Characterizing Toxicity and Risks of Hydraulic Fracturing Fluid Additives

Andrew Pawlisz, DABT ERT(UK) - Senior Toxicologist/Risk Assessor

NEMC August 2015

Orange County, CA

Disclaimer

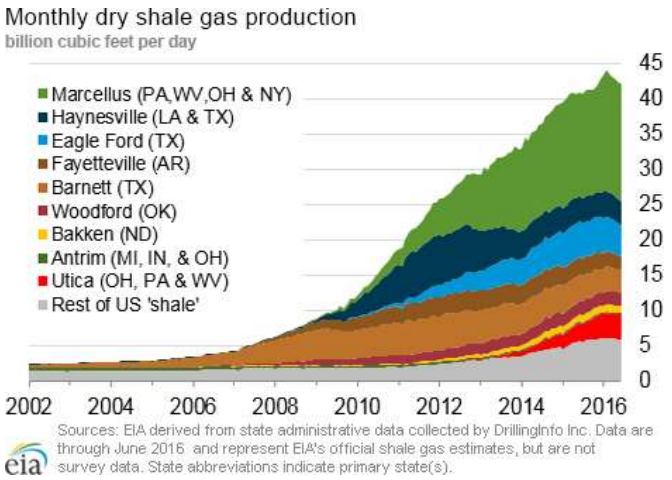
Information is from public sources as noted and views and opinions are that of the presenter alone.

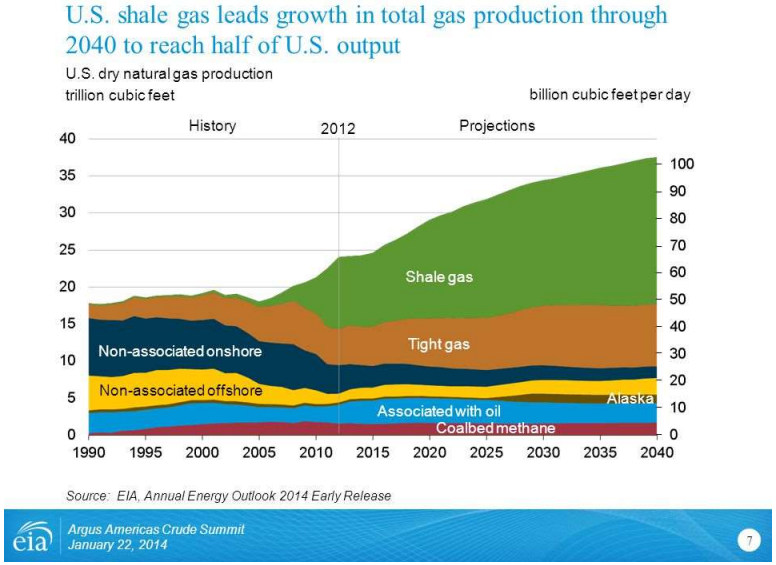
Outline

1. Introduction
2. Risk messaging to public in media
3. Reported events
4. Injury claims
5. Risk assessment process
6. Hypothetical drill rig worker risk assessment
7. Conclusions

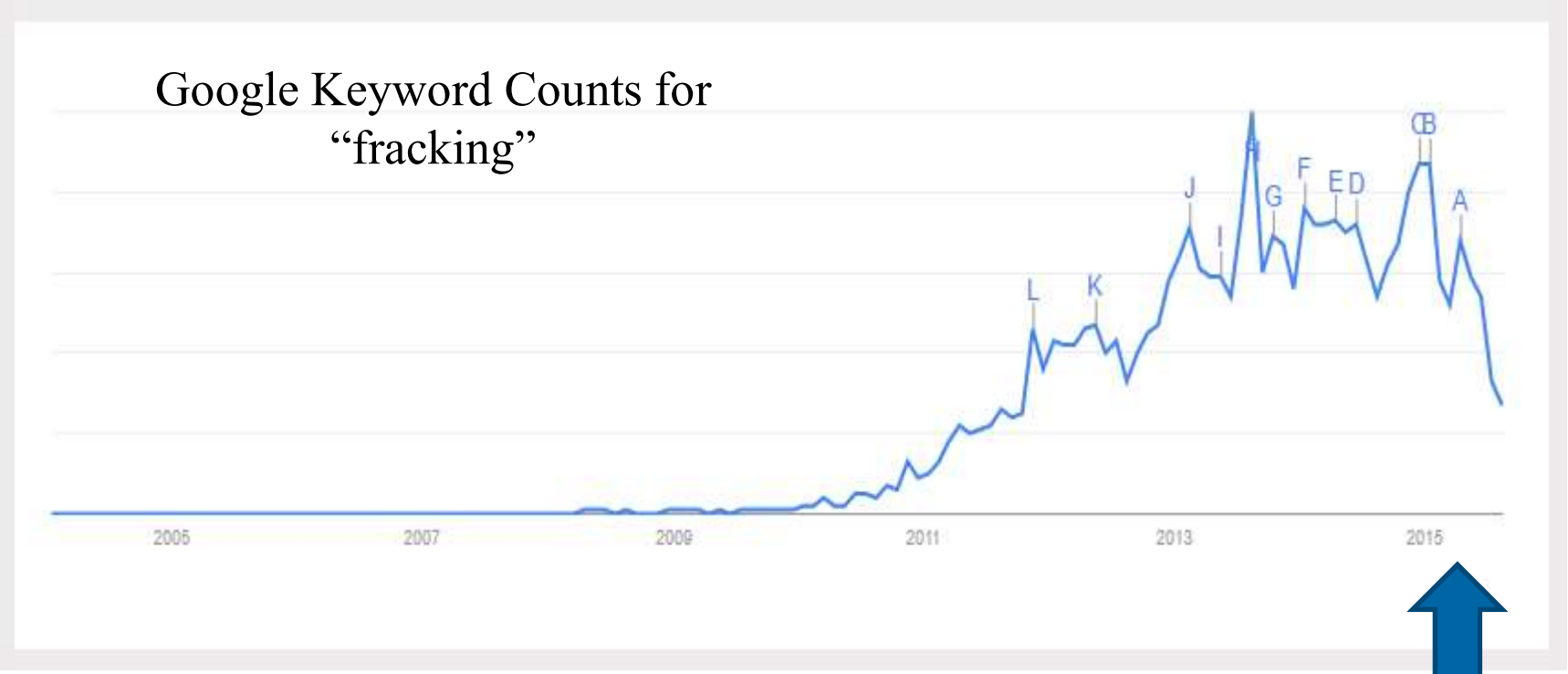
Shale Gas & Oil Exploration

- Increased application of hydraulic fracturing worldwide
- First experiment in 1947
- Over 40 North American shale plays
- Over 1 million operations completed in US
- Expansion projected despite the recent drop
- Lifting of oil export ban
- Energy prices on the rise





