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White Paper
Methanol Use in Hydraulic Fracturing Fluids

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Hydraulic Fracturing Fluids

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Acronyms and Abbreviations

°F	degrees Fahrenheit
AWQC	Ambient Water Quality Criteria
CAA	Clean Air Act
CBM	coal bed methane
cm	centimeter
CO_2	carbon dioxide
CWA	Clean Water Act
DMDC	dimethyl dicarbonate
EPA	U.S. Environmental Protection Agency
ft	feet
gpd	gallons per day
GWPC	Ground Water Protection Council
HAP	hazardous air pollutant
IOGCC	Interstate Oil and Gas Compact Commission
kg	kilogram
k_h	Henry's Law Constant
L	liter
lbs	pounds
mg	milligram
MG	million gallons
GPD	gallons per day
ml	milliliter
NEDO	New Energy Development Organization
NOAEL	no observed adverse effects level
NORM	Naturally Occurring Radioactive Material
NO_x	nitrogen oxides
NTP	National Toxicology Program
PA	Pennsylvania
PA DEP	Pennsylvania Department of Environmental Protection
RfD	reference dose
SO_2	sulfur dioxide
TDS	Total Dissolved Solids
UIC	Underground Injection Control
USGS	United States Geological Survey
VOC	volatile organic compound
WWTP	waste water treatment plant

1 Introduction

In 1999, Malcolm Pirnie (Malcolm Pirnie 1999) issued a report that provided information on the general fate and transport behavior of methanol in the environment. This report supplements the Malcolm Pirnie report and focuses on the use of methanol in hydraulic fracturing (also known as fracking) fluids: role, volumes used, determination of whether the use of methanol in fracking fluids could result in exceeding its corresponding health-based screening levels in drinking water and surface water, and methanol air emissions from fracking flowback ponds. Although this report is focused on the USA where most fracking is taking place, the report has global applicability for its findings.

In preparing this report, we relied on literature review, numerical modeling simulations, and communications with state agencies. We also relied on our personal knowledge of the fracking process, the fracking fluid suppliers, and gas well service companies. The four main sections of this report and their key conclusions include the following:

- **Methanol's Role in Hydraulic Fracturing:** This section provides information on the fracturing process (i.e., how does fracturing work), the composition of fracturing fluids, and the role methanol plays in fracturing fluids (including typical methanol volumes used per fracturing job). In summary, methanol has many chemical characteristics that make it an important additive to fracking fluids (e.g., corrosion and scale inhibitor, and friction reducer). Currently, the volumes of methanol used per fracturing job are on the order of hundreds of pounds, a small fraction of the total fracturing fluid volumes used.
- **Methanol in Flowback Water:** Even though there has not been a documented case of methanol contaminating the environment as a result of its use in fracking, this section evaluates hypothetical scenarios of methanol impacting groundwater (as a result of fracking fluid leakage from a well casing) and surface water (as a result of the discharge of treated flowback).

The scenarios show that methanol concentrations in groundwater and surface water are expected to be several times lower than the health-based screening levels for methanol.

- **Health Assessment of Methanol:** In this section, health-based screening levels for both groundwater (residential drinking water consumption) and surface water (recreational incidental ingestion) were calculated. These screening levels are applicable to the pathways of exposure to methanol as part of fracking fluids, including 1) consumption of groundwater impacted by methanol-containing fracking fluids, and 2) incidental ingestion of river and stream waters that received treated flowback. The estimated methanol intake as a result of exposure to these pathways is several times lower than the health-based screening levels for methanol.

- **Air Emissions of Methanol:** Practically, methanol will not evaporate from fracking flowback ponds. In 2010, a study conducted by the Pennsylvania Department of Environmental Protection (PA DEP) found methanol concentration in air near flowback wastewater impoundment at insignificant level (51 $\mu g/m^3$) compared to the U.S. Environmental Protection Agency (EPA) Acute Exposure Guideline levels (690,000 $\mu g/m^3$).

The United States possesses vast natural gas resources that would not be obtainable if not for hydraulic fracturing and advances in horizontal drilling. The fluids used in hydraulic fracturing must carry out a set of complex functions, and methanol has many properties that make it a desirable component in a hydraulic fracturing fluid system. While a beneficial additive for fracking operations, the actual volume of methanol used is a small fraction of the total fluid system, typically just several hundred pounds out of what may be tens of millions of pounds of fracking fluids employed at a single site. The hypothetical scenarios examined in this report of methanol reaching groundwater and surface water from leaking well casings and treated flowback water, respectively, found methanol concentrations to be several times lower than estimated health-based screening levels, indicating little or no concern for potential health impacts. Because of methanol's low tendency to volatilize out of water and into air, methanol will practically not volatize from flowback ponds.

2 Methanol's Role in Hydraulic Fracturing

Before discussing the role of methanol in the hydraulic fracturing (commonly called "fracking") process, a quick overview of the process itself is provided (i.e., how does fracking work). We then discuss the role of methanol in fracking fluids and the typical volumes used.

2.1 How Does Hydraulic Fracturing Work?

In many areas of the United States, and indeed in many places worldwide, natural gas is trapped in rocks, so it cannot be easily produced using conventional gas well drilling and production practices. [In conventional formations, natural gas flows freely into a gas well through porous rock. Figure 1a shows a conventional gas well.]

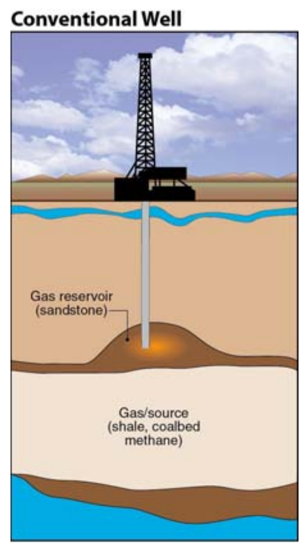

Figure 1a. Conventional gas well

However, in low permeability formations, natural gas is trapped in the pores and micro-fractures and cannot flow into the gas well. Hydraulic fracturing was invented decades ago to access resources trapped in these formations.

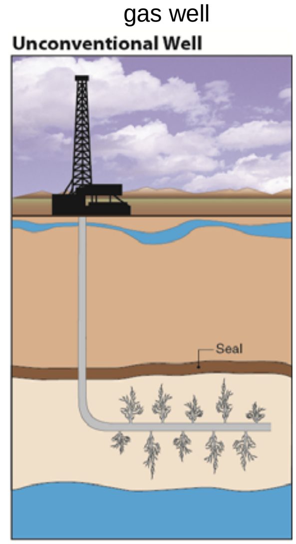

Figure 1b. Unconventional gas well

Hydraulic fracturing is a method of inducing manmade fractures in low-permeability rocks, so that the trapped natural gas can flow from the rock, into the fractures, and into the natural gas well. A horizontal well with hydraulic fractures is depicted in Figure 1b. As can be inferred from Figure 1b, drilling a well horizontally in a formation increases the length of the well casing that can drain gas from the formation. The combination of horizontal drilling with hydraulic fracturing has increased the economic success of many low-permeability natural gas-bearing formations. The U.S. Energy Information Administration estimates that shale formations in the U.S. contain 827 trillion cubic ft of recoverable natural gas. These vast resources would not be obtainable if not for hydraulic fracturing and advances in horizontal drilling.

2.2 Fracking Fluids

To create fractures in the gas-bearing formations, a “base fluid” is mixed with sand or tiny ceramic spheres (called proppants) and with chemical additives, and then pumped into the gas-bearing formation. The fluid pressure is increased until the formation rock is hydraulically fractured. Once the rock is fractured and the proppants are delivered into the fractures (to allow the fractures to stay open), the fluid pressure is reduced so that natural gas in the rock can flow through the newly formed fractures and into the well casing.[1] The volume of fluids used in a fracking job might be as much as 2 to 8 million gallons per well (University of Maryland 2010), equivalent to four to twelve Olympic-size swimming pools, with water and sand typically constituting about 99.5% of the fracking fluids. Figure 2 shows a typical fracking site.

