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Fate and Transport of Select Compounds of Interest in Fracing Fluids

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March 28, 2011

One Team. Infinite Solutions



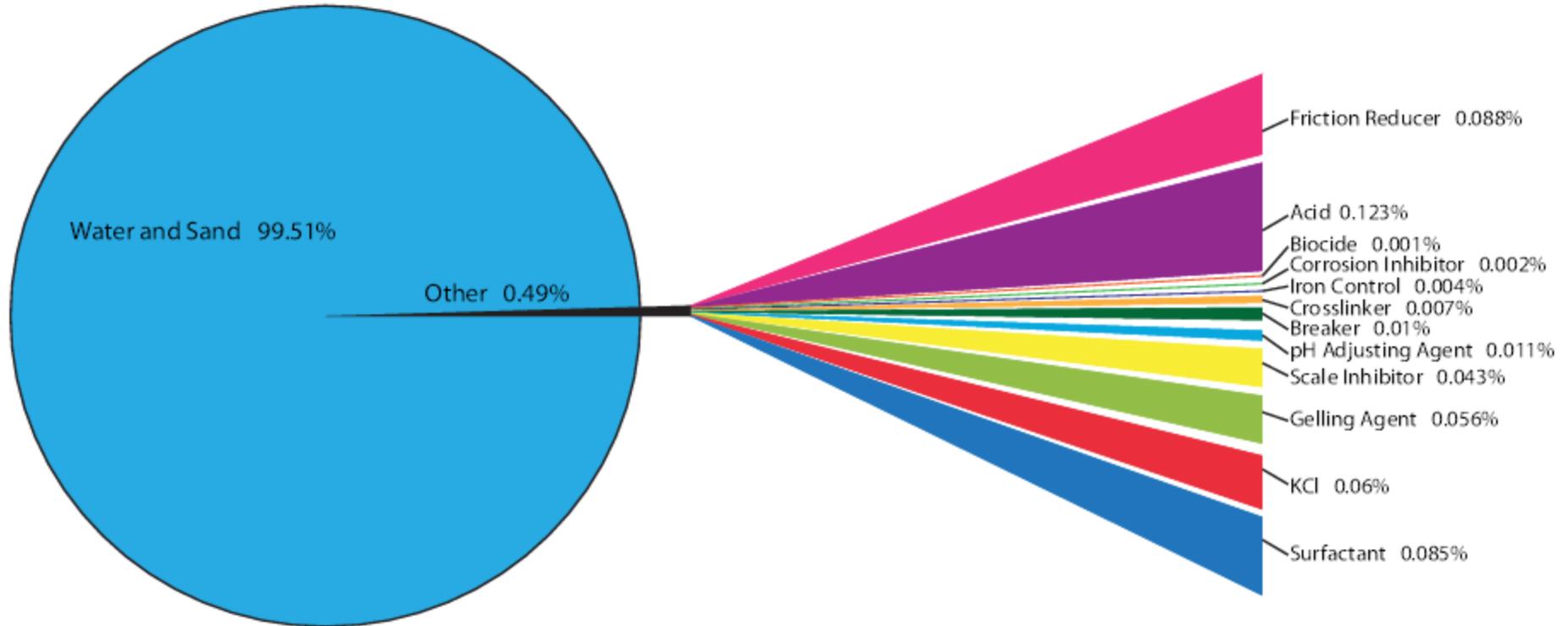
Overview



- Overview of Compounds of Interest (COIs) in Fracing Fluids
- COIs
 - Properties of Selected COIs
 - Fate and Transport of COIs
- Implications for Drinking Water Quality

Composition of Fracing Fluids

Volumetric Composition of a Fracture Fluid



Modified from: ALL Consulting, based on data from a fracture operation in the Fayetteville Shale, 2008

COIs in Fracing Fluid



Product	Chemical Composition
Linear gel delivery system	Guar gum derivative Diesel
Water gelling agent	Guar gum Water Fumaric acid
Linear gel polymer	Fumaric acid Adipic acid
Linear gel polymer slurry	Diesel oil #2
Cross-linker	Boric acid Ethylene Glycol Monoethanolamine
Cross-linker	Sodium tetraborate decahydrate