Public Interest in Fracking



Fxstreet (2015)

Production Drop

Information from Media

Fracking opponents ridiculed for claiming sand is cancer risk

Frackademia: Investigation Reveals Colorado University Involved in Pro-Fracking PR Scheme

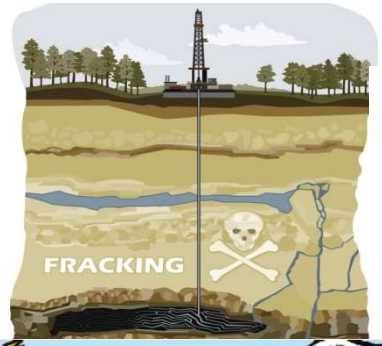
Fracking uses a miniscule amount of water

Pope inspires faith leaders to call for fracking ban in Pa.

Earthquakes Not Caused by Fracking but Are Man-Made, Says Oklahoma Geological Survey

Oklahoma Earthquakes 2015: Tremors Rise As Oklahoma Officials Struggle To Stem Fracking Wastewater Flow

US District Court Blocks Bureau of Land Management Rule For Hydraulic Fracking On Federal And Tribal Land



Texas House approves so-called 'Denton fracking ban' bill

Our Food Is Not Being Grown With Fracking Wastewater

Fracking Studies Overwhelmingly Indicate Threats to Public Health

Fracking Study Ties Water Contamination to Surface Spills

Colorado court takes up local laws limiting fracking

Johns Hopkins Study Links Fracking to Premature Births, High-Risk Pregnancies

Reported Events

- **Surface Water:**
  - Illegal dumping (Hunt 2013)
  - Pennsylvania and North Dakota (Kusnetz 2012)
  - Blacklick Creek, PA
  - Stevens Creek, PA (PR 2013)
  - Monongahela River, PA
  - Mahoning River, OH
  - Brush Run, PA
  - Ten Mile Creek, PA

Reported Events

- **Frac Fluid (on-Site):**
  - Accidental releases (Wiseman 2013)
  - Alleged exposure of worker/nurse in Durango, CO (Tsou 2012)
  - Blow-outs (TCCG 2011)
  - BMPs and controls designed to prevent exposure (Nygaard 2013)
- **Frac Fluid (off-Site):**
  - Releases to pastures in PA (PP 2010) and LA (PP 2009)
  - Treatment system residual emissions in PA (Olmstead 2012)
  - Spills (Bamberger 2012&2015)
  - Transportation accidents (King 2012)
  - Blow-outs
  - Endocrine disruptor activity (Kassotis 2015)

Worker Studies

Air (on-Site):

Air quality study at drilling pads (OSHA/NIOSH 2012)

- Levels of silica dust above work place standards
- Increased potential for lung silicosis and lung cancer
- Use of personal protective equipment will mitigate this risk
- Diesel exhaust impacts (Rodriquez 2013)
- Natural gas generators helpful

Public Health Studies

Journal of Exposure Science and Environmental Epidemiology ,
(6 January 2016) | doi:10.1038/jes.2015.81

A systematic evaluation of chemicals in hydraulic-fracturing fluids and wastewater for reproductive and developmental toxicity

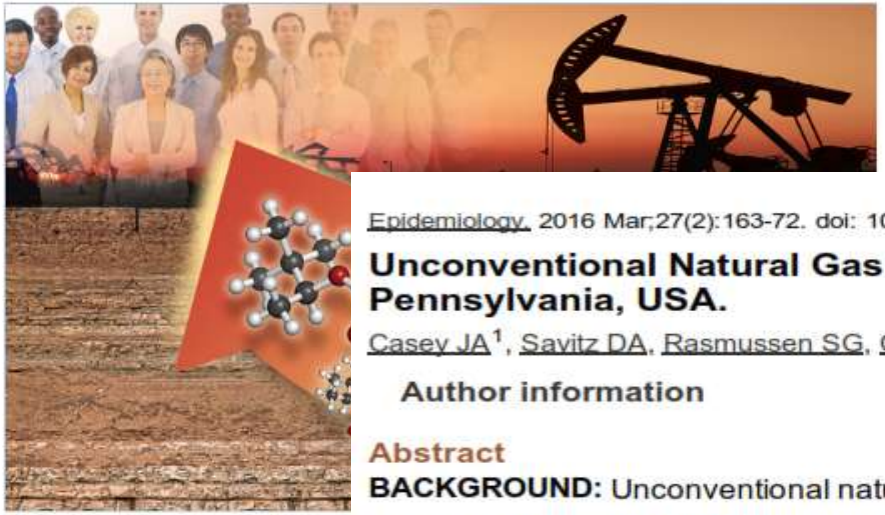
Elise G Elliott, Adrienne S Ettinger, Brian P Leaderer, Michael B Bracken and Nicole C Deziel

Publicintegrity (2016)

Yale NEWS

Toxins found in fracking fluids and wastewater, study shows

By Michael Greenwood — January 6, 2016



(Illustration by Pat Lynch / Yale University)

Epidemiology. 2016 Mar;27(2):163-72. doi: 10.1097/EDE.0000000000000387.

Wolters Kluwer | PMC FREE Full text

Unconventional Natural Gas Development and Birth Outcomes in Pennsylvania, USA.