[1] There are several animations available on the internet showing the hydraulic fracturing process. For example: http://www.youtube.com/watch?v=nvnnBcxhzNA (Accessed June 29, 2011).

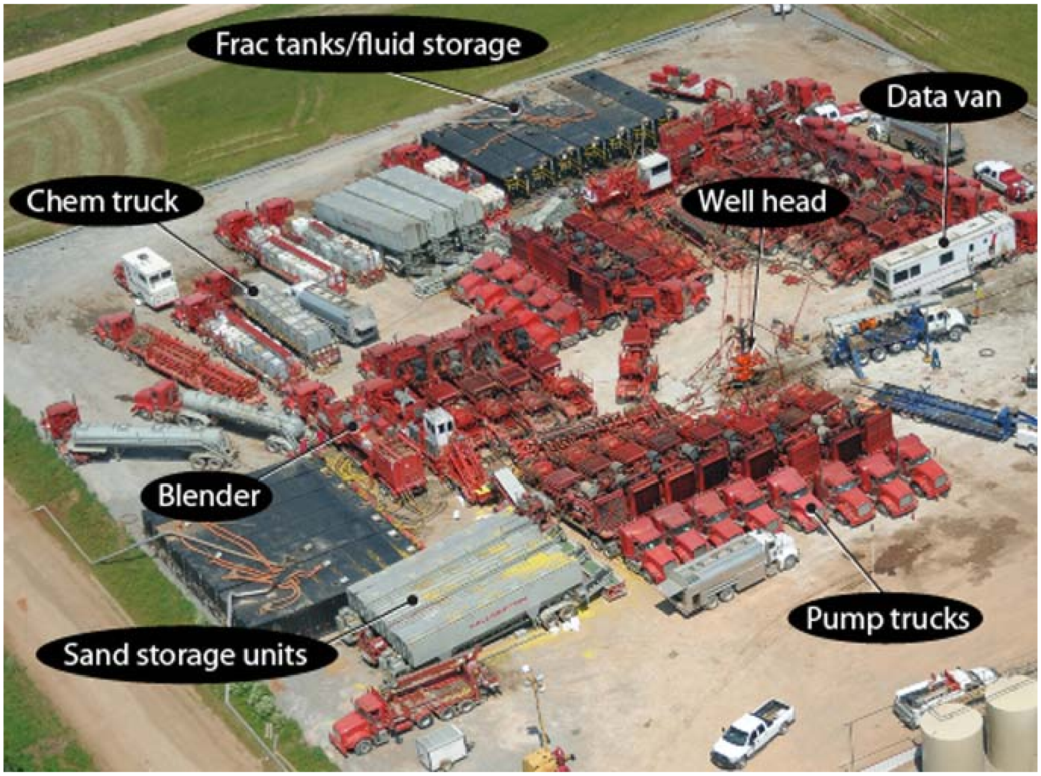

Figure 2. A typical fracking site showing water storage tanks, trucks carrying additives, and pumps for fluid mixing and injection (Source: http://www.jptonline.org/index.php?id=474)

The fluids used in hydraulic fracturing must carry out a set of complex functions: carry proppants, inhibit bacterial growth in the well casing and inhibit casing corrosion, interact with the formation minerals and water at high formation temperatures without losing their properties, deliver and stabilize the "proppants" in the formation fractures, and allow the fracking fluids and formation water to flow back easily through the well to the ground surface. These complex functions require careful design of fracking fluid components. Each component (or additive) carries out a specific function while interacting with the other additives. Because of the complexity of the design of fracking fluid recipes (or "systems"), the compositions of the different fracking fluids have been guarded. However, some producers do submit lists of chemicals used in fracking fluids to voluntary registries.[2] Further, some of the typical functions conducted by the different fracking fluid additives are known and are presented in Table 1. The general fracking fluid percent composition by volume is presented in Figure 3.

[2] The website www.fracfocus.com contains information about the fracking fluid compositions for many fracking jobs throughout the United States.

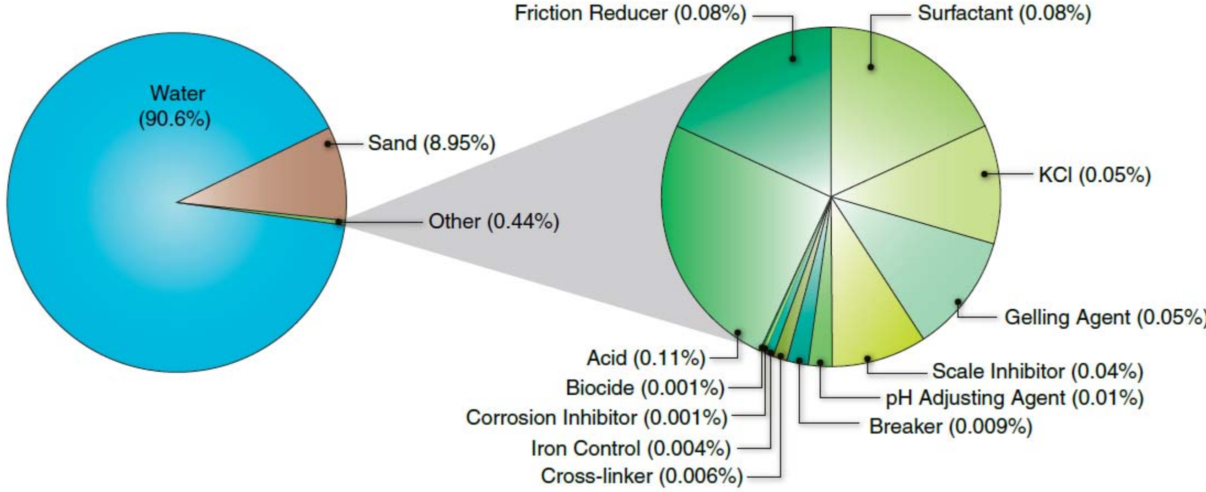

Figure 3. Typical fracking fluid percent composition and function of additives (Source: Saba et al. 2011).

Recently, news about releases of fracking fluids from holding ponds and the potential for groundwater contamination contributed to citizen concerns about fracking operations and the risk of exposure to chemicals in fracking fluids (e.g., Plagianos 2010). One of the consequences was requests for manufacturers to reveal the composition of their fracking fluids (University of Maryland 2010). Compositions of four of these fracking fluid systems are presented as examples in Tables 2, 3, 4, and 5.

Table 1. Typical fracturing fluid ingredients

Product	Purpose	Downhole Result
Water and Sand: ~ 98%		
Water	Expand fracture and deliver sand	Some stays in formation while remainder returns with natural formation water as "produced water" (actual amounts returned vary from well to well)
Sand (Proppant)	Allows the fractures to remain open so the gas can escape	Stays in formation, embedded in fractures (used to "prop" fractures open)
Other Additives: ~ 2%		
Acid	Helps dissolve minerals and initiate cracks in the rock	Reacts with minerals present in the formation to create salts, water, and carbon dioxide (neutralized)
Corrosion Inhibitor	Prevents the corrosion of the pipe	Bonds to metal surfaces (pipe) downhole. Any remaining product not bonded is broken down by micro-organisms and consumed or returned in produced water.
Iron Control	Prevents precipitation of metal (in pipe)	Reacts with minerals in the formation to create simple salts, carbon dioxide and water all of which are returned in

Product	Purpose	Downhole Result
		produced water
Anti-Bacterial Agent	Eliminates bacteria in the water that produces corrosive by-products	Reacts with micro-organisms that may be present in the treatment fluid and formation. These micro-organisms break down the product with a small amount of the product returning in produced water.
Scale Inhibitor	Prevents scale deposits downhole and in surface equipment	Product attaches to the formation downhole. The majority of product returns with produced water while remaining reacts with micro- organisms that break down and consume the product.
Clay Stabilizer	Prevents formation clays from swelling	Reacts with clays in the formation through a sodium - potassium ion exchange. Reaction results in sodium chloride (table salt) which is returned in produced water.
Friction Reducer	"Slicks" the water to minimize friction	Remains in the formation where temperature and exposure to the "breaker" allows it to be broken down and consumed by naturally occurring micro-organisms. A small amount returns with produced water.
Surfactant	Used to increase the viscosity of the fracture fluid	Generally returned with produced water, but in some formations may enter the gas stream and return in the produced natural gas
Gelling Agent	Thickens the water in order to suspend the sand	Combines with the "breaker" in the formation thus making it much easier for the fluid to flow to the borehole and return in produced water
Breaker	Allows a delayed break down the gel	Reacts with the "crosslinker" and "gel" once in the formation making it easier for the fluid to flow to the borehole. Reaction produces ammonia and sulfate salts which are returned in produced water.
Crosslinker	Maintains fluid viscosity as temperature increases	Combines with the "breaker" in the formation to create salts that are returned in produced water
pH Adjusting Agent	Maintains the effectiveness of other components, such as crosslinkers	Reacts with acidic agents in the treatment fluid to maintain a neutral (non-acidic, non-alkaline) pH. Reaction results in mineral salts, water and carbon dioxide; a portion of each is returned in produced water.

