organic carbon and inorganic binding sites, such as on clay minerals. Natural organic carbon binds strongly to many metals (Langmuir, 1997) (such as those found in flowback water), causing their migration to be significantly retarded. Similar to organic chemicals, retardation would significantly increase travel times for metals. In addition, metal mobilization will be only a short-term phenomenon, since the injection period is short and the introduced acids are expected to be neutralized in-place. The acid-neutralizing capacity of the Marcellus and overlying shales is expected to be high, since naturally present carbonate (in concretions, limestone layers, and as cementation between mineral grains) reduces acidity upon

dissolution. Thus, the ultimate fate of metals temporarily mobilized by HF injections will be to re-precipitate or adsorb back to the parent rock and remain immobile over the long-term.

Other attenuation mechanisms – dilution, dispersion, and biodegradation – are also expected to affect the fate and transport of HF constituents. Many of the HF additives are biodegradable organic compounds. Both organic and inorganic HF constituents will also be diluted by formation fluids as they slowly disperse. Given the extremely long migration periods, HF additive concentrations would be reduced significantly by these processes, if upward migration to a potable aquifer were even possible.

C.2 Potential for Upward HF Constituent Migration via Bedrock Fractures (Secondary Porosity)

A second potential migration pathway during (and after) HF stimulation is through bedrock fractures. This pathway would require an interconnected fracture network stretching many thousands of feet, however. The absence of such an interconnected network under baseline conditions is evident, given the presence of saline water and methane gas that have remained trapped in the Marcellus Shale for hundreds of millions of years (Laughrey *et al.*, 2004; Harper, 2008; USGS, 2009). Furthermore, HF stimulation is not likely to create a connected fracture network between the Marcellus Shale and potable aquifers due to the thick overlying layers of rocks, as well as the inherent design of the HF stimulation.

Natural Containment Mechanism: In-Situ Stress

In-situ stress is a compressive force associated with rock matrices that influences fracture propagation. "The *in-situ* stresses result from forces in the earth's crust and constitute the compressive far-field stresses that act to close the hydraulic fracture" (Simonson *et al.*, 1978, p. 27). In simple terms, *in-situ* stress can be described as the force that pushes rock fracture walls together and acts to close them. The magnitude of *in-situ* stress varies by rock type (*e.g.*, shale, sandstone, limestone, *etc.*). Because of their high ductility, shales tend to creep, and in doing so, convert much of the overburden weight into *in-situ* stress, thus keeping fractures closed (Van Eekelen, 1982, p. 348). In formations with layered rocks (such as the Marcellus), the *in-situ* stress may change sharply across adjacent rock layers due to differences in rock properties. This difference in stresses between adjacent rock layers is referred to as *in-situ* contrasts, which are widely considered the most important control on fracture growth (Simonson *et al.*, 1978; Warpinski *et al.*, 1982; Van Eekelen, 1982; Teufel and Clark, 1984).

During HF treatments, fluids are injected at pressures greater than the target formation's *in-situ* stress, thus opening existing fractures in the formation. Fractures tend to grow upward by augmenting the existing fracture network, but are still constrained by overlying rock layers that are barriers to natural fracture growth. Since shales have high *in-situ* stress, they serve as barriers to fracture growth (Simonson *et al.*, 1978, pp. 27-28) – a phenomenon expected to limit fracturing to the target zone. In addition, since there are multiple alternating layers of shale, sandstone, siltstone, and limestone that overlie the Marcellus, *in-situ* stress contrasts are likely to exert significant control over vertical fracture propagation.

Natural Containment Mechanism: Embedded Concretions

Common in the Marcellus and overlying shales are round limestone ellipses (concretions), up to several meters across and one meter thick (Sageman *et al.*, 2003; Lash and Blood, 2004; Lash and Engelder, 2007), which stop fractures from propagating (McConaughy and Engelder, 1999). In New York state shales, natural fractures formed over geologic time (on the order of millions of years ago), as a result of high pressures generated by hydrocarbon maturation and subsequent compaction (Lash and Engelder, 2009). However, when these natural fractures hit large limestone concretions, they ceased propagating. Thus, concretions are natural barriers that are expected to halt the growth of induced hydraulic fractures beyond the target zone.

To summarize, migration of HF constituents from the Marcellus Shale to overlying drinking water aquifers is highly unlikely either *via* rock pores or fractures. The HF process is of short duration (maximum of one to two days), whereas travel times for water from the Marcellus Shale to the nearest potable aquifer are likely to be on the order of thousands of years, even using worst-case assumptions utilized in the ICF analysis. Therefore, HF stimulation will not result in migration of HF constituents during the short treatment period. Nor will stimulation alter the overlying formation (*i.e.*, produce fractures), because natural physical constraints (*in-situ* stress and embedded concretions) will limit fracture propagation.

Containment by Design

The inherent design of the HF stimulation seeks to create a fracture network in the target formation, but not beyond it. Recent studies have shown a strong correlation between volume of fluid injected (akin to the amount of energy put into the HF stimulation) and the size of the fracture network (Mayerhofer *et al.* 2010). Thus, the designated fluid volumes inherently limit fracture growth potential, such that it is not plausible for fractures to reach an overlying aquifer. Indeed, as noted in the body of this report, a comprehensive study that mapped fracture propagation in horizontal wells in the Marcellus Shale has clearly shown that hydraulic fractures stay well below the bases of overlying aquifers (Fisher, 2010).

C.3 Hypothetical Migration From Marcellus to Overlying Aquifer

Although upward migration of HF additives from the Marcellus Shale formation to a potable aquifer is implausible for the reasons discussed in the preceding sub-section, we nonetheless undertook an extremely conservative analysis to quantify the magnitude of potential dilution and attenuation (DAF) that would occur during this hypothetical upward migration process. The analysis makes a number of simplifying assumption, which are anticipated to result in an underestimate of the anticipated DAF, but help place the human health risks posed by such hypothetical migration in proper perspective.

In order for water (and HF additives in the water) to migrate from the Marcellus Shale to a surficial potable aquifer, there must be a sufficient "hydraulic head" gradient, or driving force, to cause the water to migrate upward. Although it is not clear whether an upward gradient is even present in the Marcellus Shale, for the purposes of this analysis, we assumed that to be true.

The hydraulic head gradient between a point in the overlying aquifer and a point in the Marcellus Shale is given by:

$$\frac{dh}{dz} = \frac{H_2 - H_1}{z_2 - z_1}$$

where:

- H₁ = Hydraulic head in overlying aquifer;
- H₂ = Hydraulic head in Marcellus Shale;

- z_1 = Elevation of the overlying aquifer base; and
- z_2 = Elevation below the aquifer base (elevation of fracture zone).

The hydraulic head at any location is given by the sum of its hydraulic pressure head and its elevation head:

$$H_1 = D_{aq} + z_1$$

$$H_2 = \frac{P_{res}}{\rho g} + z_2$$

where:

- D_{aq} = Aquifer thickness (pressure head);
- P_{res} = Hydraulic head in the Marcellus Shale assumed to "Reservoir Pressure" for the purposes of this analysis;
- ρ = Density of water; and
- g = Gravitational acceleration.

Combining the above relationships, the hydraulic head gradient is given by the difference in hydraulic head divided by the distance of travel between the two locations:

$$\frac{dh}{dz} = \frac{\frac{P_{res}}{\rho g} - D_{aq} + z_2 - z_1}{z_2 - z_1}$$

This equation indicates that if the reservoir pressure (P_{res}) is great enough, fluid (*i.e.*, water or methane) can slowly migrate upward.

After stimulation, HF fluids beyond the production well's zone of influence could begin to migrate slowly upward if the prevailing head gradient is in that direction. However, if the HF fluid slowly migrates upward, HF constituent concentrations would decrease steadily due to dispersion, dilution, and biodegradation over the course of thousands of years. If the HF fluid were to reach an overlying aquifer, the constituents would be further diluted by groundwater flow within the potable aquifer. As an extreme case, in the following analysis we only considered dilution of HF fluid into bedrock formation fluids and mixing of upward seepage into an overlying aquifer. That is, we completely

ignored the attenuation that would occur over thousands of feet of multiple bedrock formations and hundreds to thousands of years.

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 that could hypothetically seep into an overlying aquifer:

$$C_{gw} = C_M \left(\frac{Q_m}{Q_M + Q_{gw}} \right)$$

- C_{gw} = Chemical concentration in shallow groundwater mixing zone ($\mu\text{g/L}$);
- C_M = Chemical concentration in Marcellus Shale groundwater ($\mu\text{g/L}$);
- Q_m = Upward HF fluid flow from Marcellus Shale into groundwater (m^3/year); and
- Q_{gw} = Flow of groundwater in the groundwater mixing zone (m^3/year).

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

$$C_{gw} = \frac{C_M}{DAF_{aq}}$$

Where DAF_{aq} is the dilution attenuation factor for upward seepage into a potable aquifer.

$$DAF_{aq} = \frac{Q_M + Q_{gw}}{Q_M}$$

The seepage of HF fluid (Q_M) from the Marcellus Shale to an overlying aquifer can be estimated by Darcy's law:¹

$$Q_M = K_{sh} A_m \frac{dh}{dz}$$

- K_{sh} = Hydraulic conductivity of shale bedrock (cm/s);

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

- dh/dz = Hydraulic head gradient (cm/cm); and
 A_m = Area of upward HF fluid seepage at the base of the potable aquifer (cm²).

For the area of upward HF fluid seepage (A_M), we have used a length scale equal to a typical horizontal gas well (4,500 ft; comparable to lengths described by dSGEIS, p. 5-22) times the width of the HF fluid plume if it were to impact an overlying aquifer. The upward head gradient was calculated as described above, assuming that reservoir pressure increases with depth at a rate of 0.6 psi per ft (rdSGEIS, p. 5-142). We applied this pressure gradient to the shallowest allowable depth of horizontal gas wells (2,000 ft bgs), corresponding to a reservoir pressure of 1,200 psi. The lateral groundwater flow in the surface aquifer, Q_{gw}, was calculated with Darcy's Law:

$$Q_{gw} = KA \frac{dh}{dx}$$

where:

- Q_{gw} = Regional groundwater flow rate (m³/s);
 K = Hydraulic conductivity of the surficial aquifer (m/s);
 A = Cross sectional area of the surficial aquifer (m²)
 h = Hydraulic head (m);
 x = Distance along direction of flow (m); and
 dh/dx = Hydraulic gradient – rate of change of head per unit of distance (unitless).

The cross-sectional area of the surficial aquifer, A, was estimated as the plume width multiplied by the aquifer thickness (either 100 or 1000 ft, depending on the scenario considered). Because the plume width is used to calculate both Q_{gw} and Q_M, it cancels out of the DAF calculation and does not need to be specified.

The key variables that control dilution are the hydraulic conductivity of the shale bedrock and the thickness of the potable aquifer. The bedrock hydraulic conductivity dictates the rate of upward HF fluid seepage, whereas potable aquifer thickness determines the size of the groundwater mixing zone where dilution occurs. We used the median hydraulic conductivity for shale of 10⁻⁹ cm/s reported by Freeze and Cherry (1979).² Although there are other rock types besides shale that also overlie the Marcellus, when

² The rdSGEIS (p. 4-3) provides a range of shale permeabilities (0.00001 to 0.1 md), which corresponds to saturated hydraulic conductivities of 10⁻⁷ to 10⁻¹¹ cm/sec, thus we used the median value (10⁻⁹ cm/sec) in our calculations. Although the rdSGEIS provided a range of permeabilities for the Marcellus shale, Hill *et al.* (Undated) discussed several problems with these permeability measurements that suggest they are unreliable. In addition, because upward seepage must traverse multiple shale

calculating the effective hydraulic conductivity across all layers, the least conductive unit (often shale) typically dominates the capacity for flow. Thus, using an hydraulic conductivity range for shale is the most appropriate choice.

Previously, ICF (2009) calculated DAF values for dilution of HF fluid within bedrock formation waters (*i.e.*, before water seeps into an overlying potable aquifer) to be at least 300³. We used the ICF DAF value of 300 and the DAF_{aq} calculations described above to determine the potential dilution for two scenarios: (1) shallow surface aquifer that is 100 ft thick, which provides for less dilution; and (2) surface aquifer thickness of 1,000 ft, as described in the r, and which provides for more dilution. Dilution factors for these scenarios are given in Table C.1.