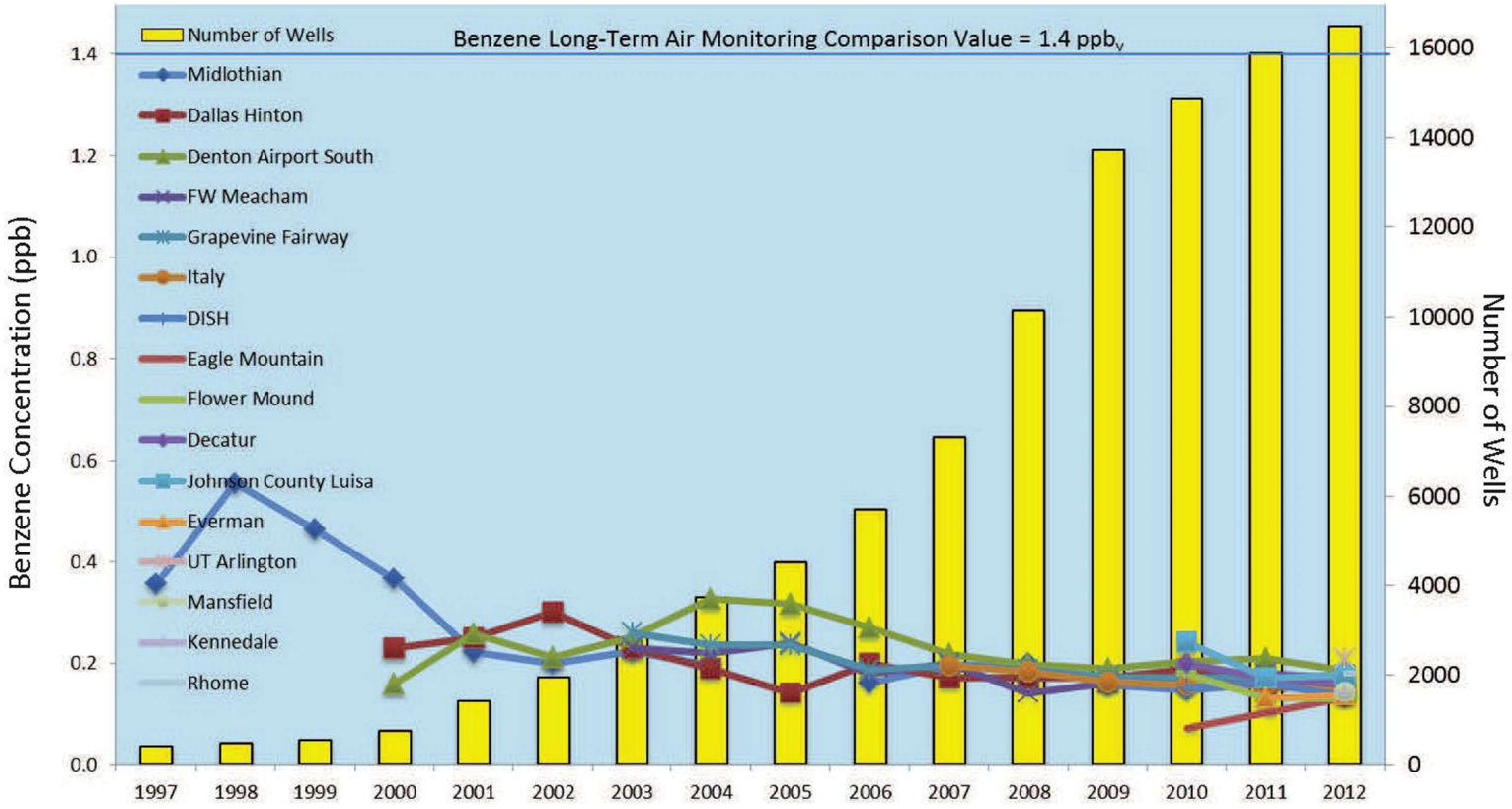
Casey JA[1], Savitz DA, Rasmussen SG, Ogburn EL, Pollak J, Mercer DG, Schwartz BS.

Author information

Abstract

BACKGROUND: Unconventional natural gas development has expanded rapidly. In Pennsylvania, the number of producing wells increased from 0 in 2005 to 3,689 in 2013. Few publications have focused on unconventional natural gas development and birth outcomes.

Annual Benzene Concentrations and Barnett Shale Production



NOTES: DISH and Eagle Mountain AutoGC monitors were installed in April 2010. Flower Mound and Decatur AutoGC monitors and Johnson County Luisa canister monitor were installed in November 2010. The Everman AutoGC monitor was installed in August 2011. The Kennedale AutoGC monitor was installed in June 2012. The UT Arlington, Mansfield, and Rhome AutoGC monitors were installed September, October, and November 2012, respectively. Data from monitors installed in 2012 are incomplete.

Injury Claims

- Presumption of liability
- Attribution challenge
- Individual and aggregate claims relating to groundwater, soil, and air
- Public nuisance, strict liability, medical monitoring, gross negligence, property value loss
- $MM health injury claims
- Plaintiffs must demonstrate causation, harm, and standing (Mullady 2012)

Recent Cases

Cerny v. Marathon

- Plaintiff has granted a mineral lease to operator in 2002 that contained the residence
- Karnes County, TX lawsuit filed in 2013 citing health problems due to alleged "*negligent oil and gas operations*"
- Damages sought:
  - medical expenses
  - loss of earning capacity
  - physical pain and suffering
  - mental pain and anguish
  - disfigurement
  - loss of enjoyment of life

Trial and Appeals Court: No-Evidence Summary Judgment in October 2015

Recent Cases

Kamuck v. Shell

- In 2009, plaintiff purchased 93 acres with mineral rights, but refused to sign agreement with defendant (neighbors sign up)
- Tioga County, PA lawsuit filed in 2011 citing "*ultra hazardous activities*" and "*toxic chemical release*" on or near property
- Damages sought:
  - strict (inherent) liability claim (societal risks vs. rewards)
  - emotional distress
  - spraying of toxic chemicals on roadways
  - nuisance damages
  - punitive damages
  - legal fees

Trial Court Decision: Case dismissed in March 2015 – multiple failures of proof and procedural missteps plus "*possum response*"

Recent Cases

Bombardiere v. Schlumberger

- In 2010, worker in West Virginia was allegedly exposed to A261 corrosion inhibitor and suffered skin burns on hands
- Damages sought:
  - medical monitoring
  - medical costs

District Court Ruling: Defendant *Motion in Limine* (evidence excluded) granted in February 2013 regarding claims of exposure and injury due to "*false expert*" involvement

Cautionary Tale – "*to be qualified as an expert, a witness must have knowledge, skill, experience, training, or education in the subject area in which he intends to testify*"

Recent Cases

Berish v. Southwestern

- Starting in 2008, due to "*insufficient casing*" allegedly fracking fluid and other constituents impacted a private well in Susquehanna County, PA
- Damages sought:
  - compensatory damages
  - punitive damages
  - emotional distress
  - medical costs
  - barring further operations

District Court Ruling: Strict liability claim was upheld in February 2011, emotional distress modified to inconvenience and discomfort