Table 2. Example composition of fracking fluid system used by the operator "Talisman Energy USA" in Bradford County, PA. Methanol concentration in the fracking fluid was 0.000007% (% by volume).

Hydraulic Fracturing (HF) Fluid Product Component Information

State:	PA
County:	Bradford
API Number:	37-015-20441-00
Operator Name:	Talisman Energy USA Inc.
Well Name:	VanBlarcom (03-004-02) R2
Completion End Date:	7/22/2010
Total Volume Pumped (bbl):	114463
True Vertical Depth (TVD):	5505.05

Hydraulic Fracturing Fluid Composition:

Trade Name	Supplier	Purpose	Ingredients**	Ingredient Concentration in additive (% by volume)*	Ingredient concentration in HF fluid (% by volume)*
Water	-	Creates a fracture network and carries sand to fractures	Surface Water	100.0%	93.91163%
Sand	CUDD	When the pressure is released the sand placed will hold the fracture open	Silicon Dioxide	95.0%	5.09318%
Friction Reducer	CUDD	Reduces friction between the fluid and the pipe	Hydrotreated light petroleum distillat	20.0%	0.010009%
Scale Inhibitor	CUDD	Mitigates scale formation on tubulars and perforations	Hydrogen Chloride	5.0%	0.000503%
Biocide	CUDD	Eliminates bacteria in carrier fluid	Sodium Chlorite	8.4%	0.003982%
Acid	CUDD	Dissolves cement and material near the wellbore to provide pumping pressure relief	Hydrogen Chloride	7.5%	0.049539%
Corrosion Inhibitor	CUDD	Prevents precipitation of metal oxides	Formic Acid	30.0%	0.000198%
			Oxyalkylated Fatty Acid	10.0%	0.000066%
			Haloalkyl heteropolycycle salt	10.0%	0.000066%
			Aromatic aldehyde	10.0%	0.000066%
			Quaternary ammonium compound	1.0%	0.000007%
			Methanol	1.0%	0.000007%
			Organic sulfur compound	1.0%	0.000007%
			Isopropanol	1.0%	0.000007%
			Benzyl Chloride	0.1%	0.000001%
Iron Control Agent	CUDD	Prevents the corrosion of the pipe	Citric Acid	35.0%	0.000694%

* Information is based on the maximum potential for concentration and thus the total may be over 100%

** Ingredients include only the hazardous components as defined by the guidelines outlined for Material Safety Data Sheets (MSDS) sheets

All component information listed was obtained from supplier Material Safety Data Sheets (MSDS). The Occupational Safety and Health Administration (OSHA) sets the criteria for the disclosure of this information. Please note that Federal Law protects "proprietary", "trade secret", and "confidential business information" and the criteria for how this information is reported on an MSDS is subject to 29 CFR 1910.1200 (i). As a result, the Operator does not have the legal authority to disclose any supplier "proprietary", "trade secret", or "confidential business information".

Source: Talisman Energy USA Inc. http://www.fortuna-energy.com/upload/well/76/01/vanblarcom-03-004-02.pdf

Table 3. Example composition of a fracking fluid used by the operator "Test C Appalachia" in Susquehanna County, PA. The maximum methanol concentration in the fluid was 0.0005% (% by mass).

Hydraulic Fracturing Fluid Product Component Information Disclosure

Fracture Date	12/1/2012
State:	Pennsylvania
County:	Susquehanna
API Number:	37-115-20299
Operator Name:	Test C Appalachia
Well Name and Number:	Test Well 1
Longitude:	-76.052537
Latitude:	41.719388
Long/Lat Projection:	NAD27
Production Type:	Gas
True Vertical Depth (TVD):	7,157
Total Water Volume* (gal):	4,764,606

Hydraulic Fracturing Fluid Composition:

Trade Name	Supplier	Purpose	Ingredients	Chemical Abstract Service Number (CAS #)	Maximum Ingredient Concentration in Additive (% by mass)**	Maximum Ingredient Concentration in HF Fluid (% by mass)**	Comments
Water		Carrier / Base Fluid			100.00%	87.19000%	
Sand (Proppant)		Proppant			100.00%	11.89718%	
Acid, Hydrochloric (1	PP CO	Acid Package	Hydrochloric Acid	007647-01-0	15.00%	0.11853%	
A999	PP CO	Acid Corrosion Inhibitor	Methanol	67-56-1	40.00%	0.00050%	
			Fatty Acid	Proprietary	30.00%	0.00037%	
			Prop-2-yn-ol	107-19-7	10.00%	0.00012%	
			Aliphatic alcohols, ethoxylated #1	Proprietary	30.00%	0.00037%	
L058	PP CO	Iron Control Agent	Sodium Erythorbate	6381-77-7	100.00%	0.00474%	
B999	PP CO	Friction Reducer	Distillates (petroleum), hydrotreated lig	64742-47-8	30.00%	0.01275%	
			Aliphatic alcohol, glycol ether	Proprietary	5.00%	0.00213%	
B-88	SPEC CHEM	Anti Bacterial Agent	Glutaraldehyde	111-30-8	27.00%	0.00992%	
			n-Alkyl dimethyl benzyl ammonium chlo	68424-85-1	5.50%	0.00202%	
			Ethanol	64-17-5	4.00%	0.00147%	
			Didecyl dimethyl ammonium chloride	7173-51-5	8.00%	0.00294%	
TS-00	SPEC CHEM	Scale Inhibitor	Sodium polyacrylate	Proprietary	30.00%	0.00325%	

*Total Water Volume sources may include fresh water, produced water, and/or recycled water

** Information is based on the maximum potential for concentration and thus the total may be over 100%

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Source: GWPC/IOGCC 2011 http://www.gwpc.org/meetings/uic/2011/proceedings/14Belieu_Stan.pdf

Table 4. Example composition of a fracking fluid used by the operator "Chesapeake Appalachia LLC" in Bradford, PA (Marcellus Shale). The maximum methanol concentration in the fluid was 0.00239% (% by mass).