Table C.1
Dilution Factors for Hypothetical Upward Flow From Marcellus

Surface Aquifer Thickness	DAF _{BR} (Dilution within Bedrock)	DAF _{aq} (Dilution in Shallow Aquifer Flow)	Combined DAF DAF _{BR} × DAF _{aq}
100 ft	300	5,500	1,650,000
1,000 ft	300	29,000	8,700,000

Note: DAF_{aq} based on migration from 4,500-foot length fracture zone upward to aquifer of specified depths.

The above analysis represents a hypothetical, worst-case scenario for the following reasons:

- We have assumed that the ambient hydraulic head gradient is upward. However, we are not aware of any field measurements of the hydraulic head gradient between the Marcellus shale and overlying shallow aquifers; hence, it is not clear even whether the natural hydraulic gradient is upward or downward. Furthermore, we used the highest reported value for the reservoir pressure gradient (0.6 psi/ft specified in the rdSGEIS, 2011, p. 5-142) to calculate the driving head for upward flow.
- We used the median literature report value for shale hydraulic conductivity in our analysis – a likely overestimate. In addition, we ignored the barriers to water flow created by gas and oil present in the Marcellus and overlying shales, as well as the tendency for brines to sink in less saline groundwater. As discussed previously, gas and oil that fill pore spaces can block the flow of water and can form effective barriers to upward water flow (*e.g.*, Figure C.1). The limited hydraulic conductivities of the shale deposits have led to the hydraulic isolation and trapping of methane and saline water in the Marcellus Shale for hundreds of millions of years – a condition that is expected to persist.

layers above the Marcellus, each with different properties, it is more appropriate to use the range of permeabilities reported in the literature rather than values only applicable to the Marcellus Shale.

³ ICF calculated dilution into bedrock formation waters overlying a gas well, assuming 40-acre spacing between gas wells—the required spacing for gas wells in New York. For a 4,500 ft horizontal well, well spacing of 40 acres would translate into a minimum mixing width of 387 ft – a relatively narrow zone for upward dispersive migration through the strongly layered bedrock above the Marcellus shale. Therefore, the dilution factor provided by ICF is likely a lower-bound estimate.

- We assumed that the shallow aquifer groundwater flow direction was parallel to the gas well and that a drinking water well in the shallow aquifer was directly downgradient of the resulting HF fluid plume. This scenario results in the narrowest plume with the least possible dilution within the shallow aquifer.
- We ignored adsorption, dispersion, chemical reactions, and biodegradation of HF additives. Since the transport distance is on the order of thousands of feet and the time of transport is on the order of thousands of years, each of these mechanisms is expected to significantly reduce HF constituent concentrations.

These calculated dilution factors (at least 1,650,000 or higher) for upward flow from a gas well to an overlying aquifer clearly demonstrate that dilution for this scenario is significant, even when making a number of conservative assumptions. As discussed in Section 5, we have also evaluated the potential migration of leaks/spills at the surface to a shallow aquifer. In comparison to that analysis, dilution for upward migration from the Marcellus is significantly greater (if upward migration occurs at all). Since greater dilution connotes lower risk, the risks for the hypothetical upward migration scenario are less than the shallow release scenario, and were not explicitly quantified in our risk analysis.

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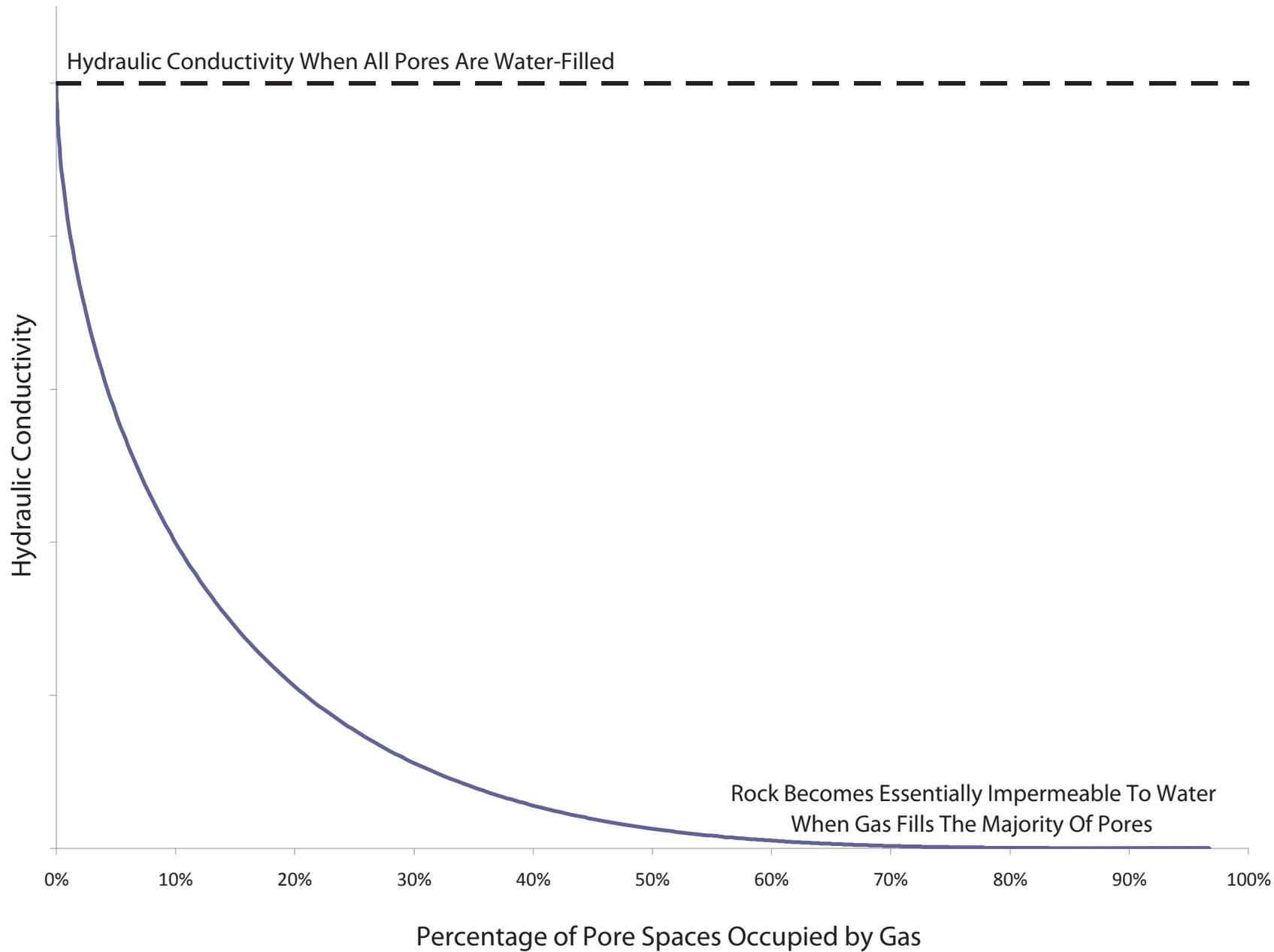
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 3) van Genuchten, 1980.



Dependence of Hydraulic Conductivity on the Percentage of Gas-Filled Pore Spaces

FIGURE C.1

Date: 12/16/2011

Appendix D

Drinking Water Hazard Quotients Using DAFs in Gradient 2009 Study

D.1 Summary of Gradient 2009 Release Scenarios and DAFs

Since preparing our 2009 risk analysis (Gradient, 2009), we have revised our release scenarios as discussed in Section 5 of this report. In part, the revision reflects a broader range of fluid volumes used for hydraulic fracturing (HF) activities. The broader range of fluid volumes includes HF systems which use smaller volumes of fluid than those previously anticipated for our 2009 analysis. For example, the Halliburton Energy Services Inc. (HESI) HF systems anticipated for use in the Marcellus Shale formation range in volume from as little as approximately 30,000 gal to 4.5 million gallons, depending on the particular HF system and the fracking stage. Thus, our revised release scenarios accommodate the wider range of spills by evaluating a 10-fold range in release volumes for the "sudden" release scenario. As summarized in Table D.1, the range of release volumes for this study – 1,000 gallons to 10,000 gallons (with 100% going to surface water or groundwater) – encompasses the release volume evaluated in our 2009 study, which was 8,500 gallons to surface water and groundwater, respectively.

The diffuse spill volume we evaluate in the present analysis, 10 gallons/day for 365 days/year, differs from our 2009 hypothetical scenario. In our 2009 study, the "diffuse" spill scenario equated to spills of 175 gallons/day, 365 days per year, with 50% impacting surface water, and 50% impacting groundwater. Spills of such a magnitude happening on a routine/daily basis are considered so implausible as to be unrealistic, and therefore we modified the diffuse spill scenario to one that is less unreasonable.

Table D.1 Comparison of Release Scenarios in Current (2011) Analysis versus 2009 Analysis.

Current (2011) Analysis			2009 Analysis	
Release Volume (gal)	Notes	Impacted Area (acre)	Release Volume (gal)	Impacted Area (acre)
<i>Sudden Release Scenario</i>				
1,000	HF Volumes ≤ 250,000 gal	0.1	8,500 to Groundwater	0.25
10,000	HF Volumes > 250,000 gal	1	8,500 to Surface Water	N/A
<i>Diffuse Release Scenario</i>				
3,500	~10 gal/day x 350 days/yr	2	32,240 to groundwater 32,240 to surface water	4 N/A

We have updated the development of the dilution attenuation factors (DAFs) for the corresponding release scenarios in the current analysis. A comparison of the DAF values used in the present analysis with those developed in our 2009 analysis is provided in Table D.2.

Table D.2 Comparison of DAF Values in Current (2011) Analysis versus 2009 Analysis.

Exposure Pathway spill volume >	Current (2011) Analysis DAF			2009 Analysis DAF	
	1,000 gal	10,000 gal	3,500 gal	8,500 gal	32,240 gal
Unsaturated Zone	50	50	150	25 – 35	78 - 108
Saturated Zone	2,740	60	33	53 – 132	15 – 36
Overall Soil + Groundwater	137,000	3,000	5,000	1,325 – 4,620	1,170 – 3,888
Surface Water (1 yr flow)	1,900,000	190,000	540,000	223,295	58,871
Surface Water (10 day flow)	52,000	5,200	N/A	not evaluated	not evaluated

As shown in Table D.2, the groundwater DAF values used in the current analysis are comparable to the values developed in our 2009 study when one compares comparable release volumes. Not surprisingly, the DAF for the 1,000 gal release scenario in the present study is clearly larger than the groundwater DAFs used in our 2006 study given that this spill volume is smaller than any release evaluated in our 2009 study. As a further note, in our 2009 study, we included an additional dilution factor for the groundwater pathway that accounted for partitioning (adsorption) of chemicals between the soil and pore water phases. As a conservative and simplifying assumption that will tend to over predict chemical migration, this pore water DAF has been eliminated from the current analysis with the exception of three compounds listed below, all of which readily adsorb to soil. These pore water DAF values were multiplied by the median soil/groundwater DAF (2,525) for these three chemicals (which was the approach applied to all chemicals for the 2009 groundwater DAF calculation).

Chemical	CAS	K _{oc}	K _d	Pore Water DAF
Cobalt acetate	71-48-7	-	125.9	630
Alkyl (C14-C16) olefin sulfonate, sodium salt	68439-57-6		2104	12.6
Naphthenic acid ethoxylate	68410-62-8		2,412	14.5

Pore water DAF derivation and soil properties used given in Appendix A

For the surface water pathway, the DAF values used for the current analysis again incorporate the range of values developed for our 2009 study. Notably, in our current analysis we have added an additional exposure scenario to evaluate the potential impacts of mixing a surface release into a smaller volume of surface water (*i.e.*, shorter duration for mixing into a surface stream). Given that the surface water DAF values used in this current study are lower than those in our 2009 study, we have not presented hazard quotients using the surface water DAFs from that prior Gradient study.