Product	Chemical Composition
Biocide	2,2-dibromo-3-nitrilo-propionamide (DBNPA)
Foaming agent	Isopropanol Salt of alkylamines Diethanolamine
Foaming agent	Ethanol 2-Butoxyethanol Ester salt Polyglycol ether Water
Acid treatment	Hydrochloric acid
Acid treatment	Formic acid
Breaker fluid	Diammonium peroxodisulfate

Common COIs



- Muriatic acid or hydrochloric acid;
- Guar gum;
- Diesel (BTEX);
- Ethanol and isopropanol;
- Sodium chloride;
- Formic acid, Fumaric and adipic acids;
- Boric acid.

Unconventional COIs



- Ethylene glycol (EG);
- Diethanolamine (DEA);
- 2,2-Dibromo-3-nitrilo-propionamide (DBNPA);
- 2-Butoxy ethanol; and
- Diammonium peroxosulfate (ammonium persulfate).

Ethylene Glycol (EG)

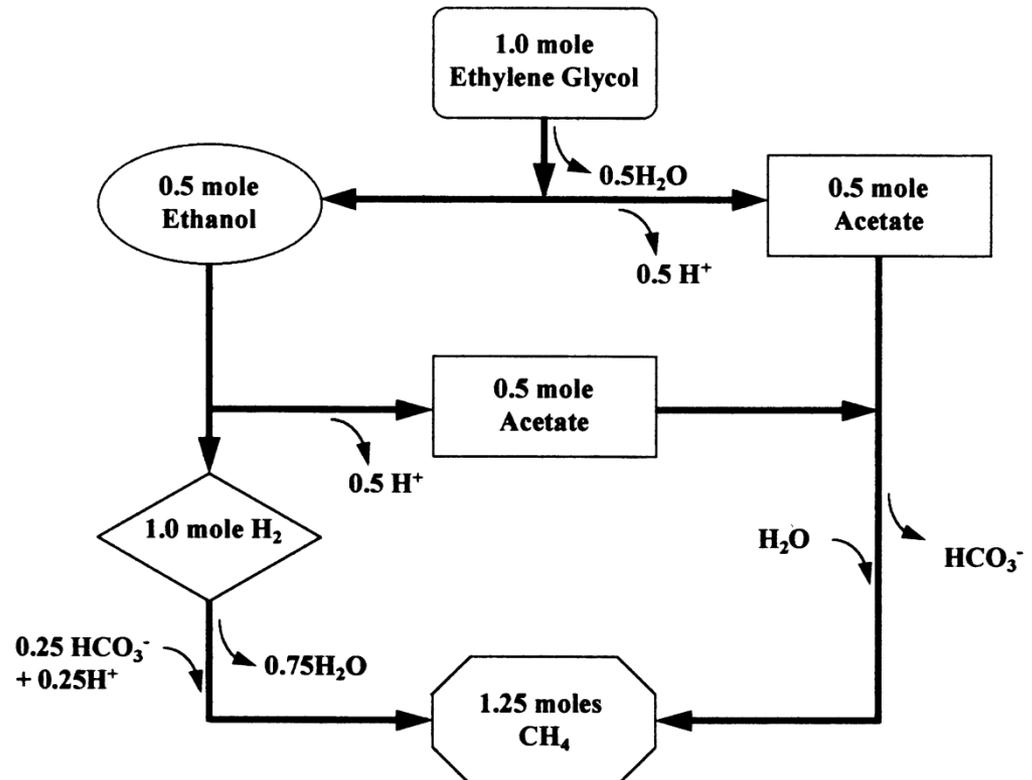


- Liquid miscible in water
- Low Kow and Henry's constant
- Common laboratory reagent – common contaminant in analyses – reason for elevated detection limits, 10 mg/L, detection limit actually ~0.2 mg/L or lower

Ethylene Glycol (EG)



- Anaerobic biodegradation pathway (Dwyer, 1983, Huang, 2005):
- Nitrate electron donor (Schramm and Schink, 1991).