Hydraulic Fracturing Fluid Product Component Information Disclosure - ATGAS 2H
CHESAPEAKE APPALACHIA LLC

API #	3701521237	County	BRADFORD	Fracture Date	4/18/2011
Surface Casing Depth (ft)	455	State	PENNSYLVANIA	Proppant Mass Pumped (lbs)	1,651,580
True Vertical Depth of Well (ft)	6,740.7	Longitude	-76.710095	Water Volume Pumped (gals)	1,565,298
Play	MARCELLUS SHALE	Latitude	41.666349	Frac Fluid Volume Total (gals)	1,647,714
Well Type	HORIZONTAL	Lat/Long Projection	NAD27	Total Fluid Mass Pumped (lbs)	14,876,546

Supplier	Product Type	Product Name	Total Product Pumped (gals)	Total Product Mass (lbs)	Component Listed on MSDS	Chemical Abstract Service Number (CAS #)	MAXIMUM Component Concentration of Product (% by Mass)	MAXIMUM Component Mass Pumped (lbs)	MAXIMUM Component Concentration Pumped (% by Mass)	MAXIMUM Parts per Million (PPM) by Mass
X CHEM OILFIELD CHEMICALS	Anti-Bacterial Agent	B84	650	5,970	Glutaraldehyde (Pentanediol)	000111-30-8	27.00%	1,612	0.01084%	108
					Didecyl Dimethyl Ammonium Chloride	007173-51-5	8.00%	478	0.00321%	32
					Quaternary Ammonium Compound	068424-85-1	5.50%	328	0.00221%	22
					Ethanol	000064-17-5	4.00%	239	0.00161%	16
	Scale Inhibitor	SC30W	201	1,829	Sodium polyacrylate	N/A	30.00%	549	0.00369%	37
					Methanol (Methyl Alcohol)	000067-56-1	15.00%	274	0.00184%	18
PUMPCO SERVICES	Friction Reducer	Plexslick 921	2,285	20,225	Water	007732-18-5	40.00%	8,090	0.05438%	544
					Petroleum Distillate Hydrotreated Light	064742-47-8	35.00%	7,079	0.04758%	476
					POLY(ACRYLAMIDE-co-ACRYLIC ACID	009003-06-9	28.00%	5,663	0.03807%	381
					Polyethoxylated Alcohol Surfactants	N/A	7.00%	1,416	0.00952%	95
	Acid	Acid HCL	4,500	43,587	Hydrochloric Acid	007647-01-0	15.00%	6,538	0.04395%	439
	Non-Emulsifier	Plexbreak 145	15	120	Water	007732-18-5	65.00%	78	0.00053%	5
					2-Butoxyethanol (Ethylene Glycol Monobutyl Ether)	000111-76-2	15.00%	18	0.00012%	1
					Methanol (Methyl Alcohol)	000067-56-1	15.00%	18	0.00012%	1
					Coconut oil, Diethanolamide	068603-42-9	7.00%	8	0.00006%	1
					Diethanolamine	000111-42-2	3.00%	4	0.00002%	0
PUMPCO SERVICES	Corrosion Inhibitor	Plexhib 256	15	108	Methanol (Methyl Alcohol)	000067-56-1	60.00%	65	0.00043%	4
					Ethoxylated Alcohols^ C14-15	068951-67-7	30.00%	32	0.00022%	2
					Modified Thiourea Polymer	068527-49-1	30.00%	32	0.00022%	2
					Propargyl Alcohol (2-Propynol)	000107-19-7	10.00%	11	0.00007%	1
					Alkenes^ C>10 alpha-	064743-02-8	5.00%	5	0.00004%	0
	Iron Control Agent	Ferriplex 40	36	391	Water	007732-18-5	60.00%	234	0.00158%	16
					Trisodium NTA	018662-53-8	40.00%	156	0.00105%	11
					Sodium Sulfate	007757-82-6	2.00%	8	0.00005%	1
					Sodium Hydroxide	001310-73-2	1.00%	4	0.00003%	0

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Table 5. Halliburton/Williams fracking fluid composition used in Denton, Texas. Methanol concentration was 0.00069% (% by mass).

Hydraulic Fracturing Fluid Product Component Information Disclosure

Fracture Date	**5/2/2011**
State:	**Texas**
County:	**Denton**
API Number:	**4212135053**
Operator Name:	**Williams**
Well Name and Number:	**Ace Unit D13H**
Longitude:	**-97.0230832**
Latitude:	**32.9951317**
Long/Lat Projection:	**NAD27**
Production Type:	**Gas**
True Vertical Depth (TVD):	**8,417**
Total Water Volume (gal)*:	**4,879,488**

Hydraulic Fracturing Fluid Composition:

Trade Name	Supplier	Purpose	Ingredients	Chemical Abstract Service Number (CAS #)	Maximum Ingredient Concentration in Additive (% by mass)**	Maximum Ingredient Concentration in HF Fluid (% by mass)**	Comments
Water	Williams	Carrier/Base Fluid	Water	7732-18-5	100.00%	87.35404%	
Sand Premium White 100 Mesh	Halliburton	Proppant	Crystalline Silica Quartz	14808-60-7	100.00%	7.10785%	
Sand Premium White 40/70	Halliburton	Proppant	Crystalline Silica Quartz	14808-60-7	100.00%	5.36323%	
Hydrochloric Acid	Halliburton	Acid	Hydrochloric Acid	7647-01-0	15.00%	0.11301%	
BE-7	Halliburton	Biocide	Sodium Hypochlorite	7681-52-9	30.00%	0.01240%	
			Sodium Hydroxide	1310-73-2	5.00%	0.00207%	
FR-66	Halliburton	Friction Reducer	Hydrotreated Light Petroleum Distillate	64742-47-8	30.00%	0.02840%	
Scalechek LP-55	Halliburton	Inhibitor	Polyacrylate	Confidential Business Information	60.00%	0.00950%	
Gelsta L	Halliburton	Stabilizer	Sodium Thiosulfate	7772-98-7	60.00%	0.00805%	
HAI-OS	Halliburton	Corrosion Inhibitor	Methanol	67-56-1	60.00 %	0.00069%	
			Propargyl Alcohol	107-19-7	10.00 %	0.00011%	
LoSurf-300D	Halliburton	Non-Ionic Surfactant	Ethanol	64-17-5	60.00%	0.00038%	
			Heavy Aromatic Petroleum Naphtha	64742-94-5	30.00%	0.00019%	
			Naphthalene	91-20-3	5.00%	0.00003%	
			Poly-alpha-omega-hydroxy, branched	127087-87-0	5.00%	0.00003%	
			1,2,4 Trimethylbenzene	95-63-6	1.00%	0.00001%	

* Total Water Volume sources may include fresh water, produced water, and/or recycled water

** Information is based on the maximum potential for concentration and thus the total may be over 100%

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Source: FracFocus Chemical Disclosure Registry. https://www.hydraulicfracturingdisclosure.org/fracfocusfind/.

2.3 Methanol in Fracking Fluids

Methanol has many properties that make it a desirable component in a hydraulic fracturing fluid system (Hossaini et al. 1989). Some of the functions that are reported in the literature to be carried by methanol include:

- **Corrosion or scale inhibitor—**Methanol prevents corrosion of pipes. This is an important function considering that small amounts of acid are used in the fracking fluids for formation fractures cleanup (e.g., see Tables 2–5).
- **Friction reducer—**Because of its low viscosity compared to water, methanol reduces the pumping pressure required to deliver the fracking fluids to the formation. [Lower piping friction requires less hydraulic power, which has significant impact on reducing cost (Antoci et al. 2001).]
- **Formation water flowback enhancer—**Methanol enhances the removal of the formation water to allow the natural gas to flow through the well (Thompson et al. 1992; Hossaini et al. 1989). As methanol dissolves in the formation water, it reduces the capillary forces that "block" the water from flowing out of the formation and into the well casing.[3] Removing the "water block" allows natural gas to flow into the well.
- **Fracking fluid flowback enhancer—**After the fracturing treatment, the well is typically closed for several hours to allow the fracking fluids to equilibrate with the reservoir high temperature. When the wellhead is opened and as the heated methanol starts to approach the wellbore, methanol is converted into vapor. This vaporization results in a significant increase of the upward driving force and enhancement of the fluids flowback (Thompson et al. 1992).

[3] In low permeability formations, the capillary force increases with the increase of the formation surface tension. Because methanol is miscible in water and has much lower surface tension (22.6 dynes/cm) than water (75 dynes/cm), the binary system of water/methanol has a lower surface tension and the capillary force that keeps the formation water trapped is reduced as methanol is introduced to the formation (Thompson et al. 1992; Hossaini et al. 1989). This allows the water/methanol mixture (and gas) to flow out of the formation.