Recent Cases

Roth et al. v. Cabot

- Dimock, PA case originating in 2006 involving methane intrusion and other groundwater quality impacts
- PADEP involved and case widely reported in media
- Claims by up to 44 plaintiffs (about 12 remain):
  - regulatory violation
  - negligence
  - nuisance
  - strict liability
  - trespass
  - inconvenience and discomfort
  - fraudulent misrepresentation

District Court Ruling: In April 2014, magistrate judge opined that natural gas drilling is not an abnormally dangerous activity and the strict liability claim does not apply (traditional negligence does)

Recent Cases

Parr v. Aruba

- 2011 toxic-tort case filed in Dallas County Court
- Decatur, TX plaintiff allegations of "*air pollution*"
- No settlement took place and jury trial ensued in 2014
- Plaintiff's September 2013 petition claimed $66M in damages to physical and mental health, pets and livestock, natural environment, and property
- Hydrocarbons and BTEX named, but no sampling conducted
- Air modeling 2009 through 2011 performed, but "*All models are wrong, some are useful*" – *G. Box*
- MSDS sheets cited as primary sources of toxicological information, where refereed and authoritative reference material existed

Recent Cases

Parr v. Aruba – cont.

- "*ethylbenzen and m,p-Xylene*" found in the bodies of plaintiffs by "*Environmental Health Specialist*"
- Residues not verified by follow-up toxicological testing/evaluation
- Plaintiffs disclaimed causes of any *disease*, focused on *discomfort*
- On April 22, 2014, jury awarded $3M in damages (pain&suffering)
- On August 4, 2014 the defendant moved for a new trial
  - Sufficient evidence of general and specific causation?
  - Reliable expert testimony?
  - Sufficient layperson understanding of how hydrocarbons impact health?
  - Nuisance vs. toxic tort case requirements (causation evidence and linkages)

Recent Cases

Parr v. Aruba – cont.

- Texas Supreme Court requirements for scientific evidence

  "*Dose makes the poison*" - *Paracelcus*

- Empirical air quality data available?
- Total hydrocarbons model has assumptions that do not reflect actual exposures integrated over time
- Incremental risk/attribution – "*substantial factor*"
- Quantitative human health risk assessment not performed
- Case under appeal

Well Integrity

- A modern well is a multi-layered casing system designed as a pressure vessel to last 40+ years (Miersmann 2010; Miskimis 2009)
- Wells fail mainly due to pipe connection leaks, cementing issues, corrosion, and mechanical stresses
- Well construction failure rates (individual barriers) range from 1 to 5% (King 2013)
- Well failure may not always lead to impacts
- Total well integrity failures range from 0.004 to 0.03% and are 10 to 100x lower than single barrier failures (King 2013)

Groundwater Protection

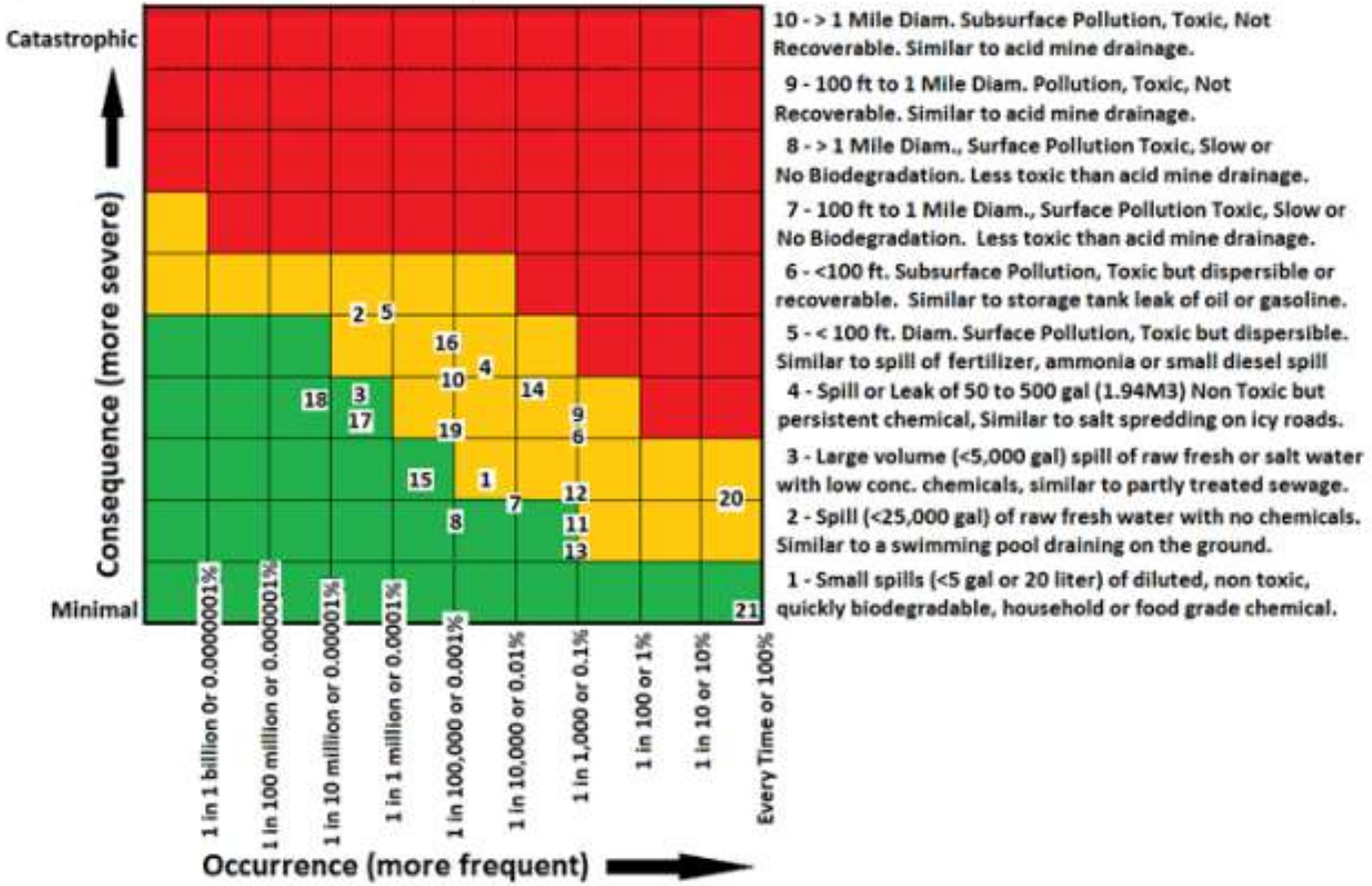
- Current evidence indicates that there have been no "*proven cases where fracking process itself has affected water-Lisa Jackson, USEPA*" *(WSJ 2010)*
- "*neither the RRC or the DMRM identified a single groundwater contamination incident resulting from site preparation, drilling, well construction, completion, hydraulic fracturing stimulation, or production operations at any of these horizontal shale gas wells*." *(Kell 2011)*
- Rare occurrences caused by non-standard conditions
- Small number of any cases relative to wells drilled (USEPA 2015)
- Fracking fluids are not moving up from fractures (Drollette 2015)

