



Modeling Drinking Water Related Human Health Risks from Hydraulic Fracturing (HF) Additives

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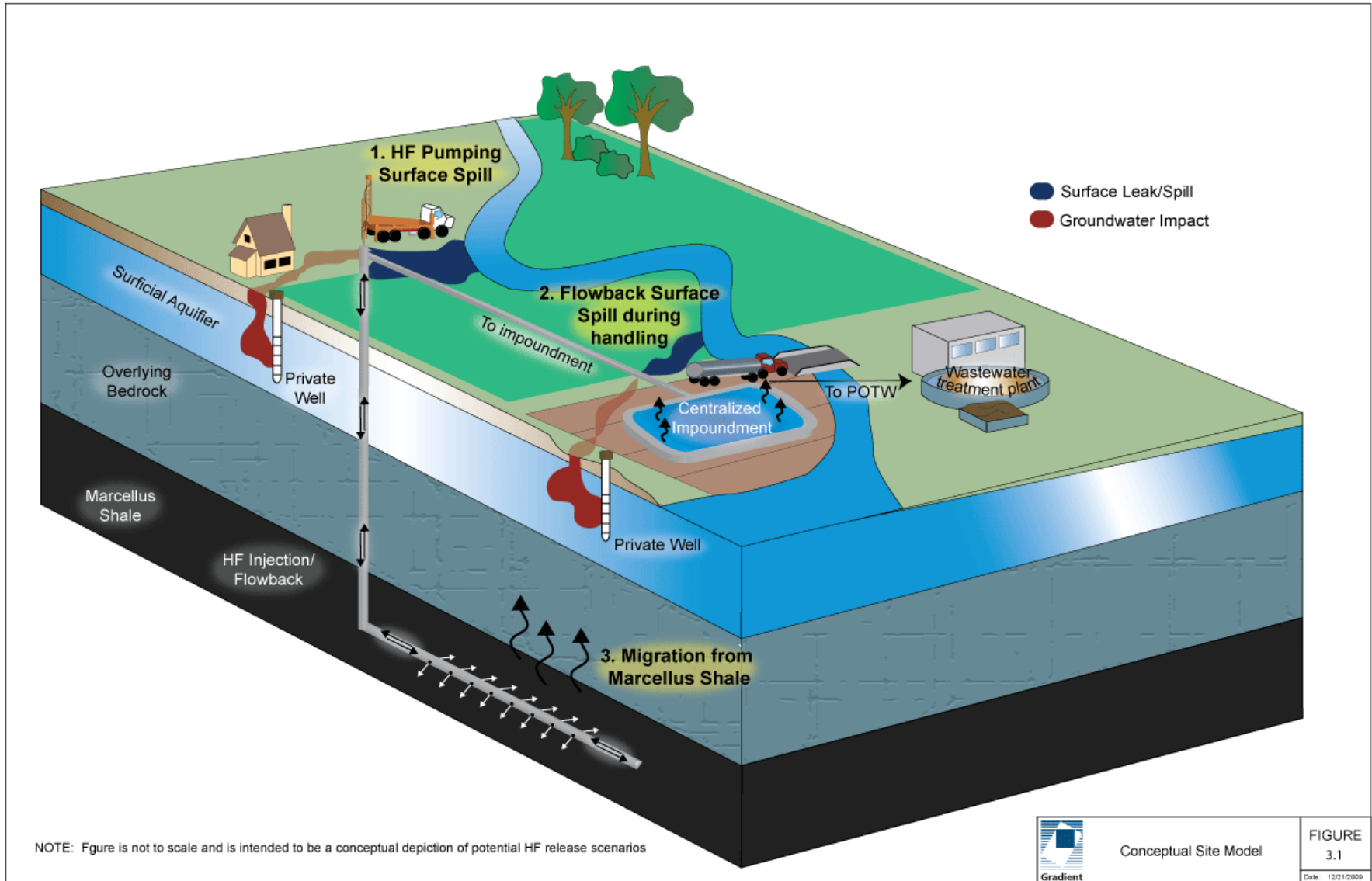
EPA HF Workshop

March 29, 2011

Analysis Objectives

- Understand potential drinking water related human health risks due to HF activities
- Use simplified models and worst-case release scenarios consistent with a screening level analysis
- Focus on New York State's Marcellus shale region
- Evaluate drinking water risks due to:
 - Surface releases to groundwater and surface water
 - Hypothetical migration from Marcellus to drinking water aquifers

Conceptual Site Model



Conceptual Site Model

FIGURE 3.1

Date: 1/21/2009

Project No.: 208135
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Model HF Fluid

- Used model fluid composition presented in NYSDEC's SGEIS (NYSDEC, 2009)

Purpose	Compound	HF Concentration (mg/L)
Surfactant/Cross Linker/Scale Inhibitor	Methanol	984
Biocide	Glutaraldehyde	90
Corrosion Inhibitor	Propargyl alcohol	1.5
Crosslinker	Ethylene glycol	180
Breaker, Surfactant	Propylene glycol	500
Breaker	Diammonium peroxidisulphate	100
Crosslinker	Monoethanolamine	18
Friction Reducer	Acrylamide	10
Gelling Agent	Naphtha (petroleum), hydrotreated heavy	275
Scale Inhibitor	Formaldehyde	0.5
Solvent	Xylene	3

Notes: 1) HF additive concentrations in model fluid, except naphtha, are less than their aqueous solubility limits.