Clearly, methanol has several chemical properties that make it a useful fracking fluid additive. The Pennsylvania Department of Environmental Protection (PA DEP) included methanol on the list of 85 chemicals used by hydraulic fracturing companies in Pennsylvania (PA DEP 2010a). In April 2011, a United States House of Representatives Committee headed by Representatives Waxman, Markey, and Degette published a report on "Chemicals used in hydraulic fracturing" ("The Waxman Report"). The Waxman Report characterized methanol as the "most widely used" chemical in hydraulic fracturing. It is important to note that "most widely used" is not an indication of the volume of methanol used. In fact, methanol represents only a small fraction of the total hydraulic fracturing fluid volume, as shown in Tables 2 to 5, and discussed below.

2.4 Volumes of Methanol Used in Fracking Fluids

In the 1990s and up until 2001, some companies (e.g., BJ Services, now part of Barker Hughes[4]) used methanol as a "base fluid" in fracking applications in Canada and Argentina (Antoci et al. 2001). "Base fluid" means that methanol was the main component in the fracking fluid (instead of water). In those cases, the fracked formations either had low permeability with high clay content,[5] low bottom-hole pressure, and/or minimal load fluid recovery (Antoci et al. 2001).

However, from our review of publications, it appears that methanol was used infrequently as a base fluid. This is because the use of methanol as a base fluid comes with safe handling issues and additional expenses to ensure that all personnel involved with methanol treatments are thoroughly trained in the proper procedures for handling flammable materials (e.g., Thompson et al. 1992).[6] Also, compared to water-based fracture fluids, methanol-based fluids are 3 to 4 times as expensive.

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4 Baker Hughes is one of the world's largest oilfield services companies, along with Schlumberger and Halliburton.

5 Reservoirs that have significant clay content may be "water sensitive". Some clays (e.g., illite and smectite) swell when absorbing water, and the swelling can reduce porosity and permeability, thereby reducing the flow of oil or water. That is, water may have had an adverse effect on the formation permeability to natural gas.

6 With regard to the safety of using methanol in field operations, special techniques have been reportedly developed by operators. The flash point of methanol is 53°F and its density is greater than that of air, which presents a safety hazard to field personnel. To minimize the potential for ignition of methanol, a "blanket" of CO_2 vapor is used to separate methanol vapor from any oxygen source. Methanol supply tanks are located at least 150 ft from the wellhead, the storage tanks are modified so that CO_2 vapor can be pumped into the tanks, engines are equipped with spark arrestors, and personnel must wear fire-resistant coveralls.

Concerns about safety and associated costs to use methanol has led to shifting away from methanol as a base fluid and limiting its use to being only an additive. Indeed, Tables 2 to 5 show that the amount of methanol in the fracking systems as an additive is not substantial. (For example, Table 4 shows that 357 lbs of methanol were pumped into the ground as part of the fracking fluids [from three product applications]; representing only 0.00239% of the 14,876,546 lbs of the total fluid pumped in that fracking job).

In summary, it appears that the use of methanol in fracking fluids is limited to being an additive, constituting a small percentage of the total fracking fluid volume. In the following section, we track methanol as it gets injected as part of the fracking fluids, and evaluate hypothetical scenarios of methanol reaching groundwater and surface water.

3 Methanol in Flowback Water

A significant portion of the water used in the hydrofracking process returns to the ground surface through the well as "flowback" water. In 2010, University of Maryland (2010) researchers predicted that approximately twenty million gallons of flowback water were going to be produced each day in Pennsylvania. Because of these large volumes, concerns about groundwater and surface water contamination from flowback water have been in the news[7]. However, as acknowledged by the U.S. Environmental Protection Agency (EPA) Administrator, Lisa Jackson, there are no documented incidents where fracturing fluid components (including methanol) have contaminated groundwater to date.[8,9,10] To our knowledge, methanol has not been reported to contaminate either surface waters or groundwater as a result of disposal of fracking fluids flowback.[11]

Nevertheless, in this section, we evaluated hypothetical scenarios that included methanol reaching groundwater and surface water as part of the fracking fluid system. (We used the fracking fluid system presented in Table 4 as an example fracking fluid.) The hypothetical scenarios we evaluated included:

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7 New York Times-Regulations Lax (2-26-11), Postgazette.com-High radioactivity (3-7-11), New York Times-Energy Dept Panel (5-6-11), New York Times-Baffled (5-13-11).

8 In a May 2011 communication with the PA DEP, we confirmed that there was not any reporting of groundwater contamination cases related to fracking.

9 Lisa Jackson's 2011 testimony to the United States Congress can be viewed via http://www.youtube.com/watch?v=L4RLzlcox5c

10 Regarding the use of fracking fluids in coal bed methane (CBM), the U.S. EPA (2004) also concluded, "*the injection of hydraulic fracturing fluids into CBM wells poses minimal threat to [*underground sources of drinking water*]… In its review of incidents of drinking water well contamination believed to be associated with hydraulic fracturing, EPA found no confirmed cases that are linked to fracturing fluid injection into CBM wells or subsequent underground movement of fracturing fluids. Further, although thousands of CBM wells are fractured annually, EPA did not find confirmed evidence that drinking water wells have been contaminated by hydraulic fracturing fluid injection into CBM wells*".

11 It is known that flowback disposal into streams adds Total Dissolved Solids (TDS) and chloride rendering the stream water murky and salty. Currently, there are no health based standards for TDS and chloride for drinking water. The secondary (non mandatory) standards for TDS and chloride are 500 mg/L and 250 mg/L, respectively. Also, flowback may contain Naturally Occurring Radioactive Material (NORM).

- Leakage of fracking fluids through a natural gas well casing, with methanol reaching groundwater and traveling toward a residential water well
- Disposal of treated flowback into surface water.

From these hypothetical scenarios, we calculated conservatively high methanol concentrations that could reach residential water wells and surface water, and compared those concentrations to the estimated health-based screening levels for methanol (we limited our evaluation to methanol and did not evaluate other fracking fluid chemicals). In each of these scenarios, we found the methanol concentration to be orders of magnitude lower than the estimated health-based screening levels for residential drinking water (17.5 mg/L) and recreational incidental ingestion of surface water (3,500 mg/L). Section 4 of this paper provides details about these methanol screening levels.

3.1 Hypothetical Scenario 1: Leakage of Methanol as Part of Fracking Fluids through a Natural Gas Well Casing, With Methanol Reaching a Residential Water Well

In order to estimate the impact of methanol in a drinking water well, a hypothetical scenario of leakage of methanol, as part of fracking fluids, was simulated using a groundwater flow and contaminant transport modeling tool.[12] In the hypothetical scenario, a residential well (screened 30 to 60 ft below ground surface) was assumed to be producing 1,000 gallons per day (gpd) from a sandy aquifer. A fracking well was installed on a neighboring property located 200 ft[13] away from the residential well. An accidental rupture of the fracking well casing was assumed to cause a rapid loss (in half a day) of 0.4 million gallons of fracking fluids with composition similar to that presented in Table 4. (In this hypothetical scenario, the amount of fracking fluid lost was approximately 25% of the total fracking fluid pumped). In this conservative (erring to the side of greater impact) scenario, the methanol concentration at the fracking well was

[12] For the simulation, the United States Geological Survey (USGS) numerical models MODFLOW (McDonald and Harbaugh 1988) and MT3D (Zheng 1990) computer codes were used.

[13] Pennsylvania Oil and Gas Law Sec 601.205 requires a minimum of 200 ft horizontal distance between a water supply well and a fracking well.

approximately 23 mg/L (based on Table 4; maximum methanol concentrations as a scale inhibitor, a non-emulsifier, and a corrosion inhibitor were 18, 1, and 4 mg/L, respectively).

For this hypothetical scenario, the simulation indicated that the methanol concentration that would reach the residential well was a maximum of 0.6 mg/L.[14] (Details of the health based methanol levels are presented in Section 4). In this hypothetical simulation, the following conditions/assumptions were made:

- Methanol is completely miscible in water and is characterized with a very low octanol-water partition coefficient of K_{OC} of 8 L/kg.
- Although methanol biodegrades aerobically with a half-life of 1–7 days, we assumed that no biodegradation occurs in this hypothetical scenario. However, it should be noted that in about 27 days, methanol concentration will drop to less than 10% of its original starting concentration.