Hypothetical Drill Rig Worker Risk Assessment

Britannica (2016)

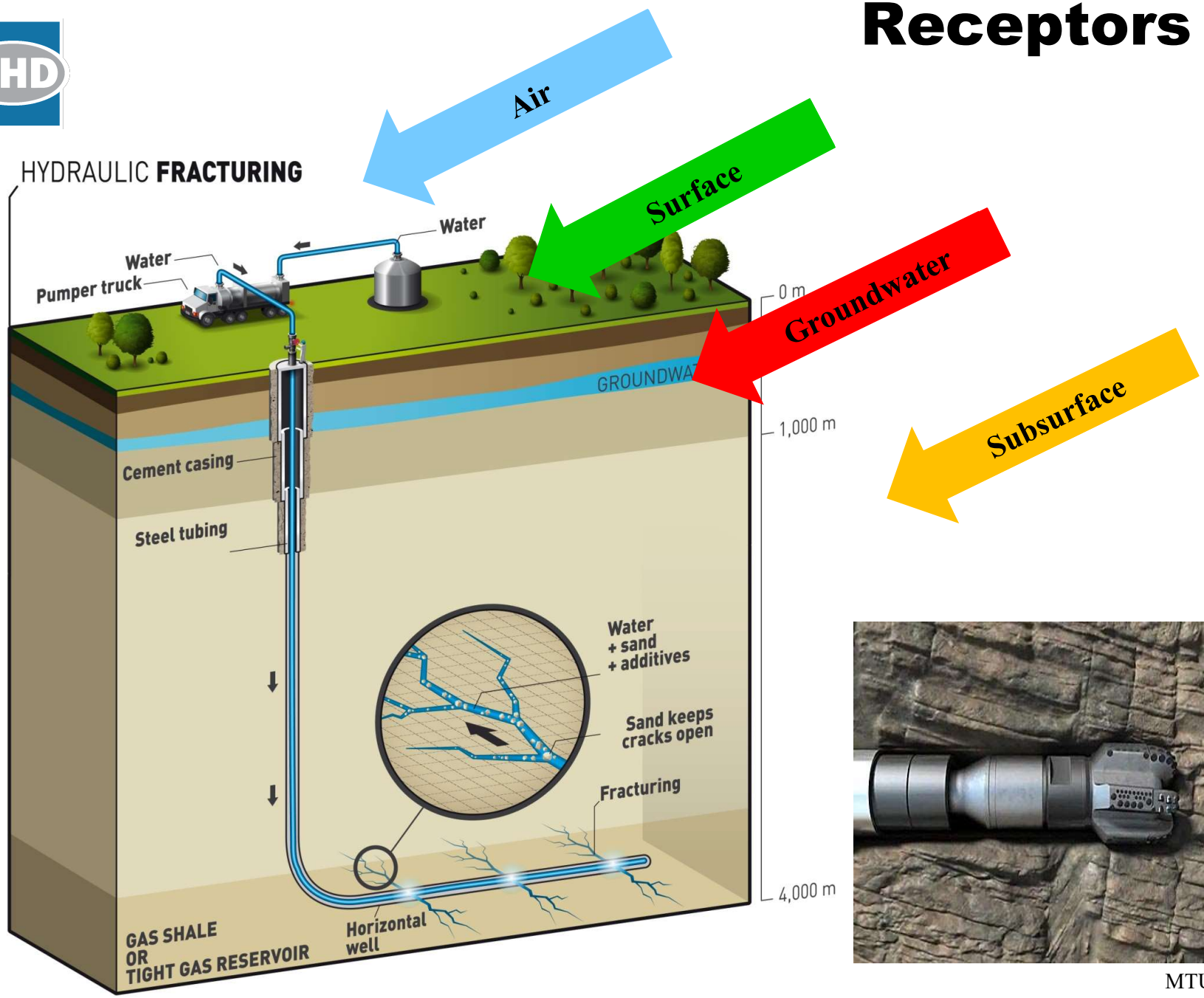
Probability of Spill

Figure 35: Estimates of Various Potential Detrimental Events. This is probability of an event without any significant use of technology that would prevent or reduce the consequence or occurrence of the event.