Flowback Characterization

Flowback data from samples collected from Marcellus shale in PA and WV (NYSDEC, 2009)

Parameter	No. Samples	No. Detected	Units	Maximum	Median
Inorganics					
Barium	34	34	mg/L	15700	661.5
Boron	26	9	mg/L	26.8	2.06
Bromide	6	6	mg/L	3070	616
Cadmium	29	5	mg/L	1.2	0.032
Cobalt	25	4	mg/L	0.58	0.3975
Copper	29	4	mg/L	0.157	0.035
Lithium	25	4	mg/L	161	55.75
Manganese	29	15	mg/L	14.5	2.18
Nickel	29	6	mg/l	0.137	0.0465
Strontium	30	27	mg/L	5841	821
Sulfate	58	45	mg/L	1270	3
Zinc	29	6	mg/l	0.09	0.048
Organics					
Benzene	29	14	ug/L	1950	479.5
Toluene	29	15	ug/L	3190	833
Ethyl Benzene	29	14	ug/L	164	53.6
Xylenes	22	14	ug/L	2670	487
Phenols	25	5	ug/L	440	191

Notes: 1) Concentrations for all organics compounds in flowback listed above are less than their aqueous solubility limits.

2) A constituent, 4-nitroquinoline -1- oxide (4-NQO), was not evaluated since the reported concentrations appear to be anomalous.

Surface Release Scenarios

- Two types of accidental releases simulated for HF additives and flowback
- Acute spill or release during down hole pumping
 - High release rate, short duration
- Diffuse or chronic spill
 - Occasional drips and leaks during handling
 - Small volumes, but possibly over longer time periods

Diffuse Spill Release Scenario

Diffuse Surface Release Scenario

HF Fluid Used (gal/well)	4,030,000
Flowback Volume @ 20% (gal/well)	806,000
Number of Wells (per pad per year)	8
Total Flowback Volume (gal)	6,448,000
Spill Volume @ 1% of Flowback Volume (gal)	64,480*
Assumed spill area (acres)	~ 4** (126m x 126m)
50% to Surface Water (gal)	32,240
50% to Soil/Groundwater Leaching (gal)	32,240

Notes:

1) * Represents 0.2% of HF used to frac 8 wells

2) ** Average pad size envisioned in New York (NYSDEC, 2009)

Acute Spill Release Scenario

Pipe/Pump Leak Scenario

HF Injection Rate (gpm)	3,400
Rupture Duration (min)	5
HF Release (gal)	17,000
Assumed Spill Area (acres)	0.25 acre (33m x 33m)
50% to Surface Water (gal)	8,500
50% to Soil/Groundwater Leaching (gal)	8,500

- Some spill data available in State databases
 - Data difficult to access and analyze
 - Largest reported spills – 8,000 to 13,000 gals

Modeling Approach

- Groundwater release:
 - Partitioning in soil between aqueous and adsorbed phases (DAF_{pw})
 - Downward migration through vadose zone (DAF_L)
 - Mixing into groundwater flowing to a well (DAF_{gw})
- Surface water release:
 - Mass-balance mixing

Groundwater Pathway

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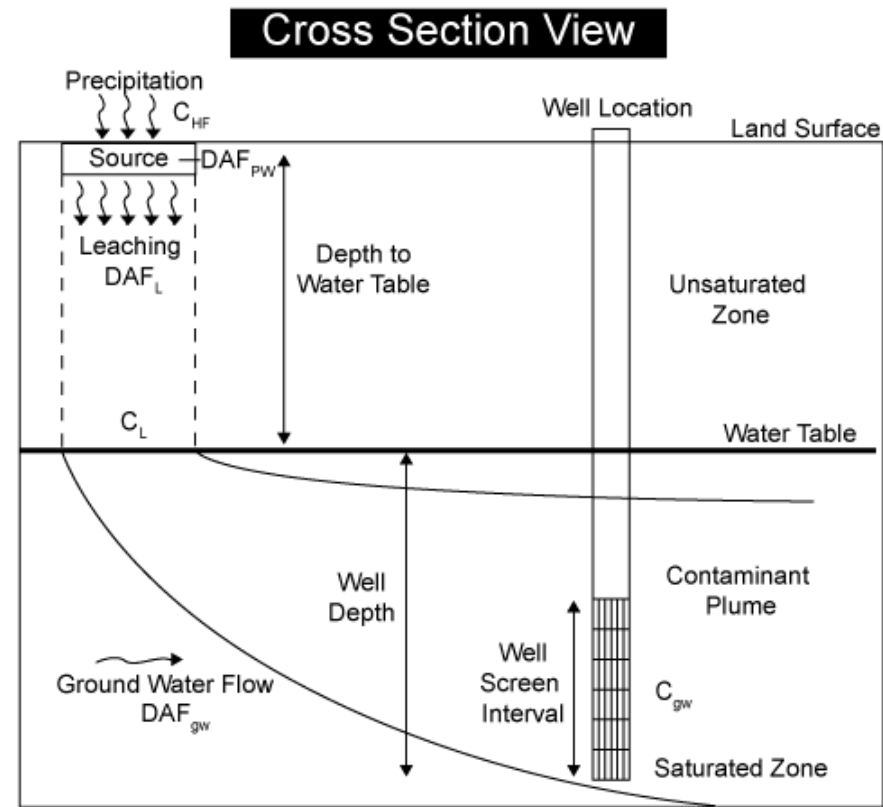
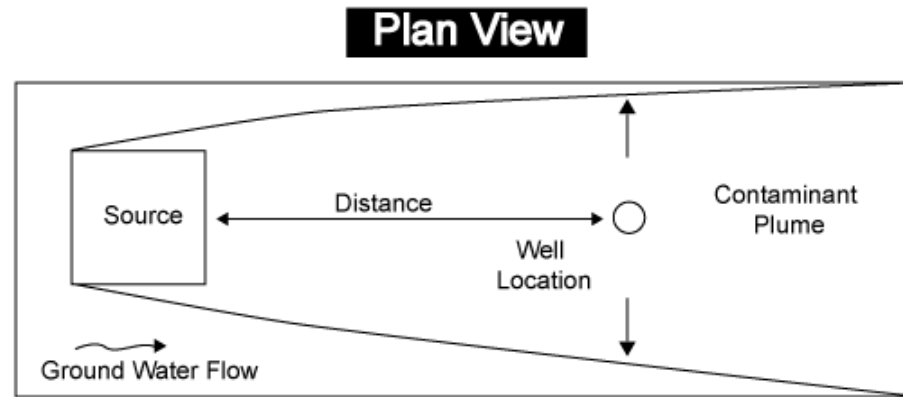
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Leaching of Surface Spill to Groundwater