Ethylene Glycol (EG)

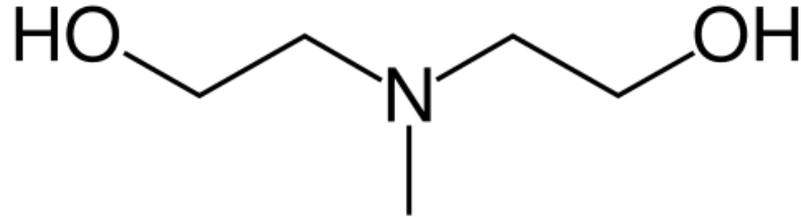


- Aerobic biodegradation pathway (Gruden et al., 2001):

EG → glycolic acid → oxalic acid → CO₂

- Persistence is moderate to low depending on microbial activity

Diethanolamine (DEA)



- Polar, colorless liquid, infinite solubility in water
- Low Kow and Henry's constant
- DEA is considered mobile by EPA (2006)
- EPA (2006) classified DEA as non-persistent in soil and groundwater (half-life of days to weeks)

Diethanolamine (DEA)

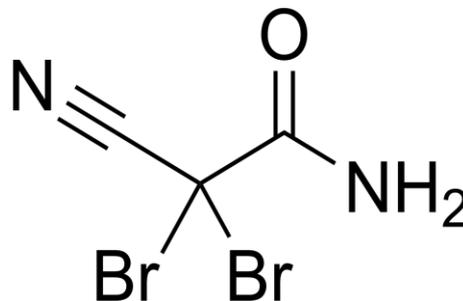


- In the presence of nitrite, DEA forms N-nitrosodiethanolamine (NDELA):

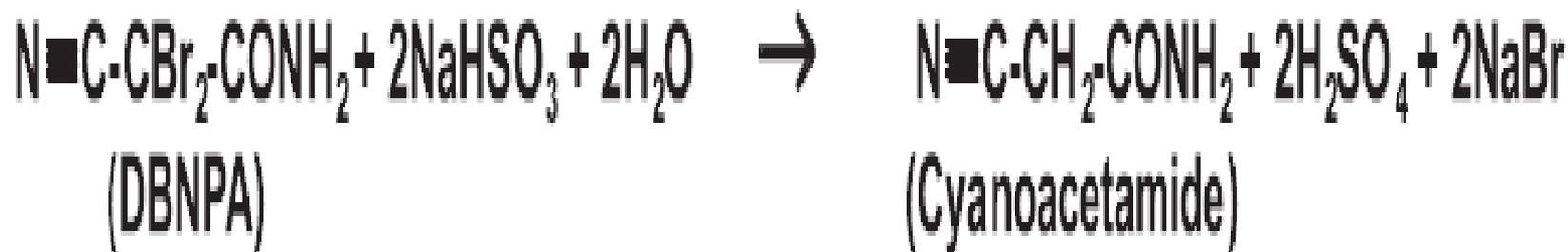


- EPA (2006) notes that NDELA persists in the environment but formation depends on NO_2^- concentration.

