Identity and Toxicological Profile of Biocides Used in Hydraulic Fracturing

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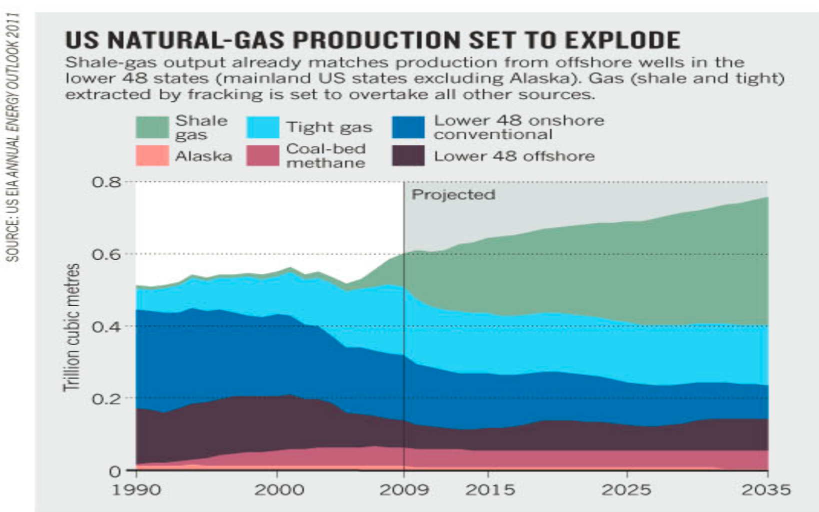
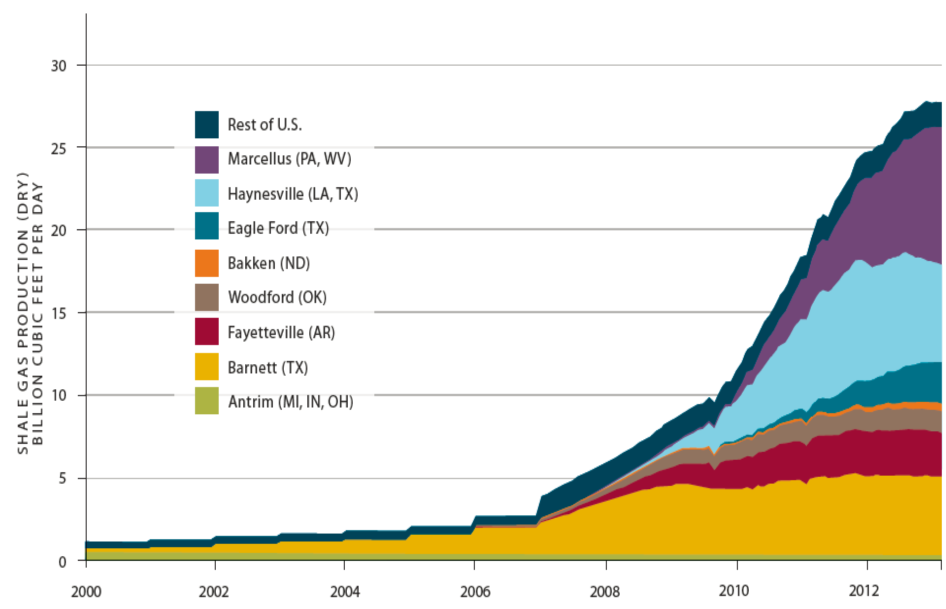
Water Energy & Resources Environment Property & Buildings Transportation

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
- Further expansion projected