For comparison purposes we have calculated the drinking water hazard quotients (HQs) for the HESI HF systems using the median groundwater DAF value that we derived from our 2009 study (2,525). These HQs for the entire list of HESI chemical additives, and the total Hazard Index for the summation of chemical HQs in each fluid system, are presented in Tables D.3 through D.6. As these summaries indicate, none of the chemicals individually, or the cumulative hazards summed over all chemicals in the HF systems, exceeds a value of 1.0. These results indicate that the HF additives would not exceed health-based drinking water benchmarks for the release scenarios evaluated here (using the DAF values derived in our 2009 study).

References

Gradient. 2009. "Human Health Risk Evaluation for Hydraulic Fracturing Fluid Additives, Marcellus Shale Formation, New York." Report to Halliburton Energy Services, Inc., Houston, TX, 127p., December 31.

Table D.3 HESI HF Additive Hazard Quotients (HQ) Using 2009 Groundwater DAF -- Sudden Spill

Chemical	CAS No	RBC ^[a]	HF Wellhead Concentration		Groundwater (2009 DAF)		Groundwater HQ ^[a]	
		(ug/L)	Min (ug/L)	Max (ug/L)	Min (ug/L)	Max (ug/L)	Min	Max
1,2,4 Trimethylbenzene	95-63-6	70	1,796	1,811	0.7	0.7	1.0E-02	1.0E-02
2-Bromo-2-nitro-1,3-propanediol	52-51-7	3,500	17,986	18,009	7.1	7.1	2.0E-03	2.0E-03
Acetic acid	64-19-7	499,800	40,307	4,303,895	16.0	1,704.5	3.2E-05	3.4E-03
Acetic anhydride	108-24-7	499,800	3,227,921	6,455,842	1,278.4	2,556.8	2.6E-03	5.1E-03
Alcohols, C12-16, ethoxylated	68551-12-2	13,125	7,944	1,045,385	3.1	414.0	2.4E-04	3.2E-02
Alcohols, C14-C15, ethoxylated	68951-67-7	13,125	133,446	133,446	52.8	52.8	4.0E-03	4.0E-03
Aldehyde	CBI	[a1]	316,979	3,169,750	125.5	1,255.3	[a1]	[a1]
Alkyl (C14-C16) olefin sulfonate, sodium salt	68439-57-6	1,155	975,504	2,359,022	386.3	934.3	5.2E-03	1.3E-02
Amines, coco alkyl, ethoxylated	61791-14-8	[a1]	98,809	616,560	39.1	244.2	[a1]	[a1]
Ammonium acetate	631-61-8	[a1]	138,584	660,754	54.9	261.7	[a1]	[a1]
Ammonium chloride	12125-02-9	7,980	9,548	952,935	3.8	377.4	4.7E-04	4.7E-02
Ammonium persulfate	7727-54-0	490	80,264	153,676	31.8	60.9	6.5E-02	1.2E-01
Ammonium phosphate	7722-76-1	30,000	59,285	59,285	23.5	23.5	7.8E-04	7.8E-04
Attapulgite	12174-11-7	4,480,000	14,680	24,822	5.8	9.8	1.3E-06	2.2E-06
Bentonite, benzyl(hydrogenated tallow alkyl) dimethylammonium stearate complex	121888-68-4	[a1]	40,987	74,557	16.2	29.5	[a1]	[a1]
Borate salt	CBI	3,100	324,146	548,110	128.4	217.1	4.1E-02	7.0E-02
C.I. Pigment Orange 5	3468-63-1	280	291	291	0.1	0.1	4.1E-04	4.1E-04
Calcium chloride	10043-52-4	11,655	6,853	24,491	2.7	9.7	2.3E-04	8.3E-04
Carbohydrate	CBI	[a1]	27,045	27,045	10.7	10.7	[a1]	[a1]
Chloromethylnaphthalene quinoline quaternary amine	15619-48-4	[a2]	5,929	1,590,803	2.3	630.0	[a2]	[a2]
Chlorous acid, sodium salt	7758-19-2	1,000	48,044	480,277	[c]	[c]	[c]	[c]
Citrus, extract	94266-47-4	[a1]	136,812	136,812	54.2	54.2	[a1]	[a1]
Cobalt acetate	71-48-7	5	104,400	104,400	41.3	41.3	1.3E-02	1.3E-02
Crystalline silica, quartz	14808-60-7	29,155	310	36,258	0.1	14.4	4.2E-06	4.9E-04
Cured acrylic resin	CBI	[a1]	32,622	32,622	12.9	12.9	[a1]	[a1]
Diethylene glycol	111-46-6	3,500	128,356	310,398	50.8	122.9	1.5E-02	3.5E-02
Diethylenetriamine	111-40-0	805	208,521	208,521	82.6	82.6	1.0E-01	1.0E-01
EDTA/Copper chelate	CBI	630	5,820	884,509	2.3	350.3	3.7E-03	5.6E-01
Ethanol	64-17-5	28,000	430,927	729,702	170.7	289.0	6.1E-03	1.0E-02
Ethoxylate fatty acid	CBI	66,792	63,777	112,693	25.3	44.6	3.8E-04	6.7E-04
Ethoxylate fatty acid	CBI	[a1]	102,304	168,970	40.5	66.9	[a1]	[a1]
Ethoxylated branched C13 alcohol	78330-21-9	13,125	54,982	71,445	21.8	28.3	1.7E-03	2.2E-03
Ethoxylated fatty acid	CBI	[a1]	99,125	168,970	39.3	66.9	[a1]	[a1]
Ethylene glycol monobutyl ether	111-76-2	1,600	385,067	931,193	152.5	368.8	9.5E-02	2.3E-01
Fatty acid ester	CBI	1,000	1,589	4,769	0.6	1.9	6.3E-04	1.9E-03
Fatty acid tall oil	CBI	29,155	132,404	988,077	52.4	391.3	1.8E-03	1.3E-02
Fatty acid tall oil amide	CBI	[a1]	7,944	23,843	3.1	9.4	[a1]	[a1]
Fatty alcohol polyglycol ether surfactant	9043-30-5	[a1]	20,981	21,265	8.3	8.4	[a1]	[a1]

Table D.3 HESI HF Additive Hazard Quotients (HQ) Using 2009 Groundwater DAF -- Sudden Spil

Chemical	CAS No	RBC ^[a]	HF Wellhead Concentration		Groundwater (2009 DAF)		Groundwater HQ ^[a]	
		(ug/L)	Min (ug/L)	Max (ug/L)	Min (ug/L)	Max (ug/L)	Min	Max
Fatty acid ester ethoxylate	CBI	350,000	1,059	3,179	0.4	1.3	1.2E-06	3.6E-06
Formaldehyde	50-00-0	3,100	294	11,765	0.1	4.7	3.8E-05	1.5E-03
Glycerine	56-81-5	93,333	30,567	30,567	12.1	12.1	1.3E-04	1.3E-04
Guar gum	9000-30-0	[a1]	2,340,833	3,490,851	927.1	1,382.5	[a1]	[a1]
Guar gum derivative	CBI	[a1]	2,340,921	5,267,613	927.1	2,086.2	[a1]	[a1]
HCl in 22 Baume Acid	7647-01-0	200	147,321	160,547,973	[c]	[c]	[c]	[c]
Heavy aromatic petroleum naphtha	64742-94-5	1,400	95,253	96,094	37.7	38.1	2.7E-02	2.7E-02
Hemicellulase enzyme	9012-54-8	[a1]	3,005	3,005	1.2	1.2	[a1]	[a1]
Hydrotreated light petroleum distillate	64742-47-8	3,500	79,436	238,433	31.5	94.4	9.0E-03	2.7E-02
Inorganic salt	CBI	[a1]	29,973	107,111	11.9	42.4	[a1]	[a1]
Isopropanol	67-63-0	350,000	257,299	2,774,519	101.9	1,098.8	2.9E-04	3.1E-03
Magnesium chloride hexahydrate	7791-18-6	175,000	13,955	49,867	5.5	19.7	3.2E-05	1.1E-04
Methanol	67-56-1	7,800	57,960	3,063,037	23.0	1,213.1	2.9E-03	1.6E-01
Naphtha, hydrotreated heavy	64742-48-9	3,500	2,179,292	2,831,831	863.1	1,121.5	2.5E-01	3.2E-01
Naphthalene	91-20-3	310	10,683	10,778	4.2	4.3	1.4E-02	1.4E-02
Naphthenic acid ethoxylate	68410-62-8	210	104,540	2,572,951	41.4	1,019.0	2.7E-03	6.6E-02
Nonylphenol ethoxylated	127087-87-0	2,345	35,911	36,228	14.2	14.3	6.1E-03	6.1E-03
Olefin	CBI	100	890	890	0.4	0.4	3.5E-03	3.5E-03
Olefin	CBI	1,000	21,351	21,351	8.5	8.5	8.5E-03	8.5E-03
Olefin	CBI	1,000	13,345	13,345	5.3	5.3	5.3E-03	5.3E-03
Olefin	CBI	1,000	890	890	0.4	0.4	3.5E-04	3.5E-04
Organic phosphonate	CBI	[a1]	97,389	3,894,092	38.6	1,542.2	[a1]	[a1]
Oxylated phenolic resin	CBI	[a1]	71,821	72,456	28.4	28.7	[a1]	[a1]
Oxylated phenolic resin	CBI	[a1]	251,374	253,595	99.6	100.4	[a1]	[a1]
Polyacrylamide copolymer	CBI	[a1]	147,752	443,486	58.5	175.6	[a1]	[a1]
Polyoxylated fatty amine salt	61791-26-2	[a1]	423,891	1,185,692	167.9	469.6	[a1]	[a1]
Potassium carbonate	584-08-7	2,345,000	562,906	1,117,790	222.9	442.7	9.5E-05	1.9E-04
Potassium formate	590-29-4	3,500	258,454	437,030	102.4	173.1	2.9E-02	4.9E-02
Potassium hydroxide	1310-58-3	2,345,000	7,697	47,170	3.0	18.7	1.3E-06	8.0E-06
Potassium metaborate	13709-94-9	[a1]	98,266	602,200	38.9	238.5	[a1]	[a1]
Propanol	71-23-8	101,675	38,802	38,802	15.4	15.4	1.5E-04	1.5E-04
Propargyl alcohol	107-19-7	31	53,378	53,378	21.1	21.1	6.8E-01	6.8E-01
Proprietary	CBI	[a2]	18,792	18,792	7.4	7.4	[a2]	[a2]
Quaternary ammonium compound	CBI	[a2]	118,653	118,653	47.0	47.0	[a2]	[a2]
Quaternary ammonium compounds, bis(hydrogenated tallow alkyl) dimethyl, salts with bentonite	68953-58-2	145,845	67,712	68,627	26.8	27.2	1.8E-04	1.9E-04
Quaternary ammonium salt	CBI	[a2]	177,856	1,193,596	70.4	472.7	[a2]	[a2]
Reaction product of acetophenone, formaldehyde, thiourea and oleic acid in dimethyl formamide	68527-49-1	[a1]	112,984	112,984	44.7	44.7	[a1]	[a1]

Table D.3 HESI HF Additive Hazard Quotients (HQ) Using 2009 Groundwater DAF -- Sudden Spill