2,2-Dibromo-3-nitrilo-propionamide



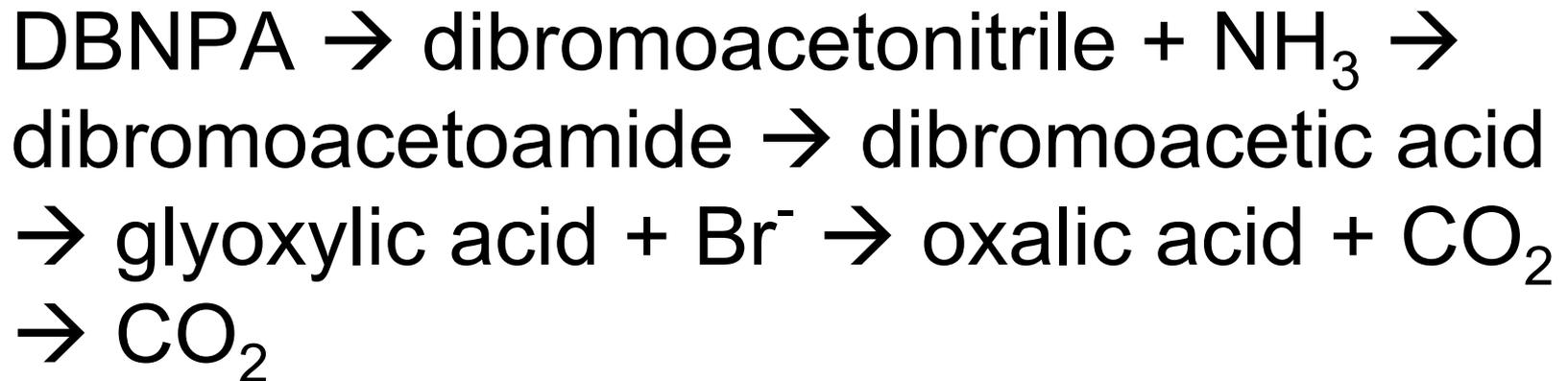
- Solid – solubility 15 g/L at 25° C
- Low Kow and Henry's constant
- Nucleophilic substitution (with reducing agents, I⁻, HS⁻, HSO₃⁻, S₂O₃²⁻, and SO₃²⁻) forms cyanoacetamide and bromide (Exner et al., 1973) – short half-life (hours)



2,2-Dibromo-3-nitrilo-propionamide



- DBNPA hydrolysis reaction has a half-life of 21 hr pH 7.4 and > 155 hr below pH 6, reaction as follows:



2,2-Dibromo-3-nitrilo-propionamide



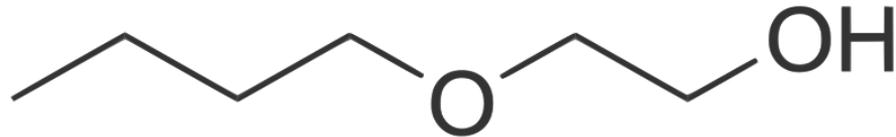
- Exner et al. (1973) reacted DBNPA with soil and soil extract (particle free) at pH 4.8 to 7.5 only ammonia and Br observed.
- Reaction has a half-life of 4 to 25 hr. Fastest rate observed at highest pH.
- Reaction attributed to microbial degradation.
- Surface catalyzed hydrolysis also possible mechanism.

2,2-Dibromo-3-nitrilo-propionamide



- DBNPA interacts with mineral surfaces retarding transport, but still a mobile compound
- Not a persistent compound due to hydrolysis and microbial degradation

2-Butoxyethanol



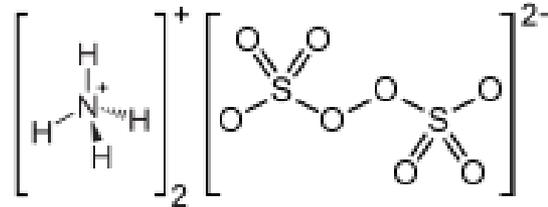
- Colorless liquid, miscible in water and most organic solvents, ether like odor
- Low Kow and Henry's constant
- Considered mobile, but not persistent
- Beihoffer and Ferguson (1994) observed that it has been detected in groundwater near US solid waste landfills (<0.4 to 84 ug/L)

2-Butoxyethanol



- Howard et al. (1991) estimated half-lives of 2-butoxyethanol of 2–8 weeks in groundwater and 1–4 weeks in soil, based on unacclimated aqueous aerobic biodegradation
- IUCLID (2000) reports 95% biodegradation in 28 days
- Hydrolysis unlikely in aqueous environment

Ammonium Persulfate



- Soluble, strong oxidant
- Dissociates into ammonium and persulfate ions
- Persulfate reacts readily with organic matter and reduced inorganic species
- Activated to form persulfate radical by heat and ferrous iron

Ammonium Persulfate



- Persulfate degrades to form sulfate ions
- Half-life in the order of minutes to days depending on reaction conditions
- Considered a mobile ion although will adsorb and react with both inorganic and organic surfaces
- Short persistence decreases potential for mobility

Summary



- Ethylene glycol poses a potential risk for mobility and false positive detections but is not persistent
- DEA mobility is retarded by mineral adsorption, but is not persistent
- DBNPA mobility is retarded by mineral adsorption, but is not persistent
- 2-Butoxyethanol is mobile with limited retardation, but is not persistent

Summary



- Ammonium persulfate is mobile but not persistent
- Monitoring for any of these compounds may only be warranted if impacts from more concentrated reagents in fracturing fluids are detected in wells
- Other geochemical considerations...