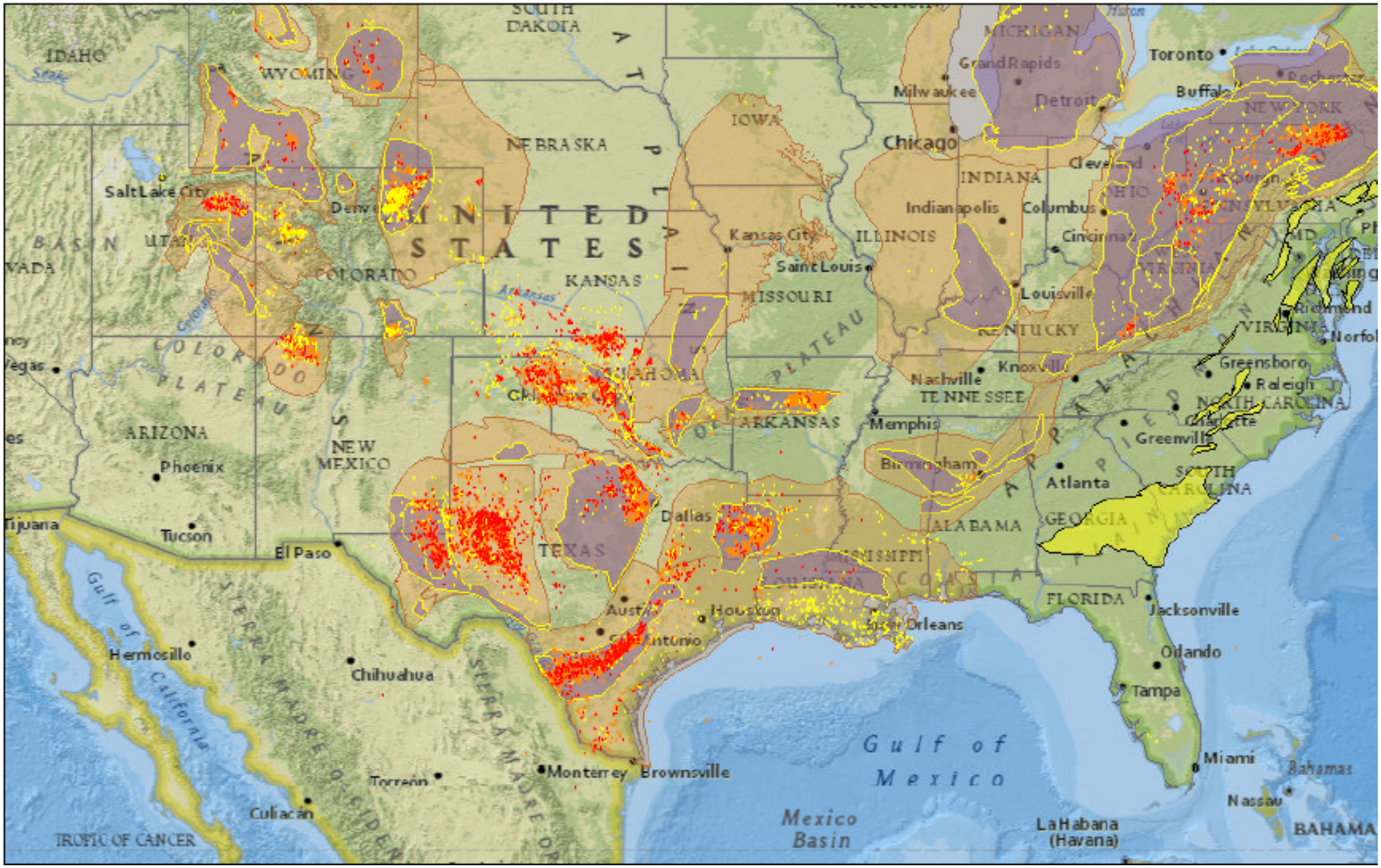
Source: King (2011); Sieminski (2013)