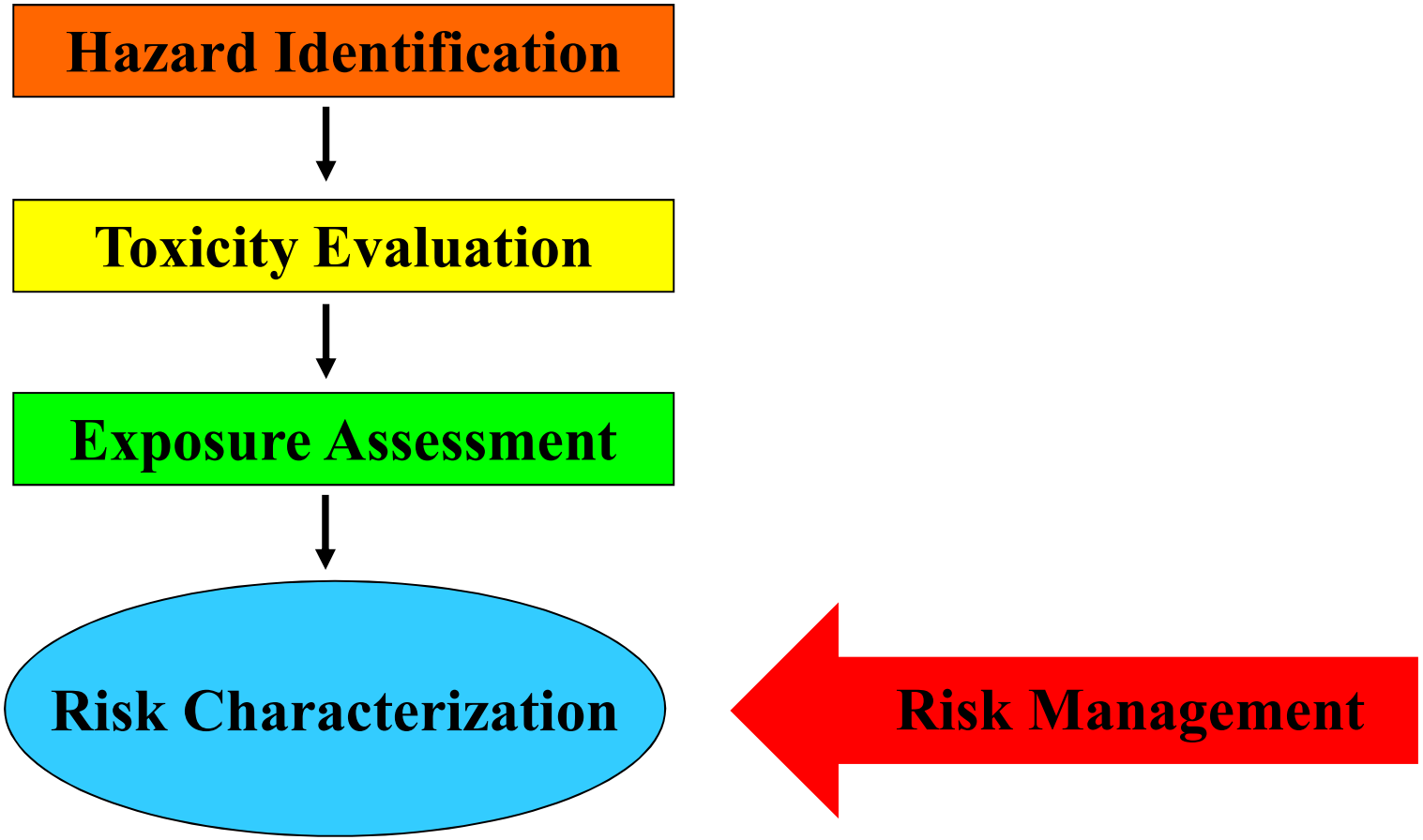
King (2011)

Receptors



MTU (2016)

Risk Assessment Process



Human Health Risk Assessment

Definition:

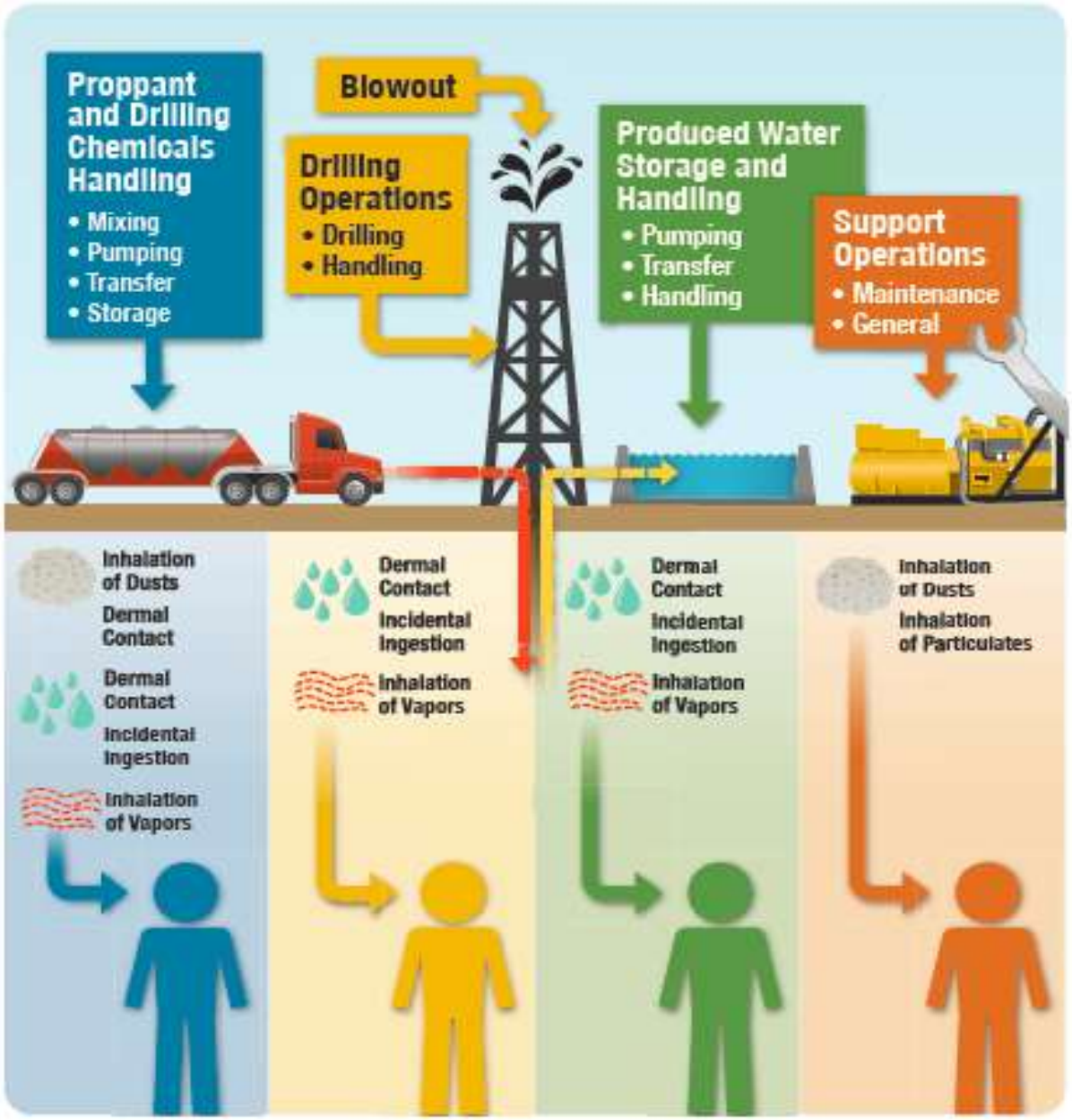
A systematic characterization of potential adverse health effects resulting from human exposure to toxic agents (chemicals)

Risk = f (**Exposure** & **Toxicity**)