In scenarios less conservative (and more realistic), methanol is expected to biodegrade before reaching a residential water well (methanol half-life is 1–7 days; Howard et al. 1991). Also, the amount of spill would likely be considerably less than the amount assumed in the conservative scenario. Thus, we conclude that methanol is not expected to be a concern if it reached groundwater as part of fracking fluids.

3.2 Hypothetical Scenario 2: Disposal of Flowback into Surface Water after Treatment

Pennsylvania appears to be the only state that has allowed for the disposal of flowback into the State's streams after treatment.[15,16] State regulators have developed strict guidelines governing the treatment of flowback water, including the establishment of a 150-ft buffer zone along

[14] The 0.6 mg/L is much lower than the 17.5 mg/L health-based screening level for methanol in residential drinking water. (Details of the health based standards are presented in Section 4 of this report).

[15] The University of Maryland Report (2010) recommended re-evaluation of whether or not municipal wastewater treatment plants that are designed to treat sewage should also be allowed to treat flowback water.

[16] Pennsylvania regulations forbid disposal of fracking flowback without any treatment.

20,000 miles of State streams.[17] Because methanol is not regulated under the Clean Water Act (CWA)[18], measured methanol concentration data from receiving streams are not available. Before discharging into the stream, fracking operators ship the flowback to a wastewater treatment plant (WWTP) that is allowed by PA DEP to accept flowback water. Upon treatment, the WWTP discharges the treated water into the receiving stream pursuant to a permit. The highest concentration of methanol in flowback received by a WWTP is assumed conservatively to be 23 mg/L (based on Table 4). In this hypothetical scenario, we conservatively assumed that the concentration in the WWTP influent and effluent remained the same (23 mg/L).

Following WWTP discharge, the river water mixes with and dilutes methanol concentration even further. The fully mixed methanol concentration C can be estimated by (U.S. EPA 1985):

$$C = \frac{C_u \; Q_u + C_w \; Q_w}{Q_w + Q_u}$$

where:

C	=	Concentration of methanol in river water following full mixing (mg/L)
C_w	=	Concentration of methanol at point source (mg/L)
C_u	=	Concentration of methanol in river water upstream of discharge (mg/L)
Q_w	=	Discharge rate at point source (gpd)
Q_u	=	Flow rate in river upstream of point source (gpd).

As an example of a stream that received effluent from a WWTP, we selected the French Creek near Phoenixville, PA, with a flow of 5,687,193 gpd (Schreffler 1998). Assuming a continuous discharge of treated fracking backflow containing 23 mg/L of methanol, the fully mixed

17 Marcellus Shale: Tough Regulations, Greater Enforcement. http://www.elibrary.dep.state.pa.us/dsweb/Get/Document-84024/0130-FS-DEP4288.pdf

18 Although methanol is considered a hazardous air pollutant under the CAA, the CAA does not specify a methanol maximum contaminant level (MCL). There is no relevance to methanol being a hazardous pollutant under the CAA and the hypothetical scenarios of methanol impacts to surface water and groundwater.

methanol concentration will be 4.75×10^{-6} mg/L. (Details of the health-based standards are presented in Section 4.)[19]

Flowback is usually disposed of by injecting fluid underground pursuant to Underground Injection Control (UIC) permits governed by the Safe Drinking Water Act. In fact, aspects of hydraulic fracturing fall under several federal regulations including the Clean Water Act, Clean Air Act, National Environmental Policy Act and Occupational Safety and Health Act. Failure to comply with these regulations results in fines and penalties for producers. Under the UIC, liquid wastes from oil and natural gas production can be injected into permitted Class II wells as long as the waste does not contain any diesel product. There are no restrictions on disposal of flowback containing methanol under the UIC program (U.S. EPA 2001).

[19] The 4.75×10^{-6} mg/L is much lower than the 3,500 mg/L health-based screening level derived for incidental ingestion of methanol in surface water.

4 Health Assessment of Methanol

This section presents a screening assessment of the potential for health effects associated with exposure to methanol from hydraulic fracturing fluids. The assessment includes a summary of background exposures to methanol as context for the exposure levels estimated from fracturing fluids, a review of relevant health effects data from toxicological studies, derivation of health-based screening levels, and a comparison of screening levels with estimated methanol water concentrations associated with fracking operations. The pathways of potential exposure to methanol in fracking fluids considered in this assessment include: 1) consumption of groundwater impacted by methanol-containing fracking fluids, and 2) incidental ingestion of river and stream waters that received treated flowback.

4.1 Methanol Exposure and Health Effects

Methanol occurs naturally and is produced from a variety of sources, including volcanic emissions, vegetative degradation, microbial activity, and from insects (NTP 2003). Methanol is not persistent in the environment, biodegrades readily and quickly under both anaerobic and aerobic conditions, and photodegrades relatively quickly (NTP 2003). People are exposed to methanol from exogenous sources, such as consumer products, cigarette smoke, and background concentrations in air and water, but dietary sources are believed to be the primary source of methanol exposure to the general population (NTP 2003). Natural sources of dietary methanol include fruits, fruit juices, alcoholic beverages, and other foods. Fruit juices contain methanol or methanol precursors at levels ranging from 12−640 mg/L with an estimated mean of 140 mg/L (NTP 2003). The estimated 90th percentile daily intake of methanol from fruit juice and wine is 48 mg/day (0.7 mg/kg-day, assuming a 70 kg body weight) (NTP 2003). The food additives aspartame and dimethyl dicarbonate (DMDC) also contribute significantly to dietary methanol exposure. The estimated 90th percentile intake level from aspartame is 0.16−0.3 mg/kg-day and from DMDC is 11 mg/day (0.16 mg/kg-day) (NTP 2003). Endogenous production of methanol can also provide a significant source of exposure. In addition to the methanol present in foods, methanol is produced in the gastrointestinal tract through microbial degradation of pectin in fruits and vegetables (Siragusa et al. 1988), as well as through metabolic processes in the body (Fisher et al. 2000). Background blood methanol levels have been measured in the range of 0.25 to 4.7 mg/L (U.S. EPA 2011a).

The health effects of acute oral and inhalation exposure to large amounts of methanol in humans are well characterized and have been summarized elsewhere (U.S. EPA 2011a; NTP 2003). Of most relevance to this health assessment of methanol in fracking fluid are studies evaluating health effects following longer term exposures to low levels of methanol (a scenario that may be relevant to methanol in drinking water). The focus of this summary is, thus, the studies that form the basis of EPA's toxicological criterion for oral exposure to methanol.

For noncancer effects following oral exposures, EPA derives a reference dose (RfD). An RfD is an intake level of a chemical, at or below which no health effects are likely to occur, even with long-term daily exposures. EPA has derived a methanol RfD of 0.5 mg/kg-day based on decreased brain weight in rats (U.S. EPA 1986). In that study, the rats were fed 0, 100, 500, or 2,500 mg/kg-day of methanol in the diet for 90 days. There were no adverse health effects in the rats exposed to 500 mg/kg-day or less. In the high dose group, brain weights were decreased and liver enzyme levels were increased in both male and female rats. Based on a no observed adverse effects level (NOAEL) of 500 mg/kg-day and applying an uncertainty factor of 1,000 (10 for extrapolation from a subchronic exposure duration; 10 for extrapolation from animals to humans; 10 to account for potentially sensitive individuals), EPA derived the RfD of 0.5 mg/kg-day.