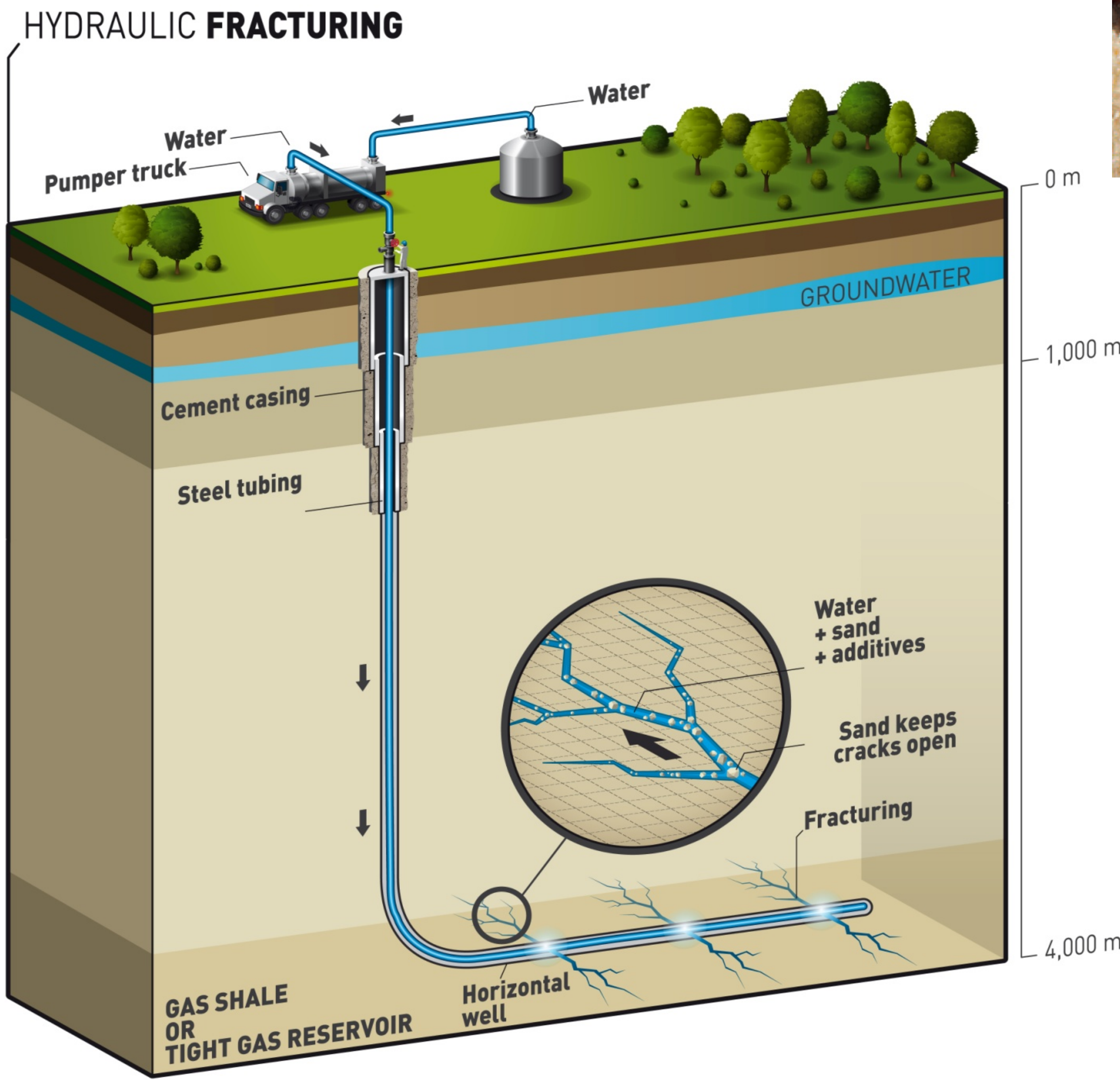


Production of natural gas (methane) from shale in the United States has expanded rapidly in the last 10 years, and is projected to continue increasing through 2040 (EIA 2013; Sieminski 2013). "Dry" means that the natural gas is extracted in gaseous form rather than in liquid form.