FIGURE 4.2

Date: 12/22/2009

HF Concentration in Drinking Water Well

$$C_{\text{well}} = \frac{C_{\text{HF}}}{\text{DAF}_{\text{pw}} \times \text{DAF}_{\text{L}} \times \text{DAF}_{\text{gw}}}$$

C_{well} = Concentration at well ($\mu\text{g/L}$)

C_{HF} = Concentration of HF additive released to the surface ($\mu\text{g/L}$)

DAF_{pw} = Dilution factor for initial pore water concentration
(unitless)

DAF_{L} = Dilution factor from pore water to leachate at the water
table (unitless)

DAF_{gw} = Dilution factor of leachate into groundwater (unitless)

Surface Spill to Surface Water

- Mass-balance mixing of spill directly into stream flow:

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

C_{sw} = HF concentration in surface water ($\mu\text{g/L}$)

Q_{HF} = Discharge of HF or flowback fluid

Q_{sw} = Stream flow

- Lowest annual mean daily discharge (LAMDD) at 10th percentile stream in the region of New York overlying the Marcellus (8.1 cfs)
- Based on data from 147 USGS stations overlying Southern New York State

Model Input Parameters

Parameter	Value	Source
Net infiltration (cm/yr)	36.8 (cm/yr)	USGS (1998)
Water content (θ)	0.3 cm ³ /cm ³	US EPA, 1996
Porosity (ϕ)	0.43 cm ³ /cm ³	US EPA, 1996
Bulk density (ρ)	1.5 g/cm ³	US EPA, 1996
Organic carbon (f_{oc})	0.006 g-oc/g-soil	US EPA, 1996
Chemical OC partition coefficient (K_{oc})	Chemical-specific (L/kg)	Compound-specific
Dispersivity	0.25, 0.5, 2.5 cm	Typical range of values
Initial soil contamination depth (x_0)	2 cm, 7 cm	Calculated based on spill characteristics

Model Input Parameters

Parameter	Diffuse Spill	Acute Spill
Spill Area (A)	~ 4 acres	0.25 acres
Spill Width (W)	126 m	33 m
Depth water table	5 m, 10 m	5 m, 10 m
Total Percolation ($q = I \times A$)	5,613 m ³ /yr	395 m ³ /yr
Groundwater Specific Discharge** (Q_D)	10 ⁻⁴ cm ³ /cm ² -sec 31.5 m ³ /m ² -yr	10 ⁻⁴ cm ³ /cm ² -sec 31.5 m ³ /m ² -yr
Groundwater Flow Volume (Q)		
Well Depth (20 m)	77,900 (m ³ /yr)	20,655 (m ³ /yr)
Well Depth (50 m)	194,743 (m ³ /yr)	51,637 (m ³ /yr)

Notes: 1) ** Assumed $K = 10^{-2}$ cm/sec and a horizontal gradient of 1% - typical values for glacial outwash (sand) deposits

Summary of DAFs

	Diffuse Spill	Acute Spill
DAF_{pw}	Compound – specific	Compound - specific
DAF_L		
Vadose Zone Depth		
5 m	57, 78, 164	18, 25, 52
10 m	78, 108, 222	25, 35, 73
DAF_{gw}		
Well Depth		
20 m	15	53
50 m	36	132
US EPA (1996) 90 th Percentile DAF	~ 15	~ 600
Combined DAF ($DAF_L \times DAF_{gw}$)**	1,170 – 3,888	1,325 – 4,620
Surface Water DAF*	59,000	n/a

*10th percentile LAMDD

** Median DAF_L used in combined DAF calculation

Risks from Diffuse HF Fluid Spills

Parameter	Groundwater Upperbound (ug/l)	Surface Water 10 th Percentile LAMDD (ug/l)	Drinking Water RBC (ug/l)	RBC Basis	Hazard Quotient	
					Groundwater Upperbound	Surface Water 10 th Percentile LAMDD
Methanol	811.2	17	18,000	EPA RSL n	0.05	0.00093
Glutaraldehyde	57.9	1.53	5,600	OPP RED RfD	0.01	0.00027
Propargyl alcohol	1.2	0.03	73	EPA RSL n	0.02	0.00035
Ethylene glycol	152.8	3.06	73,000	EPA RSL n	0.002	0.00004
Propylene glycol	422.4	8.49	730,000	EPA RSL n	0.001	0.00001
Diammonium peroxidisulphate	85.5	1.70	479.5	Derived**	0.18	0.00354
Monoethanolamine	15.1	0.31	1,400	Derived**	0.01	0.0022
Acrylamide*	NA	NA	0.015	EPA RSL c	<1	<1
Naphtha	9.4	4.67	1,300	TPHCWG, 1997	0.007	0.00359
Formaldehyde	0.3	0.01	7,300	EPA RSL n	0.00005	0.000001
Xylenes	0.2	0.05	10,000	Drinking water MCL	0.00002	0.00001

* Given its extremely short half-life, estimated to be less than 36 hours in soil, and less than 12 days in water (US EPA, 1994), acrylamide is expected to biodegrade rapidly to levels below the RBC.