In 2011, U.S EPA (2011a) released a draft toxicological review of the noncancer effects of methanol in which they derived a new RfD based on developmental toxicity. This assessment is currently under external peer review and has not been finalized. Three studies investigated the potential for reproductive and developmental effects in rodents following oral exposure to methanol during pregnancy (Fu et al. 1996; Rogers et al. 1993; Sakanashi et al. 1996). Each of these studies reported an increased incidence of cleft palate and the number of resorptions, and a decrease in the number of live fetuses. Fu et al. (1996) and Rogers et al. (1993) also reported an increased incidence of exencephaly. However, interpretation of these studies is limited by the high dose levels administered. Because of the limitations in the oral exposure studies, EPA based the proposed RfD on an inhalation exposure study in rats in which methanol exposure throughout gestation was associated with decreased brain weight, skeletal malformations/anomalies, and cleft palate (NEDO 1987). EPA decided that route-to-route extrapolation (i.e., from inhalation to oral routes of exposure) was appropriate because of: a) the similarity in effects between inhalation studies and the available oral studies (i.e., brain and skeletal effects in the developing fetus), b) the high absorption rate of methanol in both the lungs and the gut, and c) the rapid distribution of methanol throughout the body once absorbed (U.S. EPA 2011a). EPA calculated a benchmark dose from the NEDO (1987) data, applied route-to-route extrapolation, and converted the resulting dose to a human equivalent dose of 38.6 mg/kg-day. An uncertainty factor of 100 was applied (10 to account for potentially sensitive individuals, 3 for toxicodynamic differences between rats and humans; 3 for deficiencies in the toxicological database) to derive a new proposed RfD of 0.4 mg/kg-day.

There is debate in the scientific community regarding the basis for the proposed RfD in light of significant differences in methanol metabolism between rodents and humans (Sweeting et al. 2010, 2011), and inadequate consideration of background sources of methanol from the diet. In a recent meeting of the External Peer Review Panel convened to evaluate the EPA methanol assessment, panel members questioned reliance on the NEDO (1987) study, stated that the proposed RfD may not be defensible, and suggested use of a different study (e.g., Rogers et al. 1993) as the basis for the RfD.[20] Based on the calculations provided in U.S. EPA (2011a) for the inhalation exposure study reported in Rogers et al. (1993), use of data from Rogers et al. (1993) could result in an RfD that would be 5 to 7.5-fold higher than the proposed RfD based on NEDO (1987). The resulting RfD would then be greater than the current value of 0.5 mg/kg-day, implying that methanol is less toxic than current assumptions. Because the proposed RfD is still under review and could be altered during the peer-review process, this health assessment of methanol from fracking operations will rely on the current RfD of 0.5 mg/kg-day. EPA originally included a cancer assessment in the draft toxicological review for methanol but withdrew it pending further review of the available chronic toxicity and carcinogenicity study, and the unconventional methodology it used.

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[20] Reported in "Risk Policy Report", July 26, 2011.

4.2 Health-Based Screening Levels

Health-based screening levels are commonly used by public health agencies to evaluate whether additional evaluation or site-specific risk assessment is necessary (e.g., U.S. EPA 2011b). Screening levels combine chemical-specific information about toxicity (e.g., the RfD) with exposure assumptions relevant to specific media (e.g., drinking water). In order to provide a high degree of health protection, screening levels typically incorporate high-end exposure assumptions. In this section of the report, we derive health-based screening levels protective of drinking water consumption and incidental ingestion of water during recreational activities, and compare those screening levels to the high-end estimates of methanol concentrations in groundwater and surface water associated with fracking operations, which were provided in the previous section of this report.

4.2.1 Groundwater as a Primary Source of Drinking Water

If fracking fluids containing methanol were to escape through a casing defect, methanol could enter a shallow aquifer used as a residential drinking water source. Using standard high-end exposure assumptions, daily methanol intake from drinking water can be estimated using the following equation and exposure assumptions:

$$Intake = \frac{C_{GW} \times IR}{BW}$$

where:

C_{GW} = estimated concentration of methanol in groundwater = 0.6 mg/L

IR = daily water ingestion rate = 2 L/day

BW = adult body weight = 70 kg.

Assuming a high-end groundwater concentration of 0.6 mg/L described previously, the estimated methanol intake from drinking water would be 0.017 mg/kg body weight per day, or more than 40 times less than the estimated dietary intake from fruit juice and wine.

Using the same exposure assumptions and the methanol RfD of 0.5 mg/kg-day discussed previously, a groundwater screening level protective of residential drinking water consumption can be derived based on the methodology used by U.S. EPA (2011b) to derive health-based Regional Screening Levels:

$$Screening\ Level_{GW} = \frac{RfD \times BW \times HI}{IR}$$

When the assumptions are as described previously and the hazard index (HI) is set at 1.0, the groundwater screening level is 17.5 mg/L. This is 30 times as great as the maximum estimated groundwater concentration (0.6 mg/L) that could result from contamination of a drinking water supply well.

4.2.2 Full Body Contact with Surface Water

If methanol-containing fracking fluids were disposed in a WWTP, subsequent discharges into surface waters from the WWTP could potentially include methanol. An estimated intake level can be derived using the same methodology described for groundwater consumption as drinking water, but modified to account for the significantly lower water intake that would be associated with incidental ingestion.

In the latest guidance for development of Ambient Water Quality Criteria (AWQC) for human health, U.S. EPA (2000) did not recommend and thus, did not develop national criteria for incidental ingestion of surface water under the Safe Drinking Water Act. In their analysis, the amount of actual exposure from incidental ingestion, averaged over a lifetime, would be negligible. However, acknowledging that some states already have established guidance based on incidental ingestion, EPA provides limited guidance in the technical support document to the human health methodology for AWQC (U.S. EPA 1998). U.S. EPA (1998) recommends an ingestion rate of 10 mL/day for incidental ingestion during activities that could result in full body contact (swimming, water skiing, etc.), noting that the recommended value is lower than the value of 50 mL/day published in older U.S. EPA (1989) guidance. The ingestion rate is based on an assumption that a person spends an average of 1 hour in the water per day, for 4 months of the year, and swallows 30 mL of water per hour (i.e., the average volume of a mouthful of water). Averaging the 30 mL/day over a full year gives the estimate of 10 mL/day (0.01 L/day).

Using the assumptions described previously for groundwater along with the surface water ingestion rate of 0.01 L/day, the surface water screening level is 3,500 mg/L. This is 9 orders of magnitude greater than the maximum estimated surface water concentration (4.75×10^{-6} mg/L) that could result if methanol-containing fracking fluids were disposed in a WWTP.

Table 6 provides a comparison of the respective health-based screening levels with estimates of groundwater and surface water methanol concentrations from Scenarios 1 and 2 discussed above. In both cases the estimated water concentrations are considerably less than the screening levels, indicating little or no concern for potential health impacts. Even if the screening levels were modified to incorporate EPA's proposed RfD for methanol of 0.4 mg/kg-day, the estimated groundwater and surface water methanol concentrations would still be much less than their respective screening levels.

Table 6. Comparison of maximum estimated water methanol concentrations from Scenarios 1 and 2 to health-based screening levels

	Maximum Estimated Methanol Concentration	Health-Based Screening Level[a]
Groundwater[b] – residential drinking water consumption	0.6 mg/L	17.5 mg/L
Surface Water[c] – recreational incidental ingestion	4.75×10^{-6} mg/L	3,500 mg/L

[a] Health-based screening levels based on standard high end exposure assumptions and the current U.S. EPA reference dose (RfD).

[b] Estimated groundwater methanol concentration based on the modeled high end concentration in shallow aquifers, as described previously as Scenario 1.

[c] Estimated surface water methanol concentration based on the modeled high end concentration in surfaces waters receiving discharge from waste water treatment plants, as described previously as Scenario 2.

5 Methanol Air Emissions from Flowback Impoundments

In August 2011, U.S. EPA was conducting public hearings regarding their proposed emissions control regulations for the oil and gas industry, including hydraulic fracturing (U.S. EPA 2011c). The proposed EPA regulations are scheduled for implementation by April 3, 2012, and are designed to reduce emissions of hazardous air pollutants (HAP), volatile organic compounds (VOC), and methane, as well as other pollutants such as sulfur dioxide (SO_2) and nitrogen oxides (NO_x). Because methanol is classified as a HAP and a VOC, this section addresses the potential for methanol emissions into the atmosphere as a result of its use in fracking fluids. This section also provides comments on a study conducted by Harvey Consulting (Harvey 2009) that discussed air emissions of methanol from flowback ponds.