Questions?

Fate and Transport of Select Compounds of Potential Concern (COPC) in Fracing Fluids

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Use of proprietary mixtures of reagents in fracing fluids injected in deep (>1,000 feet) zones, in an effort to liberate natural gas, has led to considerable controversy regarding the potential contamination of shallower (<500 feet) drinking water aquifers. This paper focuses on the different classes of compounds identified in fracing fluids, and discusses:

1. their properties in soil/sediment and groundwater,
2. their potential fate in the environment, and
3. the potential problems analyzing for them.

The Canadian Society for Unconventional Gas (Understanding Hydraulic Fracturing, 2011) identifies the following as the typical composition of fracing fluid (citing All Consulting, based on data from a fracing operation in the Fayetteville Shale, 2008):

- Water and Sand = 99.51%
- Other 0.49% =
 - Acid = 0.123%
 - Friction Reducer = 0.088%
 - Surfactant = 0.085%
 - KCl = 0.06%
 - Gelling Agent = 0.056%
 - Scale Inhibitor = 0.043%
 - pH Adjusting Agent = 0.011%
 - Breaker = 0.01%
 - Crosslinker = 0.007%
 - Iron Control = 0.004%
 - Corrosion Inhibitor = 0.002%
 - Biocide = 0.001%

Table 2 (Adapted from the EPA, 2004) provides examples of typical compounds used in each class of chemicals listed above. This paper will focus on the less common compounds included in the list. The transport and fate of the compounds listed below is well understood and treatment options have been identified where warranted, so they will not be evaluated:

- Muriatic acid or hydrochloric acid;
- Guar gum;

- Diesel (BTEX);
- Ethanol and isopropanol;
- Sodium chloride;
- Formic acid;
- Fumaric and adipic acids; and
- Boric acid.

This paper will focus on the compounds below which are not commonly encountered in the environment and/or whose fate and transport is not clearly understood:

- Ethylene glycol;
- Mono or di-ethanol amine;
- 2,2 Dibromo-3-nitrilopropionamide, a biocide;
- 2-Butoxy ethanol; and
- Diammonium peroxosulfate (ammonium persulfate).

Compounds of Potential Concern (COPCs)

Ethylene glycol (EG) is a chemical commonly used in a variety of applications such as airplane deicing and radiator fluid. It is used in analytical laboratories and found as an impurity in alcohols and other compounds. It is a polar liquid that is miscible in water and due to its low Henry's constant and octanol-water partitioning coefficient (K_{ow}), is unlikely to volatilize or adsorb onto carbon or soil organic matter. One of the main reasons EG is not a common analyte for environmental investigations is because it is not considered very toxic (not regulated by the EPA although states, such as Pennsylvania, have set a regulatory goal of 14 milligrams per liter, mg/L) and it is a common laboratory contaminant leading to false positive detections in environmental samples at concentrations as high as 3 to 5 mg/L. With respect to its environmental fate, although it is quite mobile in soil and groundwater, EG also biodegrades readily under aerobic and anaerobic conditions which are common in areas with methane contamination through the following reaction pathway (Dwyer, 1983, Huang, 2005):



Nitrate can serve as the electron acceptor in anaerobic biodegradation of EG (Schramm and Schink, 1991), and nitrate is a common contaminant in rural groundwater as a result of agricultural practices and/or septic field contamination of drinking water.

EG is unlikely to be significantly retarded by adsorption and therefore maybe a potential concern for groundwater transport. Because it degrades readily and is not considered to be persistent in the environment, it is not likely to be a significant problem for groundwater migration.