Chemical	CAS No	RBC ^[a]	HF Wellhead Concentration		Groundwater (2009 DAF)		Groundwater HQ ^[a]	
		(ug/L)	Min (ug/L)	Max (ug/L)	Min (ug/L)	Max (ug/L)	Min	Max
Silica gel	112926-00-8	29,155	3,003	3,602	1.2	1.4	4.1E-05	4.9E-05
Silica, amorphous -- fumed	7631-86-9	29,155	12,005	27,013	4.8	10.7	1.6E-04	3.7E-04
Sodium bicarbonate	144-55-8	1,998,500	48,019	108,054	19.0	42.8	9.5E-06	2.1E-05
Sodium carboxymethyl cellulose	9004-32-4	45,500	5,321	8,998	2.1	3.6	4.6E-05	7.8E-05
Sodium chloride	7647-14-5	2,901,500	3,095	1,279,579	1.2	506.8	4.2E-07	1.7E-04
Sodium glycolate	2836-32-0	[a1]	92	155	0.0	0.1	[a1]	[a1]
Sodium hydroxide	1310-73-2	1,150,000	6,003	573,737	2.4	227.2	2.1E-06	2.0E-04
Sodium hypochlorite	7681-52-9	1,120	28,526	37,653	11.3	14.9	1.0E-02	1.3E-02
Sodium iodide	7681-82-5	160	148,211	148,211	58.7	58.7	3.7E-01	3.7E-01
Sodium perborate tetrahydrate	10486-00-7	11,667	59,975	120,060	23.8	47.5	2.0E-03	4.1E-03
Sodium persulfate	7775-27-1	2,345	1,030	377,141	0.4	149.4	1.7E-04	6.4E-02
Sodium sulfate	7757-82-6	500,000	1	241,392	0.0002	95.6	4.1E-10	1.9E-04
Sodium sulfite	7757-83-7	[a1]	30,174	30,174	12.0	12.0	[a1]	[a1]
Sodium thiosulfate	7772-98-7	500,000	3,620,876	3,620,876	1,434.0	1,434.0	2.9E-03	2.9E-03
Surfactant mixture	CBI	13,125	16,517	19,810	6.5	7.8	5.0E-04	6.0E-04
Surfactant mixture	CBI	[a1]	9,009	10,805	3.6	4.3	[a1]	[a1]
Terpenoid	CBI	2,917	21,882	136,812	8.7	54.2	3.0E-03	1.9E-02
Terpenoid	CBI	2,917	40,398	41,764	16.0	16.5	5.5E-03	5.7E-03
Tributyl tetradecyl phosphonium chloride	81741-28-8	105	12,189	24,367	4.8	9.7	4.6E-02	9.2E-02
Triethanolamine zirconate	101033-44-7	[a2]	176,136	176,136	69.8	69.8	[a2]	[a2]
Ulexite (B5H3O9.Ca.8H2O.Na)	1319-33-1	3,100	533,203	533,203	211.2	211.2	6.8E-02	6.8E-02
Zirconium, acetate lactate oxo ammonium complexes	68909-34-2	[a2]	856,536	856,536	339.2	339.2	[a2]	[a2]

Notes

Median 2009 DAF Value = 2,525

CBI - Confidential Business Information. Gradient was provided chemical-specific CAS and chemical names and used this information to evaluate chemical-specific toxicity.

[a] Chemicals with no RBC and no HQ are either classified as having low human health hazard potential or have no available human health toxicity information (see Appendix E).

[a1]: chemical listed as inert, GRAS, low priority, etc. [a2]: No toxicity information available

[b] Groundwater pathway analysis applied chemical adsorption in soil for DAF for three chemicals (see Appendix D)

[c] Hydrochloric acid and chlorous acid are expected to be readily neutralized in the environment

Table D.4 HESI HF Additive Hazard Quotients (HQ) Using 2009 Groundwater DAF -- Diffuse Spill

Chemical	CAS No	RBC ^[a]	HF Wellhead Concentration		Groundwater (2009 DAF)		Groundwater HQ ^[a]	
		(ug/L)	Min (ug/L)	Max (ug/L)	Min (ug/L)	Max (ug/L)	Min	Max
1,2,4 Trimethylbenzene	95-63-6	70	1	1,809	0.0005	0.7	7.0E-06	1.0E-02
2-Bromo-2-nitro-1,3-propanediol	52-51-7	3,500	4,914	18,009	4.2	15.4	5.6E-04	2.0E-03
Acetic acid	64-19-7	499,800	1,758	1,232,727	1.5	1,053.6	1.4E-06	9.8E-04
Acetic anhydride	108-24-7	499,800	4,413	1,786,808	3.8	1,527.2	3.5E-06	1.4E-03
Alcohols, C12-16, ethoxylated	68551-12-2	13,125	412	759,924	0.4	649.5	1.2E-05	2.3E-02
Alcohols, C14-C15, ethoxylated	68951-67-7	13,125	618	73,869	0.5	63.1	1.9E-05	2.2E-03
Aldehyde	CBI	[a1]	217	2,304,194	0.2	1,969.4	[a1]	[a1]
Alkyl (C14-C16) olefin sulfonate, sodium salt	68439-57-6	1,155	570,603	2,089,604	487.7	1,786.0	3.1E-03	1.1E-02
Amines, coco alkyl, ethoxylated	61791-14-8	[a1]	68	448,197	0.1	383.1	[a1]	[a1]
Ammonium acetate	631-61-8	[a1]	6,044	532,083	5.2	454.8	[a1]	[a1]
Ammonium chloride	12125-02-9	7,980	1,219	586,392	1.0	501.2	6.1E-05	2.9E-02
Ammonium persulfate	7727-54-0	490	77,317	109,991	66.1	94.0	6.2E-02	8.9E-02
Ammonium phosphate	7722-76-1	30,000	586	43,096	0.5	36.8	7.7E-06	5.7E-04
Attapulgite	12174-11-7	4,480,000	12,064	24,822	10.3	21.2	1.1E-06	2.2E-06
Bentonite, benzyl(hydrogenated tallow alkyl) dimethylammonium stearate complex	121888-68-4	[a1]	11,711	62,163	10.0	53.1	[a1]	[a1]
Borate salt	CBI	3,100	266,392	548,110	227.7	468.5	3.4E-02	7.0E-02
C.I. Pigment Orange 5	3468-63-1	280	281	291	0.2	0.2	4.0E-04	4.1E-04
Calcium chloride	10043-52-4	11,655	6,625	24,491	5.7	20.9	2.3E-04	8.3E-04
Carbohydrate	CBI	[a1]	969	985	0.8	0.8	[a1]	[a1]
Chloromethylnaphthalene quinoline quaternary amine	15619-48-4	[a2]	4	1,156,406	0.003	988.4	[a2]	[a2]
Chlorous acid, sodium salt	7758-19-2	1,000	34,764	346,755	[c]	[c]	[c]	[c]
Citrus, extract	94266-47-4	[a1]	88,108	97,208	75.3	83.1	[a1]	[a1]
Cobalt acetate	71-48-7	5	22,957	84,069	19.6	71.9	2.9E-03	1.1E-02
Crystalline silica, quartz	14808-60-7	29,155	35	26,651	0.03	22.8	4.7E-07	3.6E-04
Cured acrylic resin	CBI	[a1]	7,173	26,269	6.1	22.5	[a1]	[a1]
Diethylene glycol	111-46-6	3,500	75,079	274,948	64.2	235.0	8.5E-03	3.1E-02
Diethylenetriamine	111-40-0	805	1,017	1,072	0.9	0.9	5.0E-04	5.3E-04
EDTA/Copper chelate	CBI	630	4,315	5,820	3.7	5.0	2.7E-03	3.7E-03
Ethanol	64-17-5	28,000	297	710,490	0.3	607.3	4.2E-06	1.0E-02
Ethoxylate fatty acid	CBI	66,792	17,530	80,071	15.0	68.4	1.0E-04	4.7E-04
Ethoxylate fatty acid	CBI	[a1]	28,120	120,058	24.0	102.6	[a1]	[a1]
Ethoxylated branched C13 alcohol	78330-21-9	13,125	15,710	57,532	13.4	49.2	4.7E-04	1.7E-03
Ethoxylated fatty acid	CBI	[a1]	27,246	120,058	23.3	102.6	[a1]	[a1]
Ethylene glycol monobutyl ether	111-76-2	1,600	225,238	824,844	192.5	705.0	5.6E-02	2.0E-01
Fatty acid ester	CBI	1,000	203	3,388	0.2	2.9	8.0E-05	1.3E-03
Fatty acid tall oil	CBI	29,155	91	718,265	0.1	613.9	1.2E-06	9.8E-03
Fatty acid tall oil amide	CBI	[a1]	1,016	16,941	0.9	14.5	[a1]	[a1]
Fatty alcohol polyglycol ether surfactant	9043-30-5	[a1]	762	20,878	0.7	17.8	[a1]	[a1]

Table D.4 HESI HF Additive Hazard Quotients (HQ) Using 2009 Groundwater DAF -- Diffuse Spill

Chemical	CAS No	RBC ^[a]	HF Wellhead Concentration		Groundwater (2009 DAF)		Groundwater HQ ^[a]	
		(ug/L)	Min (ug/L)	Max (ug/L)	Min (ug/L)	Max (ug/L)	Min	Max
Fatty acid ester ethoxylate	CBI	350,000	135	2,259	0.1	1.9	1.5E-07	2.6E-06
Formaldehyde	50-00-0	3,100	291	2,722	0.2	2.3	3.7E-05	3.5E-04
Glycerine	56-81-5	93,333	14,884	23,494	12.7	20.1	6.3E-05	1.0E-04
Guar gum	9000-30-0	[a1]	85,034	2,910,562	72.7	2,487.7	[a1]	[a1]
Guar gum derivative	CBI	[a1]	778,086	4,590,385	665.0	3,923.4	0.0E+00	0.0E+00
HCl in 22 Baume Acid	7647-01-0	200	757	116,707,515	[c]	[c]	[c]	[c]
Heavy aromatic petroleum naphtha	64742-94-5	1,400	66	95,945	0.1	82.0	1.9E-05	2.7E-02
Hemicellulase enzyme	9012-54-8	[a1]	108	109	0.1	0.1	[a1]	[a1]
Hydrotreated light petroleum distillate	64742-47-8	3,500	10,160	169,413	8.7	144.8	1.1E-03	1.9E-02
Inorganic salt	CBI	[a1]	28,974	107,110	24.8	91.5	[a1]	[a1]
Isopropanol	67-63-0	350,000	176	2,016,888	0.2	1,723.8	2.0E-07	2.3E-03
Magnesium chloride hexahydrate	7791-18-6	175,000	13,489	49,867	11.5	42.6	3.1E-05	1.1E-04
Methanol	67-56-1	7,800	205	2,226,621	0.2	1,903.1	1.0E-05	1.1E-01
Naphtha, hydrotreated heavy	64742-48-9	3,500	84,930	2,326,482	72.6	1,988.4	9.6E-03	2.6E-01
Naphthalene	91-20-3	310	7	10,761	0.01	9.2	9.4E-06	1.4E-02
Naphthenic acid ethoxylate	68410-62-8	210	71	1,870,362	0.1	1,598.6	1.8E-06	4.8E-02
Nonylphenol ethoxylated	127087-87-0	2,345	25	36,172	0.02	30.9	4.2E-06	6.1E-03
Olefin	CBI	100	4	492	0.004	0.4	1.6E-05	2.0E-03
Olefin	CBI	1,000	99	11,819	0.1	10.1	3.9E-05	4.7E-03
Olefin	CBI	1,000	62	7,387	0.1	6.3	2.4E-05	2.9E-03
Olefin	CBI	1,000	4	492	0.004	0.4	1.6E-06	2.0E-04
Organic phosphonate	CBI	[a1]	96,426	901,081	82.4	770.2	[a1]	[a1]
Oxylated phenolic resin	CBI	[a1]	49	72,343	0.042	61.8	0.0E+00	0.0E+00
Oxylated phenolic resin	CBI	[a1]	173	253,201	0.1	216.4	[a1]	[a1]
Polyacrylamide copolymer	CBI	[a1]	18,898	315,108	16.2	269.3	[a1]	[a1]
Polyoxylated fatty amine salt	61791-26-2	[a1]	290	861,918	0.2	736.7	[a1]	[a1]
Potassium carbonate	584-08-7	2,345,000	245,793	900,118	210.1	769.3	4.2E-05	1.5E-04
Potassium formate	590-29-4	3,500	212,404	437,030	181.5	373.5	2.4E-02	4.9E-02
Potassium hydroxide	1310-58-3	2,345,000	3,748	28,064	3.2	24.0	6.3E-07	4.7E-06
Potassium metaborate	13709-94-9	[a1]	47,850	358,286	40.9	306.2	[a1]	[a1]
Propanol	71-23-8	101,675	18,894	29,824	16.1	25.5	7.4E-05	1.2E-04
Propargyl alcohol	107-19-7	31	247	29,548	0.2	25.3	3.2E-03	3.8E-01
Proprietary	CBI	[a2]	13,598	13,913	11.6	11.9	[a2]	[a2]
Quaternary ammonium compound	CBI	[a2]	76,414	84,306	65.3	72.1	[a2]	[a2]
Quaternary ammonium compounds, bis(hydrogenated tallow alkyl) dimethyl, salts with bentonite	68953-58-2	145,845	2,460	67,379	2.1	57.6	6.7E-06	1.8E-04
Quaternary ammonium salt	CBI	[a2]	122	867,664	0.1	741.6	[a2]	[a2]
Reaction product of acetophenone, formaldehyde, thiourea and oleic acid in dimethyl formamide	68527-49-1	[a1]	523	62,542	0.4	53.5	[a1]	[a1]
Silica gel	112926-00-8	29,155	2,606	3,003	2.2	2.6	3.5E-05	4.1E-05