** Derived using reported no observable adverse effects level and an uncertainty factor.

Risks from Diffuse Flowback Spills

Parameter	Groundwater Upperbound (ug/l)	Surface Water 10 th Percentile LAMDD (ug/l)	Drinking Water RBC (ug/L)	RBC Basis	Hazard Quotient	
					Leaching to Groundwater Upperbound	Surface Water 10 th Percentile LAMDD
Barium	65	267	2,000	Drinking water MCL	0.03	0.13
Boron	1	0.46	7,300	EPA RSL n	0.0002	0.0001
Bromide	2,624	52	6,000	WHO	0.4	0.01
Cadmium	0.0027	0.02	5	Drinking water MCL	0.0005	0.004
Cobalt	0.0022	0.01	11	EPA RSL n	0.0002	0.0009
Copper	0.0008	0.003	1,300	Drinking water MCL	0.0000006	0.000002
Iron	5.5	14	26,000	EPA RSL n	0.0002	0.0005
Lithium	0.09	3	70	Derived (see Section 5)	0.001	0.04
Manganese	0.04	0.25	880	EPA RSL n	0.00004	0.0003
Nickel	0.0004	0.002	730	EPA RSL n	0.0000005	0.000003
Strontium	28	99	22,000	EPA RSL n	0.001	0.005
Sulfate	1,085	22	500,000	EPA Health-based level/MCL Canada (sulfate)	0.002	0.00004
Zinc	0.0002	0.002	11,000	EPA RSL n	0.00000002	0.0000001
Organics						
Benzene	1	0.03	5	Drinking water MCL	0.1	0.007
Ethyl Benzene	0.01	0.003	700	Drinking water MCL	0.00001	0.000004
Toluene	0.30	0.054	1,000	Drinking water MCL	0.0003	0.0001
Xylenes	0.14	0.045	10,000	Drinking water MCL	0.00001	0.000005
Phenols	0.11	0.007	11,000	EPA RSL n (phenol)	0.00001	0.000001

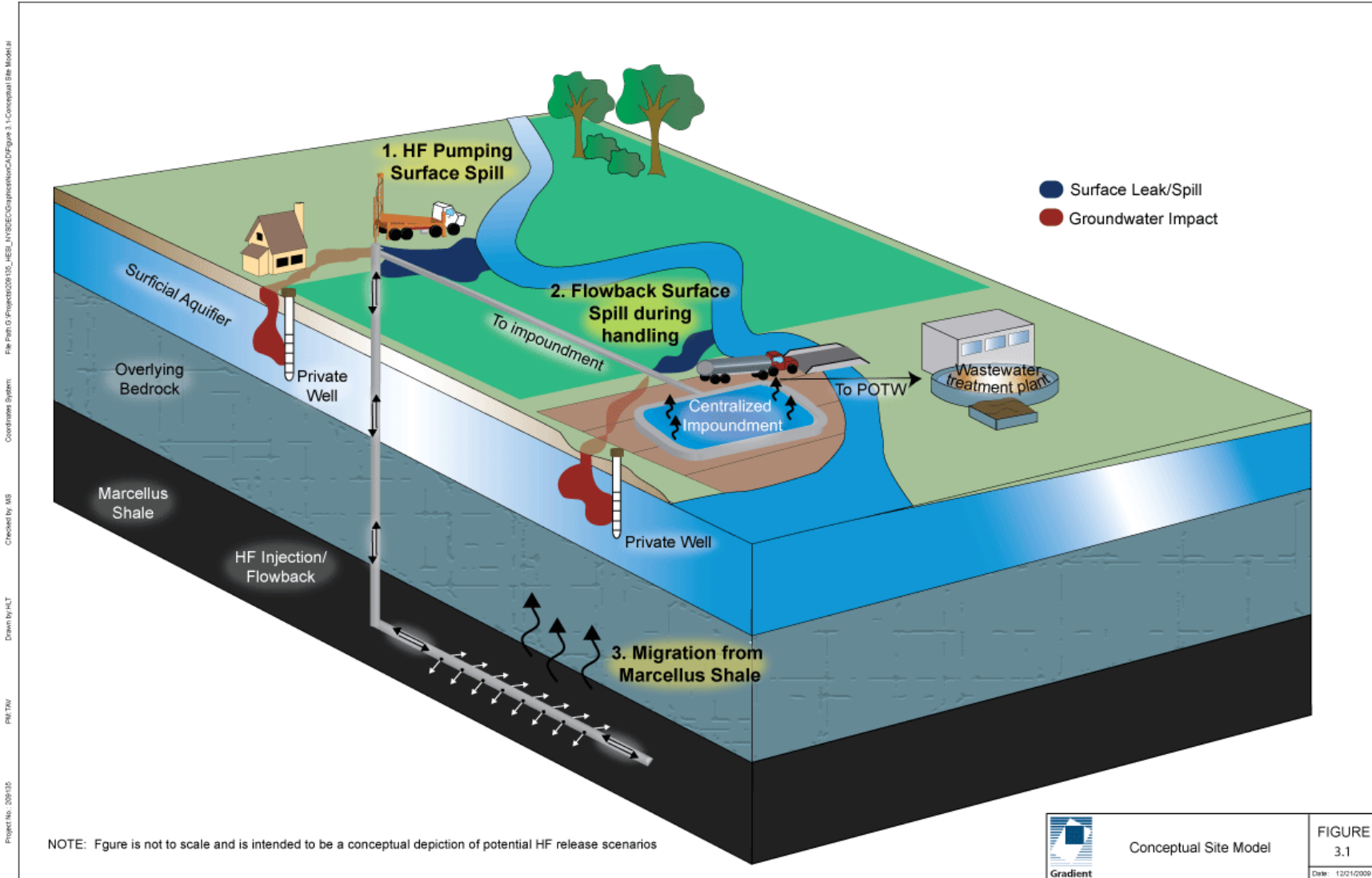
Assumptions/Limitations

- Surface release on unconsolidated deposits
- Mixing in drinking water aquifer assumes porous media system
- Complete mixing at a drinking water well – a reasonable assumption
- Releases of dissolved organics (except naphtha) – consistent with injected fluids
- Potential releases from impoundments not simulated