Mono- or di-ethanol amine is a polar, colorless liquid that, like most amines, is weakly basic. It is commonly used as a foaming agent and used in shampoo and cosmetics. The amine group allows it to be a surface active compound that can adsorb onto mineral surfaces although it has a low K_{ow} (estimate of its adsorption onto soil organic matter) and Henry's constant limiting its adsorption onto carbon and its potential to be stripped from water. As a result, diethanolamine will be difficult to treat in groundwater using conventional water treatment technologies such as granular activated carbon and air-stripping.

It undergoes moderate to rapid biodegradation and is not considered persistent. Knapp et al. (1996) isolated an anaerobe that uses diethanolamine as a carbon source and found that it grew better under reducing conditions in the presence of nitrate than under aerobic conditions. Therefore, due to its lack of persistence in the environment, diethanolamine should not pose a significant risk of migration.

2,2 Dibromo-3-nitropropionamide (DBNPA) is a water soluble (15 g/L) solid that is categorized as a "quick-kill" biocide marketed by Dow for protecting reverse osmosis membranes, paper mills, and offshore oil flooding operations. The definition of quick-kill comes from the relatively effective biocidal properties of the compound. Dow (2006) sells a formulation of DBNPA as a biocide, that includes EG to increase DBNPA solubility. Their marketing material promotes the short persistence of DBNPA in the environment.

Dow (2006) and Exner et al. (1973) explain that DBNPA reacts with nucleophiles (or reducing agents, I, HS, HSO_3^- , $\text{S}_2\text{O}_3^{2-}$, and SO_3^{2-}) in aqueous systems to form cyanoacetamide and bromide as shown in the reaction below:



Cyanoacetamide is subsequently hydrolyzed to cyanoacetic acid, its amide, and malonic acid. Exner et al. (1973) evaluated the degradation of DBNPA in soil/groundwater and surface water assessing the half-life for hydrolysis, nucleophilic substitution (as described above) and exposure to sunlight. They found that hydrolysis is rapid at pH 7.4 with a half-life of approximately 21 hours. The half-life of hydrolysis increases to 155 hours at a pH below 6. When they evaluated degradation rates in soil, they found that biodegradation under aerobic conditions occurred with a half-life of 6 to 15 hours and formed no measurable degradation byproducts besides ammonia and bromide. In order to assess the role of adsorption versus biodegradation, they washed the soil with deionized water, filtered it and added DBNPA to the extracted water. No byproducts were observed besides ammonia and bromide. The reaction was observed at a pH of 5.8, therefore the reaction was believed to be biologically mediated since hydrolysis was determined to be negligible below a pH of 6.

An evaluation of DBNA toxicity after reaction with activated sludge (simulating wastewater treatment) indicated that the DBNPA was deactivated by the reaction (Gartiser and Ulrich, 2003). The study did not evaluate for the presence degradation products, and attributed the

change to adsorption onto the activated sludge. The results of the Exner et al. (1973) appear to indicate that the deactivation was likely due to biodegradation, enhanced by the microbial enriched activated sewage sludge.

The available data appears to confirm that DBNPA has a short half-life in soil and sediments and should biodegrade rapidly in the environment. Under reducing conditions and above a pH of 7.4 the toxicity of the compound should be rapidly deactivated. Therefore, due to its short half-life, DBNPA is unlikely to pose a significant risk of migration.

2-Butoxy ethanol is a colorless liquid that is miscible in water and most organic solvents. It is used as a solvent in many surface coatings and fast drying paints and lacquers. It is also found in many cleaning agents and is therefore a common contaminant in domestic households, businesses and their wastes. Beihoffer and Ferguson (1994) reported that concentrations of 2-butoxyethanol were observed in aqueous samples from a municipal and an industrial landfill in the USA at concentrations ranging from <0.4 to 84 mg/l.

Given the common structure of its functional groups, it is relatively easily biodegraded. Howard et al. (1991) determined an aerobic surface water half-life of 1 to 4 weeks and a soil half-life of 2 to 8 weeks in soil.