Table D.4 HESI HF Additive Hazard Quotients (HQ) Using 2009 Groundwater DAF -- Diffuse Spill

Chemical	CAS No	RBC ^[a]	HF Wellhead Concentration		Groundwater (2009 DAF)		Groundwater HQ ^[a]	
		(ug/L)	Min (ug/L)	Max (ug/L)	Min (ug/L)	Max (ug/L)	Min	Max
Silica, amorphous -- fumed	7631-86-9	29,155	14,914	23,540	12.7	20.1	2.0E-04	3.2E-04
Sodium bicarbonate	144-55-8	1,998,500	59,655	94,162	51.0	80.5	1.2E-05	1.9E-05
Sodium carboxymethyl cellulose	9004-32-4	45,500	4,373	8,998	3.7	7.7	3.8E-05	7.8E-05
Sodium chloride	7647-14-5	2,901,500	5,414	1,201,010	4.6	1,026.5	7.4E-07	1.6E-04
Sodium glycolate	2836-32-0	[a1]	75	155	0.1	0.1	[a1]	[a1]
Sodium hydroxide	1310-73-2	1,150,000	5,455	482,785	4.7	412.6	1.9E-06	1.7E-04
Sodium hypochlorite	7681-52-9	1,120	27,478	37,614	23.5	32.1	9.7E-03	1.3E-02
Sodium iodide	7681-82-5	160	1,465.45	107,739.72	1.3	92.1	3.6E-03	2.7E-01
Sodium perborate tetrahydrate	10486-00-7	11,667	7,671	120,060	6.6	102.6	2.6E-04	4.1E-03
Sodium persulfate	7775-27-1	2,345	746	54,517	0.6	46.6	1.3E-04	9.2E-03
Sodium sulfate	7757-82-6	500,000	0.4	185,534	0.0003	158.6	3.0E-10	1.5E-04
Sodium sulfite	7757-83-7	[a1]	14,693	23,192	12.6	19.8	[a1]	[a1]
Sodium thiosulfate	7772-98-7	500,000	1,763,151	2,783,016	1,507.0	2,378.6	1.4E-03	2.2E-03
Surfactant mixture	CBI	13,125	14,334	16,517	12.3	14.1	4.3E-04	5.0E-04
Surfactant mixture	CBI	[a1]	7,818	9,009	6.7	7.7	[a1]	[a1]
Terpenoid	CBI	2,917	6,015	97,208	5.1	83.1	8.2E-04	1.3E-02
Terpenoid	CBI	2,917	11,104	40,664	9.5	34.8	1.5E-03	5.5E-03
Tributyl tetradecyl phosphonium chloride	81741-28-8	105	12,069	19,509	10.3	16.7	4.6E-02	7.4E-02
Triethanolamine zirconate	101033-44-7	[a2]	85,768	135,378	73.3	115.7	[a2]	[a2]
Ulexite (B5H3O9.Ca.8H2O.Na)	1319-33-1	3,100	385,811	394,764	329.8	337.4	4.9E-02	5.0E-02
Zirconium, acetate lactate oxo ammonium complexes	68909-34-2	[a2]	188,346	689,739	161.0	589.5	[a2]	[a2]

Notes

Median 2009 DAF Value = 2,525

CBI - Confidential Business Information. Gradient was provided chemical-specific CAS and chemical names and used this information to evaluate chemical-specific toxicity.

[a] Chemicals with no RBC and no HQ are either classified as having low human health hazard potential or have no available human health toxicity information (see Appendix E).

[a1]: chemical listed as inert, GRAS, low priority, etc. [a2]: No toxicity information available

[b] Groundwater pathway analysis applied chemical adsorption in soil for DAF for three chemicals (see Appendix D)

[c] Hydrochloric acid and chlorous acid are expected to be readily neutralized in the environment

Table D.5 Sum of Groundwater Chemical HQs for HESI HF Systems using 2009 Groundwater DAF - Sudden Spills

Formulation Name	Stage	HF Volume (gal)	Spill Volume (gal)	Sum of Chemical HQs
Pre-frac Acid 01	Pre-frac	34,000	1,000	0.73
Pre-frac Acid 02	Pre-frac	73,000	1,000	0.71
Pre-frac Acid 03	Pre-frac	5,000	1,000	0.11
Foam frac 01	TW	5,340	1,000	0.14
Foam frac 01	XLF	22,082	1,000	0.67
Gel frac 01	XLF	1,915,000	10,000	0.21
Hybrid frac 01	LF	170,000	1,000	0.33
Hybrid frac 01	WF	4,500,000	10,000	0.08
Hybrid frac 02	TW	816,750	10,000	0.17
Hybrid frac 02	XLF	2,329,000	10,000	0.22
Hybrid frac 03	LF	29,203	1,000	0.13
Hybrid frac 03	XLF	97,000	1,000	0.09
Hybrid frac 04	TW	393,700	10,000	0.09
Hybrid frac 04	Flush	461,993	10,000	0.08
Hybrid frac 04	XLF	2,154,500	10,000	0.65
Hybrid frac 05	TW	849,000	10,000	0.10
Hybrid frac 05	XLF	1,247,100	10,000	0.33
Hybrid frac 06	TW	7,000	1,000	0.72
Hybrid frac 06	LF	175,680	1,000	0.34
Hybrid frac 06	XLF	1,179,324	10,000	0.41
Water frac 01	WF	4,500,000	10,000	0.08
Water frac 02	WF	4,500,000	10,000	0.08
Water frac 03	WF	7,310,000	10,000	0.06
Water frac 04	Flush	204,600	1,000	0.01
Water frac 04	LF	502,200	10,000	0.07

Median 2009 DAF Value = 2,525

Table D.6 Sum of Groundwater Chemical HQs for HESI HF Systems using 2009 Groundwater DAF - Diffuse Spills

Formulation Name	Stage	HF Fluid Volume (gal)	Spill Volume (gal)	Sum of Chemical HQs
Foam frac 01	TW + XLF	27,422	3,500	0.57
Foam frac 01	TW + XLF+Pre03	32,422	3,500	0.50
Foam frac 01	TW + XLF+Pre01	61,422	3,500	0.66
Foam frac 01	TW + XLF+Pre02	100,422	3,500	0.67
Gel frac 01	XLF	1,915,000	3,500	0.21
Gel frac 01	XLF+Pre03	1,920,000	3,500	0.21
Gel frac 01	XLF+Pre01	1,949,000	3,500	0.22
Gel frac 01	XLF+Pre02	1,988,000	3,500	0.23
Hybrid frac 01	LF + WF	4,670,000	3,500	0.09
Hybrid frac 01	LF + WF+Pre03	4,675,000	3,500	0.09
Hybrid frac 01	LF + WF+Pre01	4,704,000	3,500	0.09
Hybrid frac 01	LF + WF+Pre02	4,743,000	3,500	0.10
Hybrid frac 02	TW + XLF	3,145,750	3,500	0.21
Hybrid frac 02	TW + XLF+Pre03	3,150,750	3,500	0.21
Hybrid frac 02	TW + XLF+Pre01	3,179,750	3,500	0.22
Hybrid frac 02	TW + XLF+Pre02	3,218,750	3,500	0.22
Hybrid frac 03	LF+XLF	126,203	3,500	0.10
Hybrid frac 03	LF+XLF+Pre03	131,203	3,500	0.10
Hybrid frac 03	LF+XLF+Pre01	160,203	3,500	0.23
Hybrid frac 03	LF+XLF+Pre02	199,203	3,500	0.32
Hybrid frac 04	TW+XLF+Flush	3,010,193	3,500	0.49
Hybrid frac 04	TW+XLF+Flush+Pre03	3,015,193	3,500	0.49
Hybrid frac 04	TW+XLF+Flush+Pre01	3,044,193	3,500	0.49
Hybrid frac 04	TW+XLF+Flush+Pre02	3,083,193	3,500	0.49
Hybrid frac 05	TW+XLF	2,096,100	3,500	0.23
Hybrid frac 05	TW+XLF+Pre03	2,101,100	3,500	0.23
Hybrid frac 05	TW+XLF+Pre01	2,130,100	3,500	0.24
Hybrid frac 05	TW+XLF+Pre02	2,169,100	3,500	0.25
Hybrid frac 06	LF+XLF+TW	1,362,004	3,500	0.41
Hybrid frac 06	LF+XLF+TW+Pre03	1,367,004	3,500	0.41
Hybrid frac 06	LF+XLF+TW+Pre01	1,396,004	3,500	0.42
Hybrid frac 06	LF+XLF+TW+Pre02	1,435,004	3,500	0.42
Water frac 01	WF	4,500,000	3,500	0.08
Water frac 01	WF+Pre03	4,505,000	3,500	0.08
Water frac 01	WF+Pre01	4,534,000	3,500	0.08
Water frac 01	WF+Pre02	4,573,000	3,500	0.09
Water frac 02	WF	4,500,000	3,500	0.08
Water frac 02	WF+Pre03	4,505,000	3,500	0.08
Water frac 02	WF+Pre01	4,534,000	3,500	0.09
Water frac 02	WF+Pre02	4,573,000	3,500	0.09
Water frac 03	WF	7,310,000	3,500	0.06
Water frac 03	WF+Pre03	7,315,000	3,500	0.06
Water frac 03	WF+Pre01	7,344,000	3,500	0.06
Water frac 03	WF+Pre02	7,383,000	3,500	0.07
Water frac 04	LF+Flush	706,800	3,500	0.05
Water frac 04	LF+Flush+Pre03	711,800	3,500	0.05
Water frac 04	LF+Flush+Pre01	740,800	3,500	0.08
Water frac 04	LF+Flush+Pre02	779,800	3,500	0.11

Median 2009 DAF Value = 2,525

Each HF system evaluated with different pre-frac acid treatment (Pre01, Pre02, Pre03)

Appendix E

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

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List of 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
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
TCEQ	Texas Commission on Environmental Quality
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

E.1 Overview

This appendix describes the sources of chemical toxicity information and methods we relied upon to develop health protective drinking water risk-based chemical concentrations (RBCs) for constituents in hydraulic fracturing (HF) fluid additives. These RBCs, developed in accordance with United States Environmental Protection Agency (US EPA) risk assessment guidelines and methods (US EPA, 1996, 2009a, 2010a) reflect chemical concentrations in drinking water that would not be expected to pose human health risks.

Overall, our approach involved using agency-established health-protective drinking water limits and toxicity factors, when available [*e.g.*, maximum contaminant levels (MCLs), regional screening levels (RSLs), 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 either identified toxicity information for a chemical surrogate and used that information to develop an RBC, or used route-to-route extrapolation based on existing inhalation criteria. For compounds where we could not locate an appropriate chemical surrogate or use route-to route extrapolation, we performed a qualitative hazard assessment based on one of several different evaluations performed by the United States Food and Drug Administration (US FDA), US EPA, or Health Canada.

E.2 Sources of Toxicological Information for Use in Risk Analysis

As presented in the rdSGEIS, 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 toxicity information we examined to determine RBCs for these constituents are described below (also see Table E.1).

Chemical-Specific, Quantitative Toxicity Factors: US regulatory agencies and other reputable scientific institutions are important sources of quantitative toxicity information. In particular, the US EPA has developed MCLs and tap water regional screening levels, 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 [*e.g.*, US FDA, 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 E.3, 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 ample information from long-term toxicology studies, we developed toxicity factors *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.

Quantitative Toxicity Factors Derived Using Route-to-Rout Extrapolation: If no suitable oral toxicity information was available we identified established, chemical-specific inhalation toxicity factors. Using a standard methodology (US EPA, 1994), we converted these inhalation exposures to an equivalent oral dose.