Natural Gas Plays

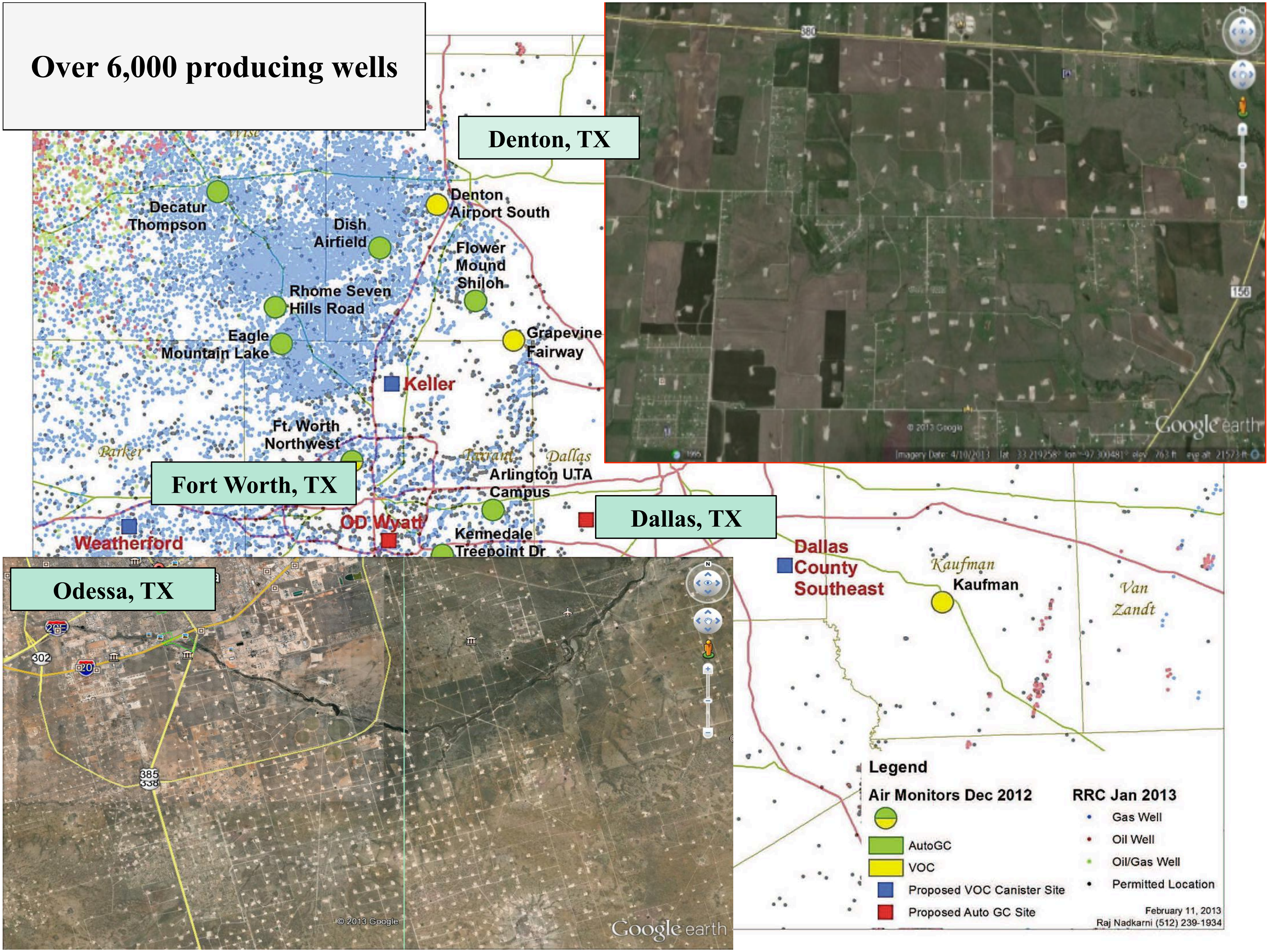


Process



Sensitive Receptor

Over 6,000 producing wells

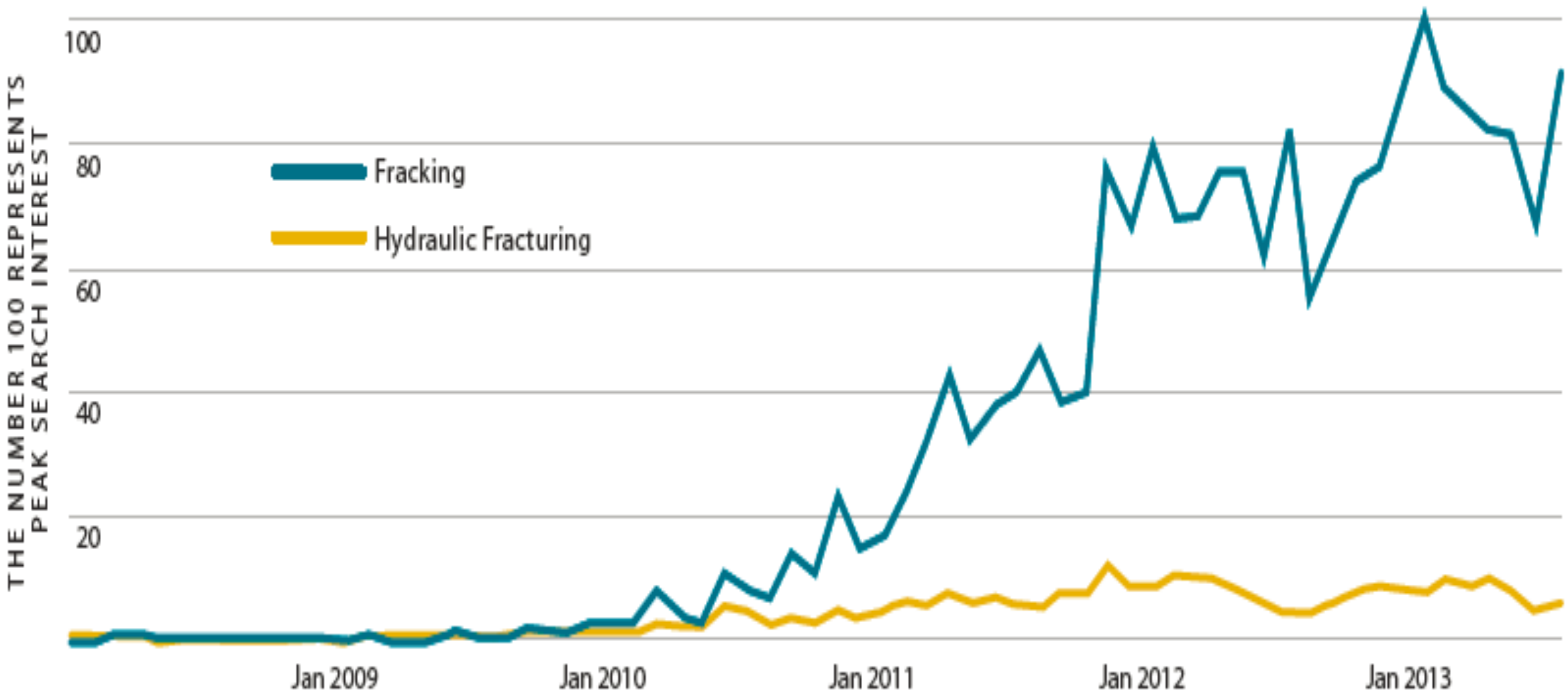


Regulatory and Public Issues

- Relatively clean alternate fossil energy source
- More energy per CO_2 than coal
- Reduction in reliance on imports