The WHO reports that 2-butoxy ethanol has a low K_{ow} and Henry's law constant making it both poorly adsorbed by organic matter in soil and not likely to volatilize into the gas phase once dissolved in water. Therefore it will be difficult to treat in solution using either adsorption or air-stripping.

Groundwater monitoring for 2-butoxy ethanol as a trace constituent in fracing fluids will be complicated by the fact that it is commonly found in house hold cleaning products and paints which maybe spilled at residential sites impacting shallow groundwater. Many domestic wells exhibit contamination from both septic and other domestic sources which could include 2-butoxy ethanol.

Although it is unlikely to be significantly retarded by adsorption, because 2-butoxy ethanol is not considered to be persistent in the environment, it is unlikely to pose a significant risk for contaminant migration. Household cleaning products and paints may pose a greater risk for exposure.

Diammonium peroxosulfate or ammonium persulfate is a salt comprised of two common ions, ammonium and persulfate. Persulfate is commonly used in the environmental remediation field to oxidize petroleum hydrocarbons, chlorinated solvents and other organic contaminants. It degrades into sulfate and can form strong sulfate and hydroxyl radicals when activated by ferrous iron or heat. Because it is a reactive oxidant, it is not persistent in soil or groundwater and will react to form sulfate within a few weeks depending on how reducing groundwater conditions are. As an oxidant, persulfate is one of the more slow reacting oxidants under

standard temperature and pressure and in the absence of a catalyst such as ferrous iron or heat.

Once reacted to form sulfate and ammonium ions, the main concern with this compound is that it increases the total dissolved solids (TDS) in groundwater and may create algal blooms in surface waters because it may increase the nitrogen concentration in surface waters. Both ions are easily removed from impacted groundwater through ion exchange or reverse osmosis treatment. It is not anticipated to pose a significant risk for migration because it will react with organic carbon and reduced materials in the aquifer.

Priorities for Groundwater Monitoring and Treatment

Based on the findings of this evaluation, none of the compounds identified appear to pose a significant risk of migration due to lack of persistence. Their chemical structure, reactivity and/or biodegradability lower their persistence in the environment and limit their potential to impact drinking water wells. That is not to say that screening and monitoring for these compounds is not warranted if there is a reason to believe, based on hydrogeologic data and other evaluations, that the fracturing fluids have the potential to reach a drinking water well.

References

- Beihoffer J, C. Ferguson. 1994. Determination of selected carboxylic acids and alcohols in groundwater by GC-MS. *Journal of Chromatographic Science*, 32, p102–106.
- Dow. 2003. Antimicrobial 7287 Water Treatment Microbiocide. Product Information Sheet.
- Dwyer, D.E. and J.M. Tiedje. 1983. Degradation of Polyethylene Glycols by Methanogenic Consortia. *Applied and Environmental Microbiology*, July, p 185-190.
- EPA Report. 2004. Evaluation of Impacts to Underground Sources of Drinking Water by Hydraulic Fracturing of Coalbed Methane Reservoirs. Chap. 4: Hydraulic fracturing fluids. EPA 816-R-04-003.
- Exner, J.H., G.A. Burk, and D. Kyriacou. 1973. Rates and products of decomposition of 2,2-dibromo-3-nitrilopropionamide. *J. Agr. Food Chem.*, 21(5), p 838-842.
- Gartiser, S. and E. Urich. 2003. Elimination of cooling water biocides in batch tests at different inoculum concentrations. SETAC Conference. Poster.
- Howard ,PH, R.S. Boethling, W.F. Jarvis, W.M. Meylan, E.M. Michalenko. 1991. Handbook of environmental degradation rates. Chelsea, MI, Lewis Publishers Inc.
- Huang, Yi-Li. 2005. Anaerobic Biodegradation of Polyethylene Glycols Using Sludge Microbes. *Process Biochemistry* 40, p 207-211.
- Knapp, J. S., N. D. Jenkey, C. C. Townsley. 1996. The anaerobic biodegradation of diethanolamine by a nitrate reducing bacterium. *Biodegradation*, 7 (3), p 183-189
- Schramm, E. and B. Schink. 1991. Ether-Cleaving Enzyme and Diol Dehydratase Involved in Anaerobic Polyethylene Glycol Degradation by a New *Acetobacterium* sp. *Biodegradation*, 2, p 71-79.