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 E.1
Sources of Toxicity Information Used in the HF Risk Evaluation

Information Type	Specific Examples
<i>Chemical-Specific, Quantitative Toxicity Factors</i>	
	MCLs RSLs US EPA Values (IRIS, PPRTV, HEAST, OPP) CalEPA values ATSDR MRLs Dietary Reference Intakes NSF RfDs TPHCWG criteria GRAS/JECFA Safe Intake Levels
<i>Sources of Chemical-Specific or Surrogate Information Used to Develop Toxicity Factors</i>	
	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
<i>Qualitative Toxicity Information on Hazard Potential</i>	
	Health Canada's Chemical Prioritization Program US EPA Low Hazard Polymer Exemption Guidance US EPA Tolerance Exempt Chemical Lists (40 CFR part 180)

E.3 Hierarchy for Selecting Toxicological Information

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 constituents. This tiered hierarchy incorporates standard risk assessment practice and US EPA guidance (US EPA, 1996, 2009a, 2010a). This sequential methodology is described below and depicted in Figure E.1:

- 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 (2010b) as the RBC, where they were available. These RSLs are based on long-term drinking water consumption (*i.e.*, 70-kg individual ingesting 2 L/day of water over a 30-year period).

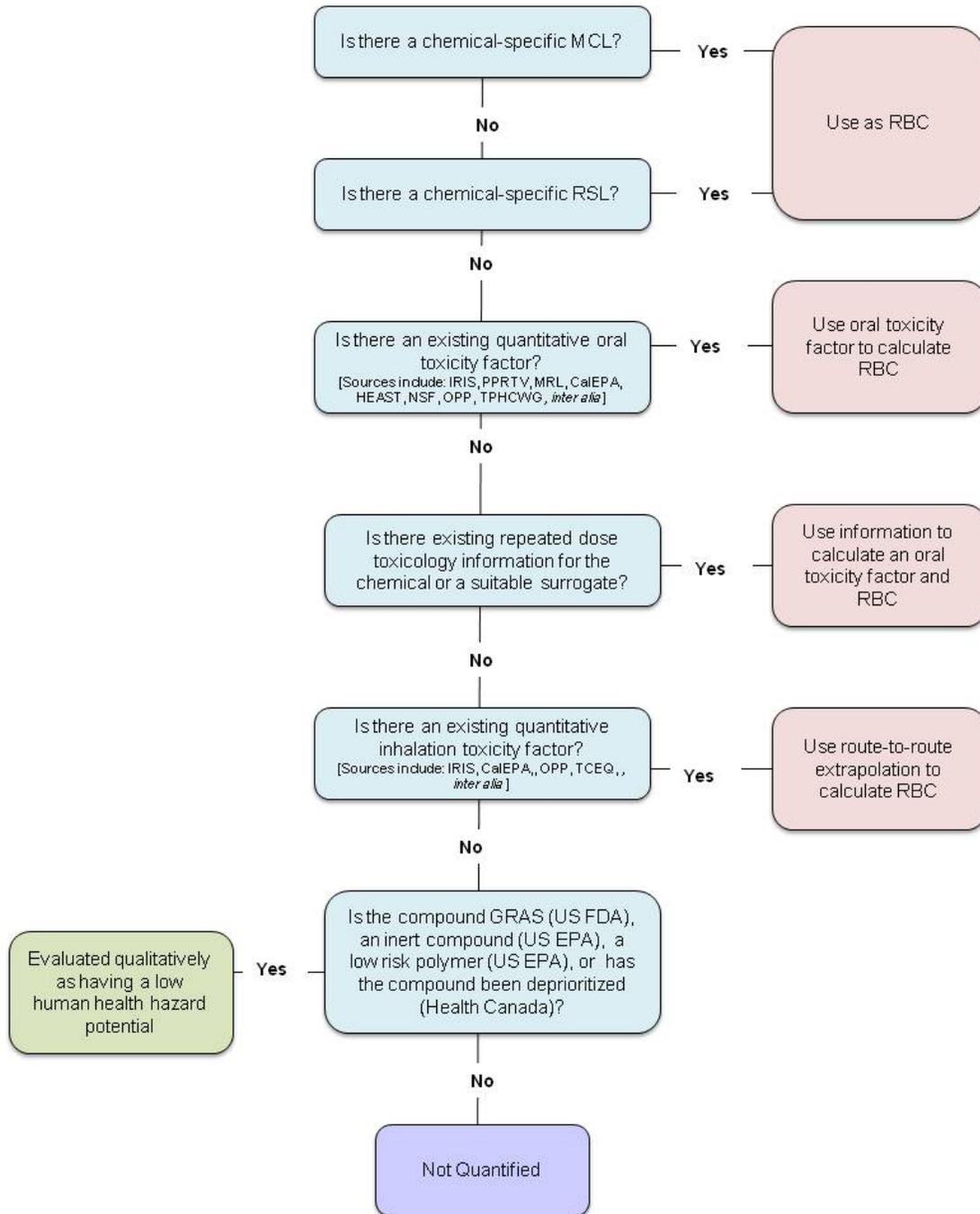
- If MCLs and RSLs were not available, we used quantitative oral toxicity factors published by various regulatory agencies to calculate health-protective RBCs. The RBCs calculated in this manner were based on exposure assumptions consistent with US EPA's RSL methodology (*i.e.*, 70-kg individual ingesting 2 L/day of water over a 30-year period). 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). We identified relevant no observed adverse effect levels (NOAELs) and/or lowest observed adverse effect levels (LOAELs) from an extensive toxicological evaluation of the chemical of interest or a suitable surrogate and, in an attempt to be health-protective, applied a generic uncertainty factor of 3,000, which is the maximum uncertainty factor recommended by US EPA guidance¹ (US EPA, 2002). If multiple studies were available we chose the lowest NOAEL or LOAEL .
- 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.
- Chemicals without MCLs, RSLs, agency-established oral toxicity factors, or repeat dose oral toxicity studies (for the chemical itself or an appropriate surrogate) were cross-referenced with lists of chemicals with established quantitative inhalation toxicity criteria [*e.g.*, Texas Commission on Environmental Quality (TCEQ) Long-Term Effect Screening Level]. If a chemical was identified with an established inhalation standard (*e.g.*, in m³/day), a health protective drinking water concentration was determined using route-to-route extrapolation and standard exposure assumptions that form the basis of the respective TCEQ inhalation guideline (*i.e.*, a 70-kg individual will breathe 20 m³/day of air).
- For chemicals that did not meet any of the above criteria, we either:
 - ▶ Cross-referenced the chemical of interest with lists of chemicals that have a low potential to pose a human health risk (*e.g.*, Health Canada Domestic Substances List, 40 CFR Part 180 "Exempt" Lists, US EPA Polymer exemptions). Chemicals designated on these lists as having a low human health hazard potential were not further quantified in our risk evaluation; or

¹ Using a combined uncertainty factor of 3,000 is highly conservative in many cases. In instances where we identified a NOAEL from a chronic study, an uncertainty factor of 100 would be more appropriate.

- ▶ Determined that, due to the lack of both quantitative and qualitative hazard information, it was not possible to evaluate the chemical of interest in this risk evaluation.

Table E.2 contains all the chemical RBCs used in this risk analysis.

Figure E.1
Hierarchy Flowchart of Toxicological Information Used in the Human Health Risk Evaluation



E.4 Toxicological Information Sources

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

E.4.1. 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 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; US EPA Region III, 2009a). For HF constituents with a promulgated MCL, we selected the MCL as the RBC.

E.4.2 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, 2010a). Unlike MCLs, RSLs are not enforceable drinking water standards; they are risk-based values that do not consider feasibility. According to the regional US EPA offices (US EPA Region III, 2009b):

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 from both cancer and non-cancer agents; 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 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). For HF constituents lacking an MCL, but for which a published drinking water RSL existed, we used the residential RSL as the RBC.

E.4.3 Agency-Established Toxicity Factors

Oral toxicity criteria can be used to develop safe levels of exposure involving chemical ingestion, including health-protective chemical concentrations in drinking water. US EPA as well as several other US agencies and leading scientific institutions have developed chemical-specific oral toxicity values. Specific resources used in this evaluation are summarized below.

E.4.3.1 RBCs Derived From US EPA Derived Toxicity Factors

The preferential source for quantitative human health risk assessment criteria is the US EPA's IRIS (US EPA, 2009c). 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).

E.4.3.2 RBC Derived From 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) (IOM, 2004). 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, 2009d).

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, 2011). 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).

E.4.3.3 RBCs Derived Using Chemical-Specific or Surrogate Toxicity Information

In the absence of an existing toxicity criterion from the above sources, we developed chemical-specific toxicity factors *de novo* using an approach consistent with the US EPA IRIS methodology. 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.

In an effort to be comprehensive and evaluate as many chemicals as possible, we conducted an extensive review of toxicology information for all HF constituents² 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." This RfD was then converted to an RBC in tap water using standard US EPA exposure assumptions. This approach was also taken for 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.

² 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 with an acceptable daily intake of 350 mg/day (for an 18-year-old adult), and not the chloride ion with an analogous acceptable daily intake of 2,300 mg/day.

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 a generic uncertainty factor of 3,000, which is the maximum UF recommended by US EPA guidance, to derive a chronic toxicity factor (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.

E.4.3.4 RBCs Based on Route-to-Route Extrapolation of Agency Toxicity Factors

If no oral toxicity data were available, but an inhalation toxicological criterion for an HF chemical existed, we used route-to-route extrapolation to convert the inhalation toxicity factor to an oral criterion. This procedure is consistent with US EPA (1994) and other state environmental regulatory agencies (*e.g.*, Texas; TCEQ, 2008) that have performed route-to-route extrapolation when no route-specific toxicity information is available.

US EPA (1994) guidance was used when conducting route-to-route extrapolations of inhalation-based toxicity criteria. While this report was published over 15 years ago, it represents the most recent guidance with respect to conducting route-to-route extrapolation (US EPA, 2009e). Specifically, Gradient's route-to-route extrapolation process assumes that a 70-kg individual will breathe at a rate of 20 m³/day.

These values should be carefully considered in more refined assessments. While our extrapolations account for both breathing and body weight, it is important to consider the potential reactivity of airborne toxicants (*e.g.*, portal-of-entry effects), the pharmacokinetic behavior of toxicants for different routes of exposure (*e.g.*, absorption by the gut versus absorption by the lung), and the significance of physicochemical properties in determining dose (*e.g.*, volatility, speciation). Given that these inhalation values were selected based on the lack of credible repeat-dose oral studies, they are used with a higher level of uncertainty as compared to oral toxicity criteria that are based on a more relevant toxicological characterization.

In this evaluation, only two RBCs were developed using route-to-route extrapolation, and both of these RBCs were based on inhalation criteria developed by TCEQ.

E.4.4 Qualitative Toxicity Information on Hazard Potential

Several available data sources have assessed the potential for a chemical to pose a public health concern. While this information is semi-quantitative or qualitative, for the purposes of this risk evaluation, we used this information to make some 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. Compounds listed in Table E-2 as "Inert Ingredients" are also shown in Table E-3 along with the specific lists on which the compound appears and specific US government exemptions for these chemicals.

E.4.4.1 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

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.

E.4.4.1.1 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, 2011). Table E.3 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.

E.4.4.1.2 US EPA Inert Ingredients

US EPA has also identified several groups of chemicals that are exempt from the requirement to derive a tolerance level (US EPA refers to these chemicals as "inert ingredients"). The term "inert ingredient" is a legal definition as defined by the Federal Insecticide, Fungicide, and Rodenticide Act that 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, 2011). 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 E.3 lists 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/f?p=901:1:1329682795855013>)

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).