Surface Release Findings

- Human health risks via drinking water affected by model HF fluid/flowback surface spills are expected to be insignificant
- Number of conservative assumptions used
 - Release scenarios
 - Limited attenuation mechanisms
 - Expected to result in overestimated exposure concentrations
- EPA case studies would be useful for validating that modeled DAFs are conservative

Marcellus Migration



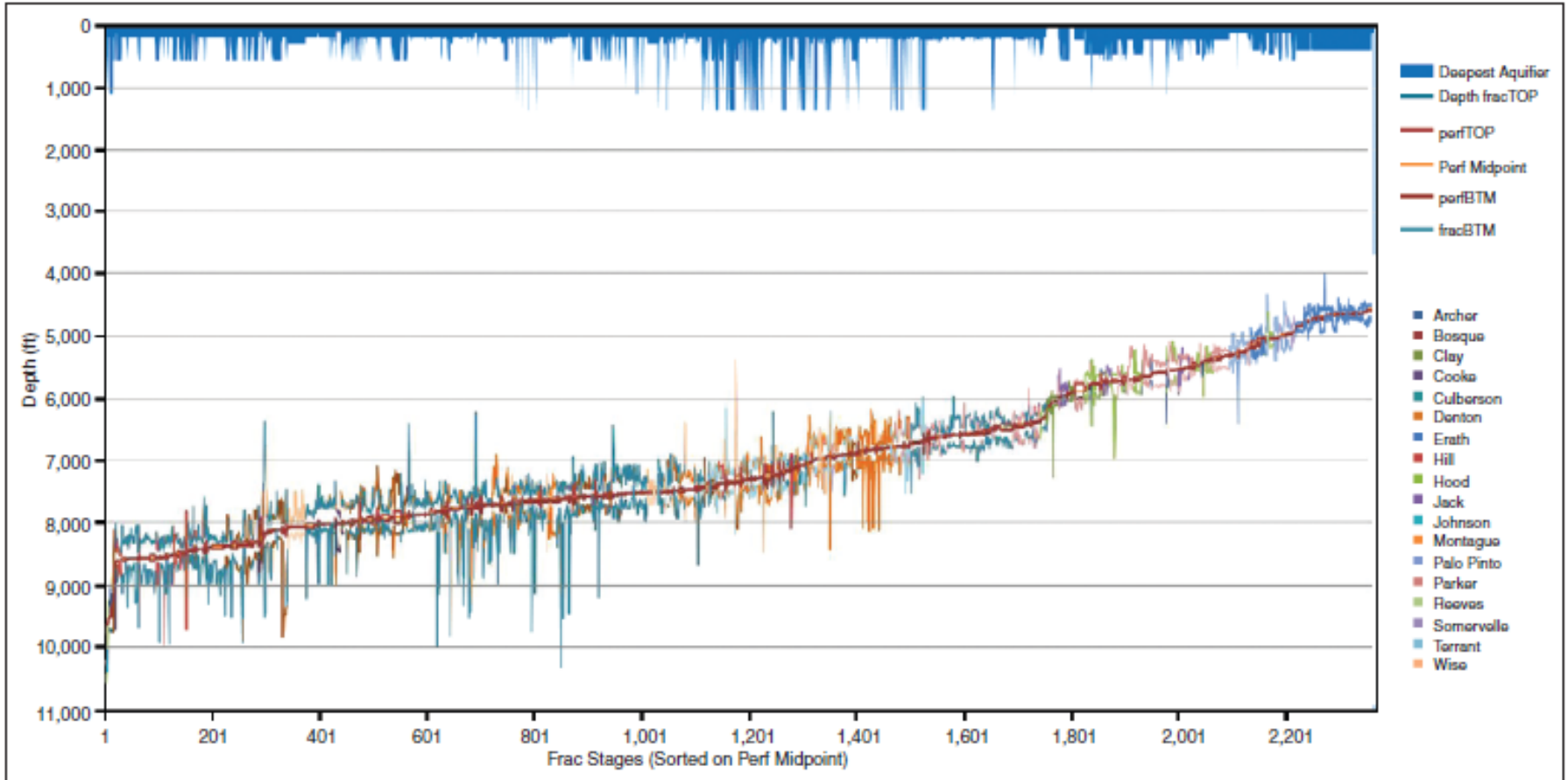

 Conceptual Site Model **FIGURE 3.1**
 Date: 12/21/2009

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Transport via Fractures

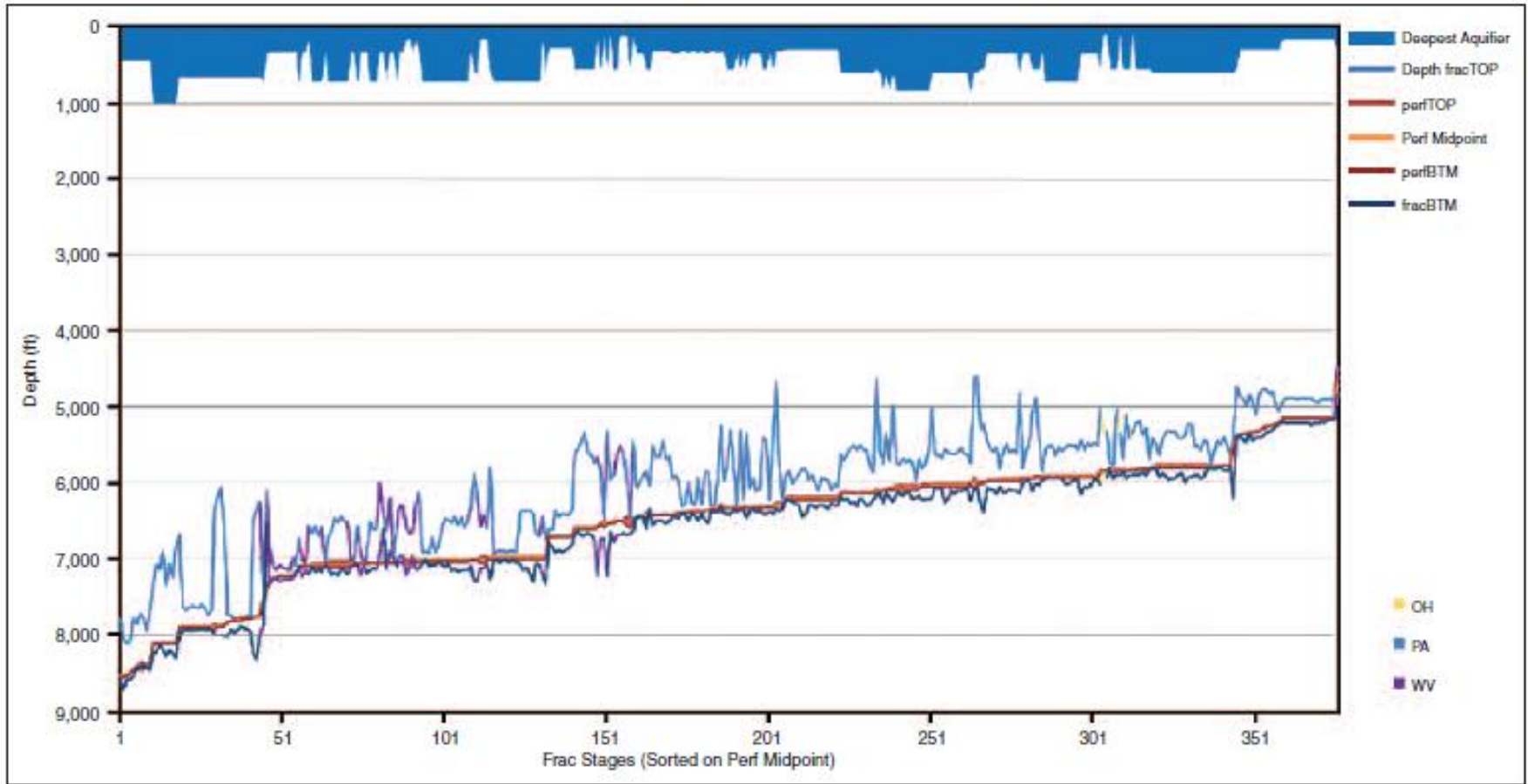
- Highly unlikely in Marcellus shale