No Exposure or Toxicity = No Injury

Case Law: "*Plaintiff must demonstrate the levels of exposure that are hazardous to human beings generally as well as the plaintiff's actual level of exposure*" *Mitchell v. Gencorp* & "*Scientific knowledge of the harmful level of exposure to a chemical, plus knowledge that the plaintiff was exposed to such quantities, are minimal facts necessary to sustain the plaintiffs' burden in a toxic tort case*" *Allen v. Penn. Eng.*

Exposure Potential: Worker



Fracking Fluid

- USEPA identified 1,000 chemicals (USEPA 2012)
- 347 unique CAS entries
- Trade secret constituents generally exempt from public disclosure
- Typical composition (Fontaine 2008):
  - Water (99%)
  - Proppants (1.9%)
  - Friction reducers (0.025%)
  - Disinfectants (0.05%)
  - Surfactants (0.002%)
  - Thickeners (not common)
  - Scale inhibitors
  - Corrosion inhibitors (0.5%)
  - Acids

Analytical Methods

- Base Methods (USEPA 2013):

Alcohols:	Methods 5030 and 8260C
Aldehydes:	Method 8315
Alkylphenols:	No standard method
Amides:	Methods 8032A
Amines (alcohols):	No standard method
Hydrocarbons:	Methods 5030 and 8260C
Carbohydrates:	No standard method
Ethoxylated alcohols:	ASTM D7485-09
Glycols:	Methods 8000C and 8321B
Halogens:	Method 9056A
Inorganics:	Methods 3015A and 6020A
Radionuclides:	Method 9310

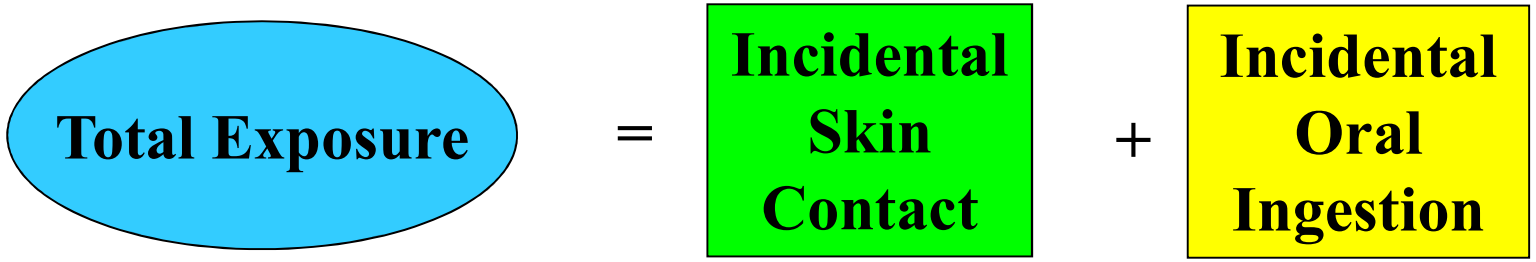
Biocidal Agents: Uses

Chemical Name	Uses	Freq.
Tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione	Biocide	19
Alkyl dimethyl benzyl ammonium chloride	Disinfectant	15
Phosphonium, tetrakis(hydroxymethly)-sulfate	Biocide	11
2,2-Dibromo-3-nitrilopropionamide	Biocide	8
Dipropylene glycol monomethyl ether	Biocide	7
5-Chloro-2-methyl-4-isothiazolin-3-one	Biocide	4
Methylene bis(thiocyanate)	Biocide	3
Magnesium chloride	Biocide	3
Ethoxylated nonylphenol	Disinfectant, surfactant, corrosion inhibitor, antiemulsant	3
2-(2-Methoxyethoxy)ethanol	Biocide	3
Oxydiethylene bis(alkyl dimethyl ammonium chloride)	Bactericide	3
Polyethylene glycol	Biocide	3
Diatomaceous earth, calcined	Biocide	2
Ammonium lauryl sulfate	Biocide	2
Ethanol	Biocide, disinfectant, corrosion inhibitor, foaming agent, surfactant	2
2-Bromo-3-nitrilopropionamide	Biocide	2
Didecyl dimethyl ammonium chloride	Biocide	2
2-(Thiocyanomethylthio)benzothiazole	Biocide	2
1,2-Bromo-2-nitropropane-1,3-diol	Biocide	2
Dialkyl dimethyl ammonium chloride	Disinfectant	2
Heavy aromatic petroleum naphtha	Biocide, antiemulsant, acid inhibitor, corrosion inhibitor, proppant, surfactant	1
Glutaraldehyde	Biocide, corrosion inhibitor	1

Biocidal Agents: Toxicity

Chemical Name	Reference Dose *(mg/kg BW-day)*	Reference Concentration *(mg/m^3)*
Acrolein	5.00E-04	2.00E-05
Naphthalene	2.00E-02	3.00E-03
2-(Thiocyanomethylthio)benzothiazole	3.00E-02	1.70E-01
Glutaraldehyde	5.00E-02	8.00E-05
Methyl-4-isothiazolin	5.30E-02	Not Available
Methylene bis(thiocyanate)	5.50E-02	Not Available
Didecyl dimethyl ammonium chloride	8.40E-02	NA
2,2-Dibromo-3-nitrilopropionamide	1.18E-01	5.33E-02
Tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione	1.20E-01	8.40E+00
2-Bromo-3-nitrilopropionamide	1.78E-01	5.33E+01
1,2-Bromo-2-nitropropane-1,3-diol	1.80E-01	5.00E+00
5-Chloro-2-methyl-4-isothiazolin-3-one	2.10E-01	Not Available
Dibromoacetonitrile	2.45E-01	Not Available
Phosphonium, tetrakis(hydroxymethly)-sulfate	2.48E-01	9.17E-01
Trichloroisocyanuric acid, dry	4.06E-01	8.33E+01
Alkyl dimethyl benzyl ammonium chloride	4.26E-01	Not Available
Magnesium nitrate	5.00E-01	Not Available
Tetrasodium ethylenediaminetetraacetate	6.30E-01	Not Available
N, N'-Methylene bis(5-methyl oxazolidine)	9.00E-01	3.33E-01
Ethoxylated nonylphenol	1.31E+00	2.10E-01
Sodium dichloro-s-triazinetrione	1.42E+00	Not Available