E.4.4.2 Health Canada Assessments

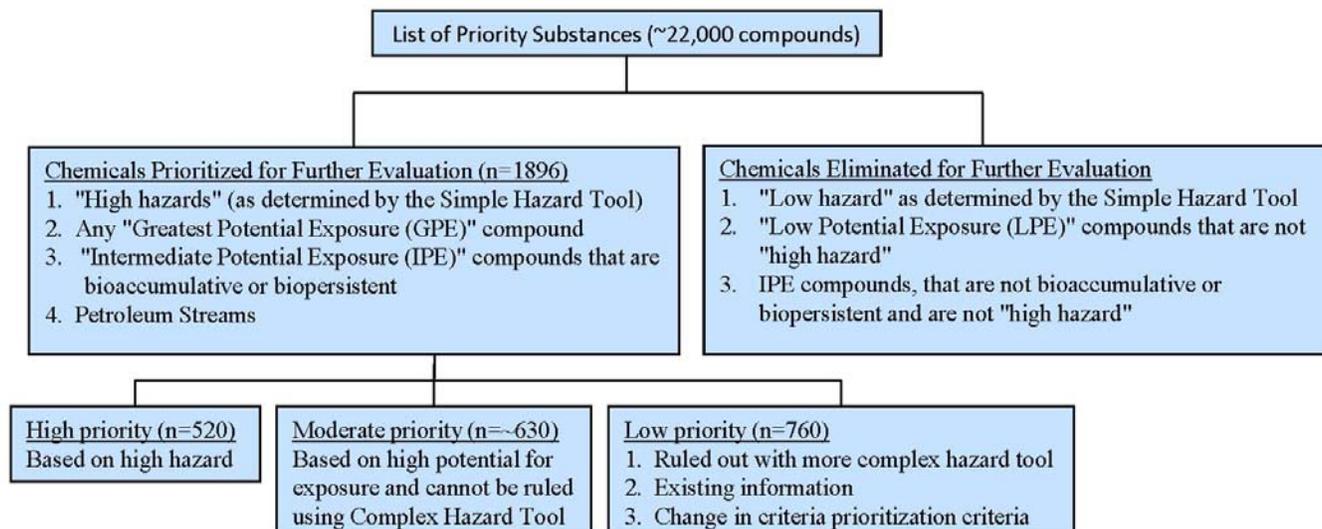
E.4.4.2.1 Health Canada Food Additives

Health Canada defines a substance as a food additive if it is a chemical that is "added to food during preparation or storage and either becomes a part of the food or affects its characteristics for the purpose of achieving a particular technical effect" (Health Canada, 2006). For example, substances that are used to enhance the appearance or texture of a food or serve as essential aids in the processing of food are all considered to be food additives.

E.4.4.2.2 Health Canada Lists of Priority Substances

Beginning in 1999, under a government mandate, Health Canada undertook efforts to prioritize chemicals that could pose human health and ecological risks for approximately 22,400 substances. These were chemicals used, imported, or manufactured in Canada for commercial purposes between January 1, 1984 and December 31, 1986 (at a quantity of greater than 100 kg per year). In 2006, Health Canada (2009) completed this initial evaluation and determined which chemicals due to high toxicity and/or a high potential for exposure required a more detailed risk assessment (see Figure E.2).

**Figure E.2
Health Canada Prioritization Scheme**



In the initial assessment, all 22,400 substances were screened for potential toxicity using the "Simple Hazard Tool." This tool identified all chemicals with existing evidence of carcinogenicity, genotoxicity, developmental toxicity, and reproductive toxicity according to several key agencies, including the European Community, Health Canada, International Agency for Research on Cancer, US National Toxicology Program, and US EPA. Any compound meeting hazard criteria established by these agencies for particular health endpoints, was considered a "high hazard" compound (Health Canada, 2009).

Using the Simple Hazard tool, all chemicals were also screened against low hazard criteria. More specifically, if a chemical appeared on a designated low hazard list, the chemical was de-prioritized for further consideration. The low hazard lists included the following:

- Health Canada's Pesticide Formulant 4A List: Formulants of Minimal Toxicological Concern
- US EPA's List 4A: Minimal Risk Inert Ingredients
- Organisation for Economic Co-operation and Development's draft list of chemicals that do not need assessment in the High-Production Volume (HPV) Chemicals Program

- European Community's Annex II to Council Regulation 793/93 of 23 March 1993 on the evaluation and control of the risks of existing substances: List of substances exempt from the provisions of Articles 3 and 4
- US EPA's HPV Challenge Program chemicals not considered to be candidates for testing under the HPV Challenge Program, based on preliminary US EPA review indicating that testing using the SIDS base set would not further understanding of the chemicals' properties (Indicator 1)

In addition to the simple hazard tool, the initial chemical evaluation also considered the potential for human exposure and the potential for ecological toxicity. Under these considerations, chemicals with the greatest potential for human exposure and chemicals with an intermediate potential for human exposure, which were also biopersistent and bioaccumulative, were prioritized for further consideration (Health Canada, 2009).

Using these criteria, Health Canada indentified 1,896 substances that would be further considered in additional stages of the prioritization/screening assessment (*i.e.*, categorization). Specifically, these remaining chemicals were divided into "high," "moderate," and "low" priority. High priority chemicals included all chemicals that had a high potential to pose a human health hazard. Moderate priority compounds had the potential for higher exposure, but were not considered hazardous by the simple hazard tool (and could not be ruled out using a more complex hazard tool).³ Low priority substances either had extensive existing information (and thus were not prioritized for human study) or were considered low toxicity using more sophisticated tools to assess hazard (Health Canada, 2009).

We compared the subset of HESI HF constituents lacking MCLs/RSLs or other reliable toxicity factors with the chemicals that underwent prioritization by Health Canada. Those HF constituents that were deemed be an unlikely health concern according to the Health Canada prioritization approach, were not included in our quantitative risk analysis. These included chemicals that were either not prioritized in the initial Health Canada assessment (*i.e.*, were not among the 1,896 chemicals prioritized for further evaluation) or when prioritized were subsequently determined to have low toxicity.

³ The complex hazard tool uses more quantitative information to assess a wider array of health endpoints than the simple hazard tool. Quantitative structure activity relationship information can also be used in the complex hazard tool in the absence of chemical-specific data.

E.4.4.3 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 is as follows (US EPA, 2009f):

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."

Polymers meeting the above criteria were determined to have a low human health hazard potential and were not considered further in our risk analysis (Table E.2).

E.4.5 Chemicals Lacking Reliable Toxicity Information

We determined that for several compounds, due to the lack of chemical-specific information and lack of a suitable surrogate, it was not possible to reliably calculate a toxicity factor. Therefore, we excluded these compounds from risk consideration (see Table E.2).

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Table E.2 Human Health Risk Based Concentrations (RBC) For Drinking Water Consumption.

Chemical	HF Chemical CAS Number	Basis for Chemical Risk Based Concentration (RBC)	RBC (ug/L)	RBC Note ^[a]	RBC Basis Notes
1,2,4 Trimethylbenzene	95-63-6	1,2,4 Trimethylbenzene	70	A	PPRTV -derived RfC of 7x10 ⁻³ mg/m ³ , (route-to-route extrapolation)
2-Bromo-2-nitro-1,3-propanediol	52-51-7	2-Bromo-2-nitro-1,3-propanediol	3500	A	Existing OPP toxicity factor (US EPA, 1995)
Acetic acid	64-19-7	Acetic acid	499800	B	Quantitative JEFCA information (JEFCA, 1974)
Acetic anhydride	108-24-7	Acetic acid	499800	B	Quantitative JEFCA information (JEFCA, 1974)
Alcohols, C12-16, ethoxylated	68551-12-2	Ethoxylated Alcohols	13125	B	Working group derived toxicity factor (HERA, 2009)
Alcohols, C14-C15, ethoxylated	68951-67-7	Ethoxylated Alcohols	13125	B	Working group derived toxicity factor (HERA, 2009)
Aldehyde	CBI	Aldehyde	--	C	No RBC (US FDA GRAS; US EPA Inert [InertFinder]; Health Canada)
Alkyl (C14-C16) olefin sulfonate, sodium salt	68439-57-6	Alkyl (C14-C16) olefin sulfonate, sodium salt	1155	B	Repeat-dose toxicity study
Amines, coco alkyl, ethoxylated	61791-14-8	Amines, coco alkyl, ethoxylated	--	D	No RBC (US EPA Inert CFR180.91 & 180.93; Health Canada)
Ammonium acetate	631-61-8	Ammonium acetate	--	C	No RBC (US FDA GRAS; US EPA Inert [InertFinder]; Health Canada)
Ammonium chloride	12125-02-9	Ammonium chloride	7980	B	Repeat-dose toxicity study (OECD, 2004)
Ammonium persulfate	7727-54-0	Ammonium persulfate	490	B	Repeat-dose toxicity study (OECD, 2005)
Ammonium phosphate	7722-76-1	Ammonium phosphate	30000	A	US EPA (2006b) lifetime health advisory level for ammonia
Attapulgate	12174-11-7	Attapulgate	4480000	B	Prescription drug use information (MedicineNet, 1999)
Bentonite, benzyl(hydrogenated tallow alkyl) dimethylammonium stearate complex	121888-68-4	Bentonite, benzyl(hydrogenated tallow alkyl) dimethylammonium stearate complex	--	D	No RBC (US EPA Inert [InertFinder])
Borate salt	CBI	Boron	3100	C	US EPA ingestion RSL
C.I. Pigment Orange 5	3468-63-1	CI Pigment Red	280	D	Repeat-dose toxicity study (CPMA, 2006)
Calcium chloride	10043-52-4	Calcium chloride	11655	C	Repeat-dose toxicity study (OECD, 2002c)
Carbohydrate	CBI	Carbohydrate	--	B	No RBC (US FDA GRAS; US EPA Inert CFR180.950e; Health Canada)
Chloromethylnaphthalene quinoline quaternary amine	15619-48-4	Chloromethylnaphthalene quinoline quaternary amine	--	E	Unable to locate any relevant information.
Chlorous acid, sodium salt	7758-19-2	Chlorous acid, sodium salt	1000	A	US EPA MCL
Citrus, extract	94266-47-4	Citrus, extract	--	D	No RBC (US EPA Inert [InertFinder])
Cobalt acetate	71-48-7	Cobalt	5	A	US EPA ingestion RSL
Crystalline silica, quartz	14808-60-7	silicas/silicates	29155	B	Repeat-dose toxicity study (OECD, 2004)
Cured acrylic resin	CBI	Cured acrylic resin	--	D	No RBC (no repeat-dose toxicity information)
Diethylene glycol	111-46-6	Diethylene glycol	3500	D	Repeat-dose toxicity study (Wagner, 2006)
Diethylenetriamine	111-40-0	Diethylenetriamine	805	B	Repeat-dose toxicity study (AP&G, 2003)
EDTA/Copper chelate	CBI	Copper	630	C	US EPA ingestion RSL
Ethanol	64-17-5	Ethanol	28000	B	Repeat-dose toxicity study (OECD, 2004)
Ethoxylate fatty acid	CBI	Ethoxylate fatty acid	66792	D	Repeat-dose toxicity study
Ethoxylate fatty acid	CBI	Ethoxylate fatty acid	--	C	No RBC (US FDA GRAS; US EPA Inert CFR180.91 & 180.93)
Ethoxylated branched C13 alcohol	78330-21-9	Ethoxylated Alcohols	13125	B	Working group derived toxicity factor (HERA, 2009)
Ethoxylated fatty acid	CBI	Ethoxylated fatty acid	--	D	No RBC (US EPA Inert [InertFinder])
Ethylene glycol monobutyl ether	111-76-2	Ethylene glycol monobutyl ether	1600	A	US EPA ingestion RSL
Fatty acid ester	CBI	Fatty acid ester	1000	D	TCEQ (2010) Long-Term Effect Screening Level (Inhalation)
Fatty acid tall oil	CBI	Fatty acid tall oil	29155	B	Repeat-dose toxicity study
Fatty acid tall oil amide	CBI	Fatty acid tall oil amide	--	D	No RBC (US EPA Inert [InertFinder]; Health Canada)
Fatty alcohol polyglycol ether surfactant	9043-30-5	Fatty alcohol polyglycol ether surfactant	--	C	No RBC (US EPA Inert CFR180.91, 180.93, 180.94a, 180.96; Health Canada)
Fatty acid ester ethoxylate	CBI	Fatty acid ester ethoxylate	350000	B	Repeat-dose toxicity study
Formaldehyde	50-00-0	Formaldehyde	3100	A	US EPA ingestion RSL
Glycerine	56-81-5	Glycerine	93333	B	Repeat-dose toxicology study (ECHA, 2011)
Guar gum	9000-30-0	Guar gum	--	B	No RBC (US FDA GRAS; US EPA Inert CFR180.950e; Health Canada)
Guar gum derivative	CBI	Guar gum derivative	--	D	No RBC (US EPA Inert CFR180.920; Health Canada)
Heavy aromatic petroleum naphtha	64742-94-5	Petroleum Distillate	1400	B	Working group derived toxicity factor (TPHCWG, 1997)
Hemicellulase enzyme	9012-54-8	Hemicellulase enzyme	--	D	No RBC (US EPA Inert [InertFinder])
Hydrochloric Acid	7647-01-0	Hydrochloric Acid	200	D	IRIS RfC Inhalation of 2.0 x10 ⁻² mg/m ³ (route-to-route extrapolation)
Hydrotreated light petroleum distillate	64742-47-8	Petroleum Distillate	3500	B	Working group derived toxicity factor (TPHCWG, 1997)
Inorganic salt	CBI	Inorganic salt	--	C	No RBC (US FDA GRAS; US EPA Inert [InertFinder];)
Isopropanol	67-63-0	Isopropanol	350000	B	Repeat-dose toxicity study (Gentry et al., 2002)
Magnesium chloride hexahydrate	7791-18-6	Magnesium	175000	A	Dietary Reference Intake Value (IOM, 2001)
Methanol	67-56-1	Methanol	7800	A	US EPA ingestion RSL
Naphtha, hydrotreated heavy	64742-48-9	Petroleum Distillate	3500	B	Working group derived toxicity factor (TPHCWG, 1997)
Naphthalene	91-20-3	Naphthalene	310	A	US EPA ingestion RSL
Naphthenic acid ethoxylate	68410-62-8	Naphthenic Acids	210	D	Repeat-dose toxicity study (Rogers et al., 2002)
Nonylphenol ethoxylated	127087-87-0	Nonylphenol ethoxylated	2345	C	Repeat-dose toxicity study (DOW, 2007)
Olefin	CBI	Olefin	100	D	TCEQ (2010) Long-Term Effect Screening Level (Inhalation)
Olefin	CBI	Olefin	1000	D	TCEQ (2010) Long-Term Effect Screening Level (Inhalation)