- Aquifers separated by thousands of feet of low conductivity rock
 - Multiple rock units
 - Isolate high TDS water from drinking water aquifers
 - Have resulted in trapped methane for geologic time scales
- HF induced fractures are expected to be constrained
 - Short duration of HF treatment (1 to 2 days)
 - Layered rock system
 - Many stress contrasts limit fracture growth
 - Embedded concretions stop hydraulic fractures
 - Field data show that actual fracture growth is limited and remains thousands of feet below drinking water aquifers (Fisher, 2010)

Barnett Shale Mapped Fracture Treatments (TVD)



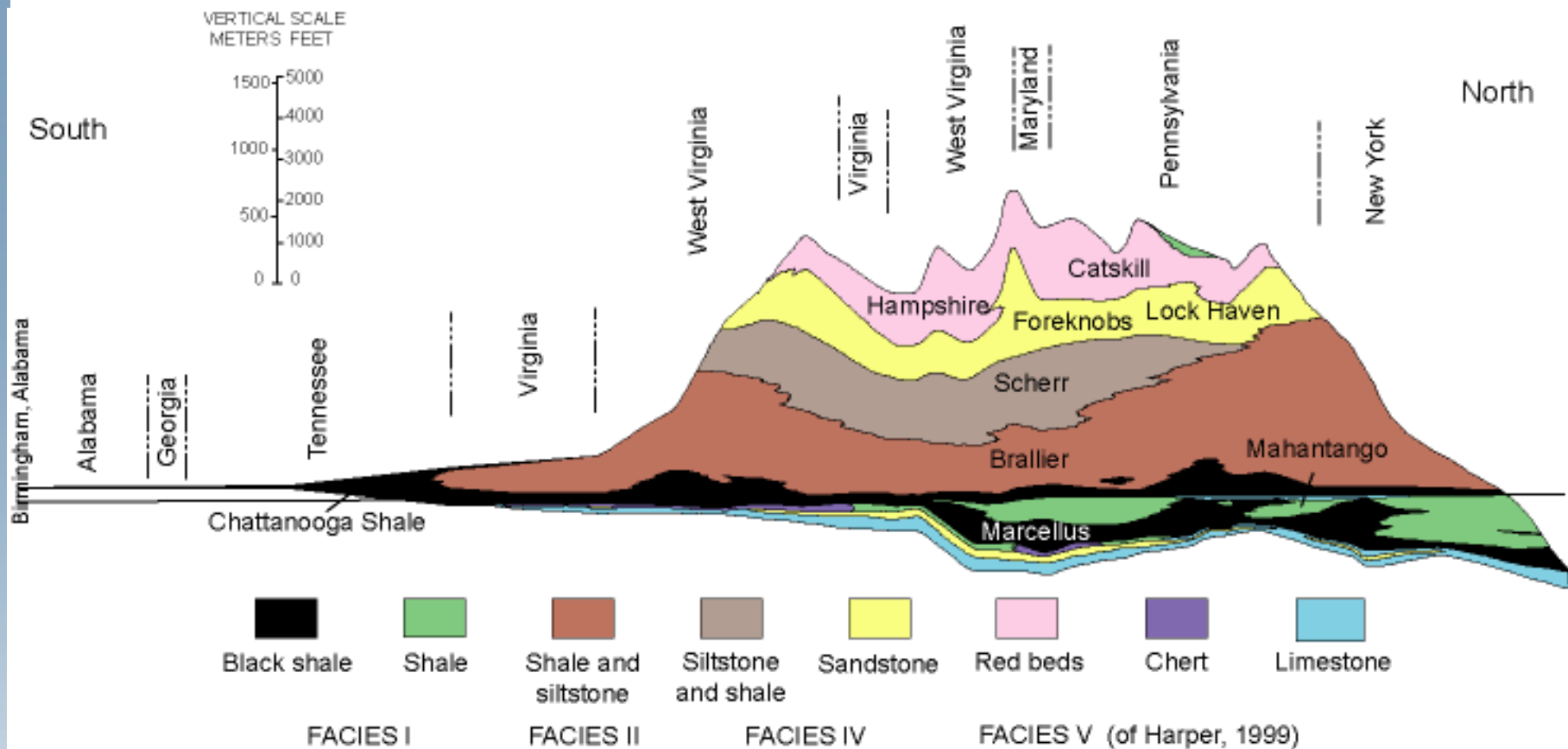
Source: Fisher (2010)