Rig Worker Exposure Model



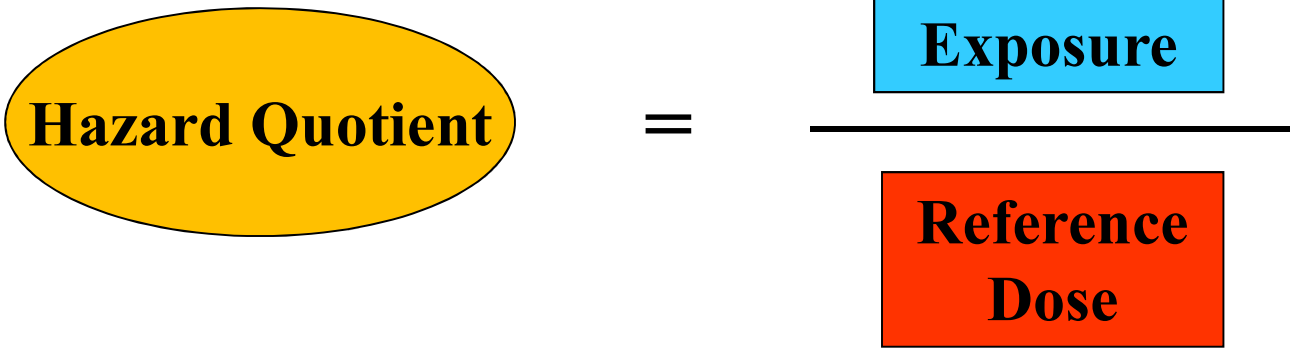
Exposure Assumptions:

- Each shift of 8 hrs
- Oral ingestion of 16 mL fracking fluid per shift
- 14% transdermal influx via exposed hands and arms
- 250 days per year
- Occupational exposure of 10 years

Biocidal Agents: Exposure Ranking

Chemical Name	Fracturing Fluid Concentration *(mg/L)*	Incidental Consumption Exposure *(mg/kg-day)*	Incidental Contact Exposure *(mg/kg BW-day)*	**Total Exposure**
Polyethylene glycol	4.20E+01	5.75E-03	1.16E-01	**1.22E-01**
Diatomaceous earth, calcined	3.28E+01	4.49E-03	9.04E-02	**9.49E-02**
Ethanol	1.88E+01	2.57E-03	5.18E-02	**5.43E-02**
Glutaraldehyde	1.29E+01	1.77E-03	3.57E-02	**3.74E-02**
2,2-Dibromo-3-nitrilopropionamide	6.85E+00	9.38E-04	1.89E-02	**1.98E-02**
Alkyl dimethyl benzyl ammonium chloride	2.54E+00	3.48E-04	7.00E-03	**7.35E-03**
5-Chloro-2-methyl-4-isothiazolin-3-one	1.91E+00	2.62E-04	5.27E-03	**5.53E-03**
Magnesium nitrate	1.91E+00	2.62E-04	5.27E-03	**5.53E-03**
Tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione	1.90E+00	2.60E-04	5.24E-03	**5.50E-03**
Dibromoacetonitrile	1.09E+00	1.49E-04	3.00E-03	**3.15E-03**
Didecyl dimethyl ammonium chloride	9.80E-01	1.34E-04	2.70E-03	**2.84E-03**
Phosphonium, tetrakis(hydroxymethly)-sulfate	9.10E-01	1.25E-04	2.51E-03	**2.63E-03**
Magnesium chloride	3.90E-01	5.34E-05	1.08E-03	**1.13E-03**
1,2-Bromo-2-nitropropane-1,3-diol	3.80E-01	5.21E-05	1.05E-03	**1.10E-03**
Methyl-4-isothiazolin	1.30E-01	1.78E-05	3.58E-04	**3.76E-04**
2-Bromo-3-nitrilopropionamide	3.00E-02	4.11E-06	8.27E-05	**8.68E-05**

Worker Risk Model



Risk Decision Process:

- HQ ≤ acceptable exposure
- HQ > estimated exposure may be associated with elevated risks

Biocidal Agents: Risk Ranking

Chemical Name	Total Exposure *(mg/kg-day)*	RfD *(mg/kg-day)*	**HQ**
Glutaraldehyde	3.74E-02	5.00E-02	**0.749**
2,2-Dibromo-3-nitrilopropionamide	1.98E-02	1.18E-01	**0.168**
Tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione	5.50E-03	1.20E-01	**0.046**
Didecyl dimethyl ammonium chloride	2.84E-03	8.40E-02	**0.034**
Polyethylene glycol	1.22E-01	4.00E+00	**0.030**
5-Chloro-2-methyl-4-isothiazolin-3-one	5.53E-03	2.10E-01	**0.026**
Ethanol	5.43E-02	3.00E+00	**0.018**
Alkyl dimethyl benzyl ammonium chloride	7.35E-03	4.26E-01	**0.017**
Dibromoacetonitrile	3.15E-03	2.45E-01	**0.013**
Magnesium nitrate	5.53E-03	5.00E-01	**0.011**
Phosphonium, tetrakis(hydroxymethly)-sulfate	2.63E-03	2.48E-01	**0.011**
Methyl-4-isothiazolin	3.76E-04	5.30E-02	**0.007**
1,2-Bromo-2-nitropropane-1,3-diol	1.10E-03	1.80E-01	**0.006**
2-Bromo-3-nitrilopropionamide	8.68E-05	1.78E-01	**0.000**
Magnesium chloride	1.13E-03	2.80E+00	**0.000**
Tetrasodium ethylenediaminetetraacetate	5.79E-05	6.30E-01	**0.000**

Summary

- All HQs<1 for hypothetical drill rig worker
- Highest potential exposures:
  - Polyethylene glycol
  - Diatomaceous earth
  - Ethanol
  - Glutaraldehyde
  - Brominated nitrilopropionamide
- Relative risk ranking:
  - Glutaraldehyde
  - Brominated nitrilopropionamide
  - Methylated thiodiazine
  - Methylated ammonium chloride
  - Polyethylene glycol

Conclusions

- Air exposure findings can be variable (exc. for silica dust exposure)
- Reports suggest no widespread impacts on groundwater (except surface spills, non-spec operations, and accidents)
- Growth in oil and gas play exploration likely to continue
- Increasingly larger footprint of the potential for exposure
- Public concerns and injury claims (*Parr v. Aruba?*)
- Long-term fate of wells? – due diligence/well abandonment
- The risk assessment process can help to better quantify the potential for adverse impacts, along with health studies

Pawlisz (2013)