Table E.2 Human Health Risk Based Concentrations (RBC) For Drinking Water Consumption.

Chemical	HF Chemical CAS Number	Basis for Chemical Risk Based Concentration (RBC)	RBC (ug/L)	RBC Note ^[a]	RBC Basis Notes
Olefin	CBI	Olefin	1000	D	TCEQ (2010) Long-Term Effect Screening Level (Inhalation)
Olefin	CBI	Olefin	1000	D	TCEQ (2010) Long-Term Effect Screening Level (Inhalation)
Organic phosphonate	CBI	Organic phosphonate	--	D	No RBC (Health Canada)
Oxylated phenolic resin	CBI	Oxylated phenolic resin	--	D	No RBC (US EPA Low Hazard Polymer)
Oxylated phenolic resin	CBI	Oxylated phenolic resin	--	D	No RBC (US EPA Low Hazard Polymer)
Polyacrylamide copolymer	CBI	Polyacrylamide copolymer	--	D	No RBC (Health Canada)
Polyoxylated fatty amine salt	61791-26-2	Polyoxylated fatty amine salt	--	C	No RBC (US EPA Inert CFR180.92 & 180.93)
Potassium carbonate	584-08-7	Potassium carbonate	2345000	A	Dietary Reference Intake Value
Potassium formate	590-29-4	Calcium Formate	3500	D	Repeat-dose toxicity study (ACC, 2001)
Potassium hydroxide	1310-58-3	Potassium hydroxide	2345000	A	Dietary Reference Intake Value (IOM, 2005)
Potassium metaborate	13709-94-9	Potassium metaborate	--	D	No RBC (Health Canada)
Propanol	71-23-8	Propanol	101675	C	Repeat-dose toxicity study (Wagner, 2005)
Propargyl alcohol	107-19-7	Propargyl alcohol	31	A	US EPA ingestion RSL
Proprietary	CBI	Proprietary	--	E	Unable to locate any relevant information (Natural clay material)
Quaternary ammonium compound	CBI	Quaternary ammonium compound	--	E	Unable to locate any relevant information.
Quaternary ammonium compounds, bis(hydrogenated tallow alkyl) dimethyl, salts with bentonite	68953-58-2	Quaternary ammonium compounds, bis(hydrogenated tallow alkyl) dimethyl, salts with bentonite	145845	B	Repeat-dose toxicity study (OECD, 2007)
Quaternary ammonium salt	CBI	Quaternary ammonium salt	--	E	Unable to locate any relevant information.
Reaction product of acetophenone, formaldehyde, thiourea and oleic acid in dimethyl formamide	68527-49-1	Reaction product of acetophenone, formaldehyde, thiourea and oleic acid in dimethyl formamide	--	D	No RBC (Health Canada)
Silica gel	112926-00-8	silicas/silicates	29155	B	Repeat-dose toxicity study (OECD, 2004)
Silica, amorphous -- fumed	7631-86-9	silicas/silicates	29155	B	Repeat-dose toxicity study (OECD, 2004)
Sodium bicarbonate	144-55-8	Sodium bicarbonate	1998500	C	Over the counter drug use information.
Sodium carboxymethyl cellulose	9004-32-4	Sodium carboxymethyl cellulose	45500	C	Repeat-dose toxicity study (Rowe et al., 1944)
Sodium chloride	7647-14-5	Sodium chloride	2901500	A	Dietary Reference Intake Value (IOM, 2001)
Sodium glycolate	2836-32-0	Sodium glycolate	--	D	No RBC (US EPA Inert [InertFinder]; Health Canada)
Sodium hydroxide	1310-73-2	Sodium	1150000	A	Dietary Reference Intake Value (IOM, 2005)
Sodium hypochlorite	7681-52-9	Sodium hypochlorite	1120	B	Repeat-dose toxicity study (Kurokawa et al., 1986 (cited in IRIS Chlorine record))
Sodium iodide	7681-82-5	Iodine	160	A	US EPA ingestion RSL
Sodium perborate tetrahydrate	10486-00-7	Sodium perborate tetrahydrate	11667	B	Repeat-dose toxicity study (HERA, 2004)
Sodium persulfate	7775-27-1	Sodium persulfate	2345	B	MCL Health Canada (sulfate)
Sodium sulfate	7757-82-6	Sulfate	500000	D	US EPA Health-Based Advisory; MCL Health Canada (sulfate)
Sodium sulfite	7757-83-7	Sodium sulfite	--	C	No RBC (US FDA GRAS; US EPA Inert [InertFinder]; Health Canada)
Sodium thiosulfate	7772-98-7	Sulfate	500000	D	US EPA Health-Based Advisory; MCL Health Canada (sulfate)
Surfactant mixture	CBI	Surfactant mixture	--	D	No RBC (Health Canada)
Surfactant mixture	CBI	Surfactant mixture	13125	B	Working group derived toxicity factor (HERA, 2009)
Terpenoid	CBI	Terpenoid	2917	C	IRIS record: NOAEL is 250 mg/kg-d
Terpenoid	CBI	Terpenoid	2917	C	IRIS record: NOAEL is 250 mg/kg-d
Tributyl tetradecyl phosphonium chloride	81741-28-8	Tributyl tetradecyl phosphonium chloride	105	B	Repeat-dose toxicity study (Malish, 2009)
Triethanolamine zirconate	101033-44-7	Triethanolamine zirconate	--	E	Unable to locate any relevant information.
Ulexite (B5H3O9.Ca.8H2O.Na)	1319-33-1	Boron	3100	C	US EPA ingestion RSL
Zirconium, acetate lactate oxo ammonium complexes	68909-34-2	Zirconium, acetate lactate oxo ammonium complexes	--	E	Unable to locate any relevant information.

Table E.2 Human Health Risk Based Concentrations (RBC) For Drinking Water Consumption.

Chemical	HF Chemical CAS Number	Basis for Chemical Risk Based Concentration (RBC)	RBC (ug/L)	RBC Note ^[a]	RBC Basis Notes
Flowback Constituents					
Aluminum	7439-90-5	Aluminum	16,000	A	US EPA ingestion RSL
Aqueous ammonia	7664-41-7	Aqueous ammonia	30,000	A	EPA Lifetime health advisory level
Arsenic	7440-38-2	Arsenic	10	A	Drinking water MCL
Barium	7440-39-3	Barium	2,000	A	Drinking water MCL
Benzene	71-43-2	Benzene	5	A	Drinking water MCL
Boron	7440-42-8	Boron	3,100	A	US EPA ingestion RSL
Bromide	24959-67-9	Bromide	6,000	A	WHO
Cadmium	7440-43-9	Cadmium	5	A	Drinking water MCL
Calcium	7440-70-2	Calcium	1,249,500	A	Derived from Upper Limit of tolerable intake/70kg
Chromium	7440-47-3	Chromium	100	A	Drinking water MCL
Cobalt	7440-48-4	Cobalt	4.7	A	US EPA ingestion RSL
Copper	7440-50-8	Copper	1,300	A	Drinking water MCL
Ethyl Benzene	100-41-4	Ethyl Benzene	700	A	Drinking water MCL
Iron	7439-89-6	Iron	11,000	A	US EPA ingestion RSL
Lead	7439-92-1	Lead	15	A	Drinking water MCL
Lithium	7439-93-2	Lithium	70	A	Derived from RfD - PPRTV
Magnesium	7439-95-4	Magnesium	175,000	A	Derived from Upper Limit of tolerable intake/70kg
Manganese	7439-96-5	Manganese	320	A	US EPA ingestion RSL
Molybdenum	7439-98-7	Molybdenum	78	A	US EPA ingestion RSL
Nickel	7440-02-0	Nickel	300	A	US EPA ingestion RSL
Phenols	64743-03-9	Phenols	4,500	A	US EPA ingestion RSL
Potassium	7440-09-7	Potassium	2,345,000	A	Derived from Acceptable Intake
Sodium	7440-23-5	Sodium	1,151,500	A	Derived from Upper Limit of tolerable intake/70kg
Strontium	7440-24-6	Strontium	9,300	A	US EPA ingestion RSL
Sulfate	14808-79-8	Sulfate	500,000	A	MCL Health Canada
Toluene	108-88-3	Toluene	1,000	A	Drinking water MCL
xylenes	1330-20-7	xylenes	10,000	A	Drinking water MCL
Zinc	7440-66-6	Zinc	4,700	A	US EPA ingestion RSL
NORM ^[b]			pCi/L		
Cs-137		Cs-137	1.74	A	US EPA Preliminary remediation goal for drinking water.
Ra-226		Ra-226	5	A	MCL (Ra 228/226 combined)
Ra-228		Ra-228	5	A	MCL (Ra 228/226 combined)

Notes:

[a] See Table E.3

[b] Naturally occurring radioactive material.

CBI - Confidential Business Information. Gradient was provided chemical-specific CAS and chemical names and used this information to evaluate chemical-specific toxicity.

Table E.3 RBC Notes

RBC Note	Examples of Respective RBC Derivation
A	<p>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).</p> <p>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).</p>
B	<p>The criterion or safe level was developed by a non-US governmental agency (e.g JECFA).</p> <p>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.</p> <p>The COC was not further considered because it is listed as "minimal risk inert ingredient" for pesticide use</p>
C	<p>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.</p> <p>The toxicological criterion was developed from an existing inhalation criterion using route-to-route extrapolation (e.g., an inhalation RfC was used to derive an ingestion risk estimate). Substantial data on the ADME⁺ and target organ effects for this chemical are available (e.g., IRIS documentation for an RfC)</p>
D	<p>The toxicological criterion has been derived from an existing criterion using route-to-route extrapolation (e.g., an inhalation RfC was used to derive an ingestion risk estimate). Limited data are available on the ADME⁺ and target organ effects for this chemical (e.g., TCEQ LT ESL).</p> <p>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.</p> <p>The COC was not further considered because it has been identified as a "low-priority" chemical by an authoritative agency (e.g., US EPA Polymer Guidance; Health Canada Non-Priority Substance).</p> <p>The COC is listed as an inert ingredient in consumer products (e.g., household cleaners, cosmetics). No quantitative data on safe levels of intake per person are available.</p>
E	<p>No data are available to evaluate the toxicological hazard of chronic exposure.</p>

Table E.3 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 E – Table E.2 References

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