Marcellus Shale Mapped Fracture Treatments (TVD)



Source: Fisher (2010)

Marcellus Cross-Section



Source: USGS, 2005

Transport via Pore Spaces

- Migration during HF process infeasible
 - HF takes 1 to 2 days
 - ICF (2009) concluded that HF pressure would have to remain applied for years to thousands of years for transport to drinking water aquifers
- Migration of “trapped fluids” post-HF also not expected
 - Low hydraulic conductivity of shale and overlying rocks
 - Multiple phases (water, oil, and gas) further reduce ability to transmit water
 - High capillary pressures
 - Unclear if there is a driving head, especially considering brine density
 - Extreme-case migration analysis undertaken

Extreme-Case Migration Analysis

- Darcy's law based analysis with simplifying assumptions
 - Ignore brine density and multi-phase effects
 - Ignore retardation and biodegradation
- Only considers mixing with porewater in bedrock and in drinking water aquifer

Predicted Dilution-Attenuation Factors for Upward Migration

Extreme-case analysis indicate that additive concentrations would be significantly attenuated if they were to reach drinking water aquifers

Surface Aquifer Thickness	DAF_{BR} (Mixing within Bedrock)*	DAF_{aq} (Mixing in Shallow Aquifer Flow)	Combined DAF DAF_{BR} × DAF_{aq}
100 ft	>300	5,500	>1.65 x 10 ⁶
1,000 ft	>300	29,000	>8.7 x 10 ⁶

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

** From ICF (2009).*

Conclusions

- Generalized scenarios provide a framework to understand potential human health risks to drinking water from HF activities
 - Upward migration from Shale implausible exposure pathway
 - Risks from surface spills and vertical migration from Marcellus Shale expected to be insignificant for model HF fluid and flowback
 - Additional model sensitivity analyses being undertaken to define effect of input parameter variability and uncertainty
- EPA case studies and other data could help validate modeling results

Equations and References

Porewater DAF

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

or

$$DAF_{pw} = \frac{(\rho K_d + \theta)}{\theta}$$

Where: DAF_{pw} = Pore Water DAF
 C_{pw} = Concentration in pore water
 θ = Soil water content (cm^3 – water/ cm^3 – soil)
 K_d = Soil water partition coefficient (L/Kg); and
 S = Soil dry bulk density (g/cm^3)

Leaching DAF

- Downward transport through the vadose zone (Enfield *et al.*, 1982)

$$C_L = \frac{1}{2} C_o \left\{ \left[\operatorname{erf} \frac{z + z_o - vt}{2(Dt)^{1/2}} \right] - \left[\operatorname{erf} \frac{z - vt}{2(Dt)^{1/2}} \right] \right\}$$

Where:

- C_o = Initial concentration in leachate
- Z_o = Initial contaminant depth
- D = Dispersion coefficient
- C_L = Leachate concentration at water table
- v = Percolation rate

- $DAF_L = 1/(C_L/C_o)$ – averaged over the time period that leachate enters the water table

Groundwater DAF

- Transport of chemicals to a drinking water well:

$$C_{gw} = C_L \frac{Q_I}{(Q_I + Q_{gw})}$$

$$DAF_{gw} = \frac{Q_I + Q_{gw}}{Q_I}$$

- C_{gw} = Concentration at a well
- Q_I = Volumetric rate of downward seepage
- Q_{gw} = Groundwater flow rate through aquifer cross section to drinking water well screen bottom

References

- Enfield, CG; Carsel, RF; Cohen, SZ; Phan, T; Walters, DM. 1982. "Approximating pollutant transport to ground water." *Ground Water* 20(6):711-722.
- Fisher, K. 2010. "Data Confirm Safety of Well Fracturing." *The American Oil & Gas Reporter*, July.
- Gradient. 2009. "Human Health Risk Evaluation For Hydraulic Fracturing Fluid Additives Marcellus Shale Formation, New York." 127p., December 31.
- ICF International. 2009. "Technical assistance for the draft supplemental generic EIS: oil, gas and solution mining regulatory program—Well permit issuance for horizontal drilling and high-volume hydraulic fracturing to develop the Marcellus shale and other low-permeability gas reservoirs." August 7.
- New York State Dept. of Environmental Conservation (NYSDEC). 2009. "Supplemental Generic Environmental Impact Statement on the Oil, Gas and Solution Mining Regulatory Program: Well Permit Issuance for Horizontal Drilling and High-Volume Hydraulic Fracturing to Develop the Marcellus Shale and other Low-Permeability Gas Reservoirs (Draft)." Division of Mineral Resources, Bureau of Oil & Gas Regulation, 804p., September.
- US EPA. 1996. "Soil Screening Guidance: Technical Background Document." Office of Solid Waste and Emergency Response. NTIS PB96-963502; EPA-540/R-95/128; OSWER Publication 9355.4-17A. Accessed on January 29, 2001 at www.epa.gov/oerrpage/superfund/resources/soil/toc.htm, May.
- United States Geological Survey (USGS). 1998. "Water Resources of the Batavia Kill Basin at Windham, Greene County, New York." USGS Water-Resources Investigations Report 98-4036. 105p.
- United States Geological Survey (USGS). 2005. "Assessment of Undiscovered Natural Gas Resources in Devonian Black Shales, Appalachian Basin, Eastern U.S.A." U.S. Geological Survey Open File Report 2005-1268.