Table 1: Characteristics of Undiluted Chemicals Found in Hydraulic Fracturing Fluids (Based on MSDSs)				
Product	Chemical Composition Information	Hazards Information ¹	Toxicological Information ²	Ecological Information
Linear gel delivery system	1) Guar gum derivative 2) Diesel	<ul style="list-style-type: none"> Harmful if swallowed Combustible 	<ul style="list-style-type: none"> Chronic effects/Carcinogenicity – contains diesel, a petroleum distillate and known carcinogen Causes eye, skin, respiratory irritation Can cause skin disorders Can be fatal if ingested 	Slowly biodegradable
Water gelling agent	1) Guar gum 2) Water 3) Fumaric acid	None	May be mildly irritating to eyes	Biodegradable
Linear gel polymer	1) Fumaric acid 2) Adipic acid	Flammable vapors	Can cause eye, skin, and respiratory tract irritation	Not determined
Linear gel polymer slurry	1) Diesel oil #2	<ul style="list-style-type: none"> Causes irritation if swallowed Flammable 	<ul style="list-style-type: none"> Carcinogenicity – Possible cancer hazard based on animal data; diesel is listed as a category 3 carcinogen in EC Annex 1 May cause pain, redness, dermatitis 	Partially biodegradable
Cross-linker	1) Boric acid 2) Ethylene Glycol 3) Monoethanolamine	<ul style="list-style-type: none"> Causes irritation if swallowed Combustible 	<ul style="list-style-type: none"> Chronic effects/carcinogenicity D5 may cause liver, heart, brain, reproductive system, and kidney damage, birth defects (embryo and fetus toxicity) Cause eye, skin, respiratory irritation Can cause skin disorders and eye ailments 	Not determined
Cross-linker	1) Sodium tetraborate decahydrate	May be mildly irritating: <ul style="list-style-type: none"> to eyes and skin if swallowed 	May be mildly irritating	<ul style="list-style-type: none"> Partially biodegradable Low fish toxicity
Foaming agent	1) Isopropanol 2) Salt of alkylamines 3) Diethanolamine	<ul style="list-style-type: none"> Harmful if swallowed Highly flammable 	<ul style="list-style-type: none"> Chronic effects/carcinogenicity – may cause liver and kidney effects Causes eye, skin, respiratory irritation Can cause skin disorders and eye ailments 	Not determined
Foaming agent	1) Ethanol 2) 2-Butoxyethanol 3) Ester salt 4) Polyglycol ether 5) Water	Harmful if swallowed or absorbed through skin	<ul style="list-style-type: none"> May cause nausea, headache, narcosis May be mildly irritating 	Harmful to aquatic organisms
Acid treatment-hydrochloric acid	1) Hydrochloric acid	<ul style="list-style-type: none"> May cause eye, skin and respiratory burns Harmful if swallowed 	<ul style="list-style-type: none"> Chronic effects/carcinogenicity – prolonged exposure cause erosion of teeth Causes severe burns and skin disorders 	Not determined
Acid treatment-hydrochloric acid	1) Formic acid	<ul style="list-style-type: none"> May cause mouth, throat, stomach, skin, and respiratory tract burns May cause genetic changes 	<ul style="list-style-type: none"> May cause heritable genetic damage in humans Cause severe burns Causes tissue damage 	Not determined
Breaker fluid	1) Diammonium peroxodisulphate	<ul style="list-style-type: none"> May cause respiratory tract, eye or skin irritation Harmful if swallowed 	May cause redness, discomfort, pain, coughing, dermatitis	Not determine
Biocide*	1) 2,2-Dibromo-3-nitriopropionamide			

Table 2. Adapted from Table 4-1, Chapter 4, EPA Report 816-R-04-003. Hazard and toxicological information sources from MSDS according to EPA. Biocide not included in original table. Identified by multiple sources as a biocide for hydraulic fracturing.