In summary, methanol's tendency to volatize from fracking fluids is orders of magnitude lower than the other fracking fluid constituents, and will practically not evaporate from fracking flowback ponds. The Harvey (2009) report did not make correct assumptions regarding the amount of methanol used in fracking fluids or methanol's tendency to volatilize from ponds, which resulted in unrealistic estimates of the amount of methanol that may evaporate from flowback ponds.

5.1 Potential for Methanol Emissions into the Atmosphere

Volatilization of a pure chemical compound into the atmosphere is determined by its vapor pressure (Schwarzenbach et al. 1993). Methanol has a relatively high vapor pressure of about 127 mmHg at 25°C[21] This number is higher (which means that methanol is more volatile) than benzene (94.8 mmHg) and ethylbenzene (9.6 mmHg), for example.

However, once dissolved in water, the tendency of methanol or any other chemical to volatilize into the air is no longer simply described by the vapor pressure. Instead, the tendency to volatilize is described by a parameter called the Henry's Law constant (K_h; Schwarzenbach et

[21] All chemical parameter values are from the Risk Assessment Information System website. http://rais.ornl.gov/tools/profile.php?analysis=Methanol (accessed January 3, 2012).

al. 1993).[22] K_h may be thought of as simply the ratio of a compound's abundance in air to its abundance in water at equilibrium. Low K_h means that the chemical has a low tendency to volatilize out of the water and into the air.

Because methanol is infinitely soluble in water (unlike benzene, ethylbenzene, and most other fracking fluid components), methanol has a very low K_h of about 1.86×10^{-4} at 25°C [23]. For comparison, K_h for benzene, ethylbenzene, and n-hexane are 2×10^{-1}; 3×10^{-1}; and 69.1 at 25°C, respectively. These K_h values are orders of magnitude higher than that of methanol, which means a much higher tendency to volatize from fracking fluids than methanol. As a result, once in water-based fracking fluids, methanol will practically not volatilize.

Indeed, the evaporation rate for dissolved methanol is 35,000 times lower than that of water. In a dry atmosphere above an open flowback impoundment, the methanol air concentration is calculated to be 4.3×10^{-6} mg/L.[24] The water concentration in air is calculated to be 0.15 mg/L.[25] Therefore, the expected rate of methanol evaporation is approximately 35,000 times lower than that of water.

5.2 Methanol Air Emissions from Fracking Flowback Impoundments

Because the volume of methanol used in a fracking fluid system is typically a few hundred pounds out of what may be tens of millions of pounds of fracking fluids,[26] methanol air emissions are not a concern.

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22 For fracking fluids containing many chemical species but where the bulk fluid is water, Henry's Law constant is used as an approximation (Schwarzenbach et al. 1993).

23 K_h value is unitless.

24 Methanol concentration in the air = Henry's Law constant (k_h) for methanol × methanol concentration in flow back water = $1.86\times10^{-4}\times23$ mg/l (see Table 4 for details regarding methanol concentration in flowback water) = 4.3×10^{-6} mg/L. This calculation assumes that there is sufficient mixing due to diurnal heating and other factors to maintain methanol concentrations near the surface at 23 mg/L.

25 Water concentration in air = Pv/RT, where P_v is the vapor pressure of water (23.8 mmHg at 25°C), R is the gas constant (62.36367 mmHg-L/mol-K) and T is the temperature in degrees K (298.15 at 25°C). This gives 1.28×10^{-3} mol/L or, for 18 gm/mol, a concentration of 0.15 gm/L for the water concentration in air.

26 The website www.fracfocus.org contains information about composition of fracking fluids used in fracking jobs throughout the United States.

Indeed, the Pennsylvania Department of Environmental Protection (PA DEP), Bureau of Air Quality, monitored ambient air pollutant concentrations from an open and active fracturing-fluid wastewater impoundment (the Yeager Impoundment) near Washington, Pennsylvania (Washington County) (PA DEP 2010b). Results from a 4-day monitoring event reported methanol detection on only 1 day, with a concentration of 51 $\mu g/m^3$. This value is orders of magnitude lower than EPA's 690,000 $\mu g/m^3$ acute exposure guideline level and the Department of Energy Emergency Removal Program Guidelines for mild or transient effects level. The PA DEP finding confirms that methanol does not have tendency to volatilize from flowback ponds.

5.3 Comments on the Harvey (2009) Report

In September 2011, Exponent attended the EPA public hearing on the new regulations for the oil and gas industry, and the only air pollutants mentioned were benzene, ethylbenzene, n-hexane, and methane. Methanol was mentioned only in the context that limitations on current air emission models include "*poor*" estimates of methanol emission rates (U.S. EPA 2011c).

An example of the "*poor*" estimate of methanol emission was presented in a report by Harvey (2009), prepared for the Natural Resource Defense Counsel—the Harvey Report. This report was cited by "Inside EPA" in their September 13, 2011, issue as a source of information regarding methanol emissions from its use in fracking fluids. The Harvey Report discussed a hypothetical scenario of 10 wells discharging 12,500,000 gallons of flowback water to a pond, which would result in a "*theoretically possible*" methanol air emission of **32.5** tons/year (Harvey 2009). The Harvey Report does not provide details of their calculations.

It appears that the Harvey Report either confused methanol for a different chemical, or committed several errors while addressing methanol emissions, for example:

- The Harvey Report stated, *"(methanol and heavy naphtha) are emitted at relatively large rates and quantities due to **their low solubility** in water and **large concentrations in the flowback water**"* [emphasis added]

  This statement is factually incorrect. Methanol has infinite solubility in water and not low solubility as the Harvey Report claims. Also, methanol has a low concentration in flowback water;[27] the opposite of what the Harvey Report claims.

- The Harvey Report described the behavior of methanol in flowback water by stating, *"Since methanol has **a relatively high vapor pressure**, its release to the atmosphere could possibly occur within only about two days after the recovered water is transferred to the impoundment"*.

  This statement is misleading. As described above, the controlling parameter for methanol emissions from water is not the vapor pressure. Rather, it is Henry's Law constant (K_h). Methanol has a very low K_h and hence has a very low tendency to volatilize; the opposite of what the Harvey Report claims.

- The Harvey Report calculated that 32.5 tons/year of methanol could be emitted from the flowback of ten (10) fracturing wells. This estimate is neither realistic nor "theoretically possible" (as the Harvey Report describes in its the analysis). From the review of the Fracfocus website (www.fracfocus.org), methanol use per fracturing job is in the order of hundreds of pounds. Assuming an average methanol use of 350 lbs per fracturing job,[28] ten (10) fracturing wells would use 3,500 lbs. The methanol content in the flowback water from these 10 wells would be 875 lbs (flowback water is 25% of the injected fracturing fluids per Harvey's Report assumptions). In an unrealistic scenario of the entire methanol in the flowback water being emitted into the air (875 lbs), it is still several orders of magnitude less than what the Harvey Report had estimated (65,000 lbs of methanol emitted in the air). [Note that methanol is infinitely soluble in water, and does not readily volatilize because of its low K_h and thus has a tendency to remain in the water phase. Even if the entire flowback water pond evaporated, only 875 lbs of methanol would evaporate and not

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[27] In this report, we used a methanol concentration of 23 mg/l in flowback water as a conservative high estimate.

[28] Table 4 of this report shows that methanol use was 357 lbs (representing only 0.00239% of the 14,876,546 lbs of the total fluid pumped in that fracking job). We used an average methanol use of 350 lbs in this example.

65,000 lbs as the Harvey Report claims]. The PA DEP study confirmed that methanol does not have tendency to volatilize from flowback ponds.

The website www.fracfocus.org (which provides the chemical composition in hydraulic fracturing fluids) was not available in 2009 when the Harvey Report was published, and may explain the erroneous estimate of methanol content in fracturing fluids by those authors. However, the errors about the basic behavior of methanol in the environment in the Harvey Report have no explanation.

In summary, the tendency of methanol to volatize from fracking fluids are orders of magnitude lower than the other fracking fluid constituents, and methanol will practically not evaporate from fracking flowback ponds as confirmed by the PA DEP study (PA DEP 2010b).

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