Modeling Drinking Water Related Human Health Risks from Hydraulic Fracturing Additives

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Gradient

The statements made during the workshop do not represent the views or opinions of EPA. The claims made by participants have not been verified or endorsed by EPA.

Potential impact of hydraulic fracturing (HF) activities on drinking water aquifers is being studied by the United States Environmental Protection Agency (US EPA) at the request of Congress. Although HF has been widely used for natural gas development for many years, this topic is receiving greater attention in the media and the scientific community as large new natural gas reserves are being proposed for development. A number of regulatory agencies, including the US EPA (2004),² have previously assessed potential impacts to drinking water aquifers, and concluded that HF activities are not expected to affect drinking water aquifers. Among them, is a comprehensive evaluation undertaken by the New York State Department of Environmental Conservation (NYSDEC), which published a Draft Supplemental Generic Environmental Impact Statement (SGEIS) addressing permitting requirements for the development of natural gas production wells in the Marcellus Shale formation (NYSDEC, 2009).³ Our presentation relies on the HF-related information presented in the NYSDEC SGEIS, and evaluates potential human health risks associated with HF-related releases that could affect groundwater or surface water.

Using the HF fluid composition of the "model HF fluid" used by NYSDEC, as well as HF flowback fluid composition from the Marcellus Shale reported in the SGEIS for samples from Pennsylvania/West Virginia, and published information on chemical toxicity, we examined potential HF fluid release scenarios and their associated potential impacts on human health. We focused on possible contamination of drinking water resources – in particular either groundwater aquifers or surface water bodies.

Exposure Analysis

We examined potential contamination of drinking water resources and quantified risk to human health for the following scenarios:

² US EPA. 2004. "Evaluation of impacts to underground sources of drinking water by hydraulic fracturing of coalbed methane reservoirs (Final)." Office of Water, June.

³ New York State Department of Environmental Conservation (NYSDEC). 2009. "Draft Supplemental Generic Environmental Impact Statement on the Oil, Gas and Solution Mining Regulatory Program—Well Permit Issuance for Horizontal Drilling and High-Volume Hydraulic Fracturing to Develop the Marcellus Shale and Other Low-Permeability Gas Reservoirs." Division of Mineral Resources, September.

Groundwater

- Migration of HF fluid additives that remain in the Marcellus Shale after fracturing, up through the overlying shale and multiple bedrock layers to an overlying drinking water aquifer.
- Spills/releases of HF fluid to the surface during HF operations or from flowback management (*i.e.*, pumping, handling), and subsequent migration to a nearby drinking water well.

Surface Water

- Spills/releases of HF fluid to the surface during HF operations or from flowback management at a surface impoundment, and migration to a nearby stream/river.

For each scenario, we adopted conservative (health-protective) assumptions that tend to overstate, rather than understate, the potential for human exposure *via* drinking water. For example:

- We examined shallow drinking water aquifers with water tables (WTs) from ~15 to 30 feet (ft) below the surface (5 to 10 meters).
- We examined scenarios for shallow drinking water wells, ranging from 65 to 165 ft deep (20 to 50 meters).
- We assigned a hydraulic conductivity to the drinking water aquifer that is lower (less mixing and dilution) than typical values for productive aquifers of the Southern Tier of New York State (NYS).
- We assumed no "setback" for the surface releases in our analysis of impacts to shallow drinking water wells or surface waters, whereas setback requirements are typically used for well siting purposes.

Overall, these assumptions are conservative (health-protective) and expected to yield an upper-bound estimate of human health risks.

Toxicity Evaluation

We adopted established risk analysis methods to evaluate chemical toxicity and potential human exposures. Agency-established toxicity criteria (e.g., drinking water standards, or risk-based benchmarks) were available for most of the model HF fluid and flowback constituents. For HF additives lacking these "agency-established" health drinking water benchmarks or toxicity factors, we developed risk-based concentrations (RBCs) for drinking water based on published toxicity data in order to evaluate the health risks of the HF additives.

Risk Analysis Results

None of the conservatively-modeled HF/flowback constituent concentrations in shallow groundwater and surface water exceeded a risk-based concentration for drinking water. Furthermore, our analysis confirms that migration of HF fluid additives from the Marcellus Shale up through overlying bedrock to a surface aquifer is an implausible contamination pathway. Even if such a pathway were plausible, the rate of migration would be such that the dilution/attenuation of groundwater would be significant, thereby reducing the model HF fluid additive concentrations in drinking water (from the overlying aquifer), to concentrations well below health-based standards/benchmarks and not pose a threat to human health.

Conclusions

To summarize, our analysis indicates that even using conservative (health-protective) exposure assumptions and a combination of agency-developed/Gradient-derived toxicity factors, the potential human health risks associated with model HF fluid additives and measured flowback constituents *via* drinking and household use of water are expected to be insignificant, as defined by agency-based guidelines:

- The migration of HF additives from the Marcellus Shale formation to overlying potable aquifers is implausible, given the thickness of the overlying confining rock layers and the effective hydraulic isolation that these overlying layers have provided for millions of years (resulting in trapping of the natural gas). Even using extreme case assumptions, the migration of HF additives from the Marcellus Shale to potable aquifers would not be sufficient to exceed health-based drinking water concentrations.
- Human health risks associated with surface releases of the model HF fluid additives are also 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. In addition, typically used setback requirements and mitigation measures are expected to further protect these water resources and human health.