- US#1 top energy producer
- Concerns with environmental impacts, groundwater, and flowback/produced water
- Regulatory, public, and political pressures
- Attribution challenge: conventional vs. unconventional

Source: Vidic (2013)

Regulatory and Public Issues

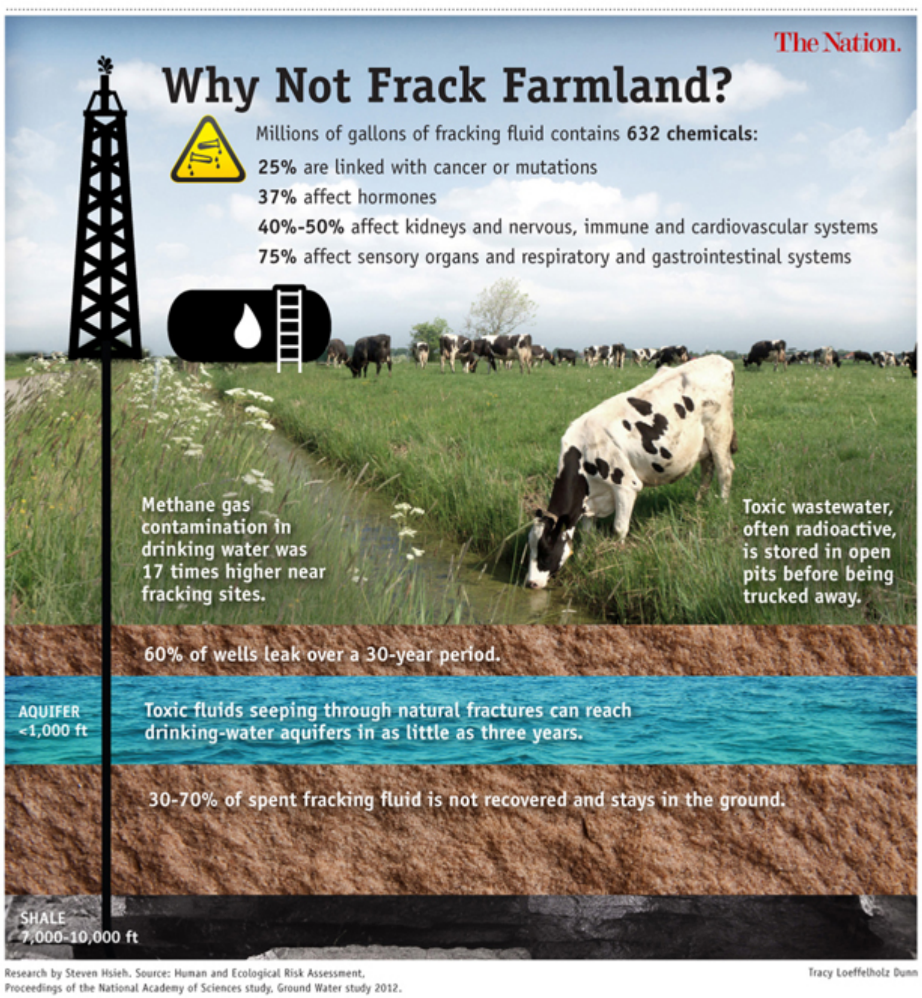


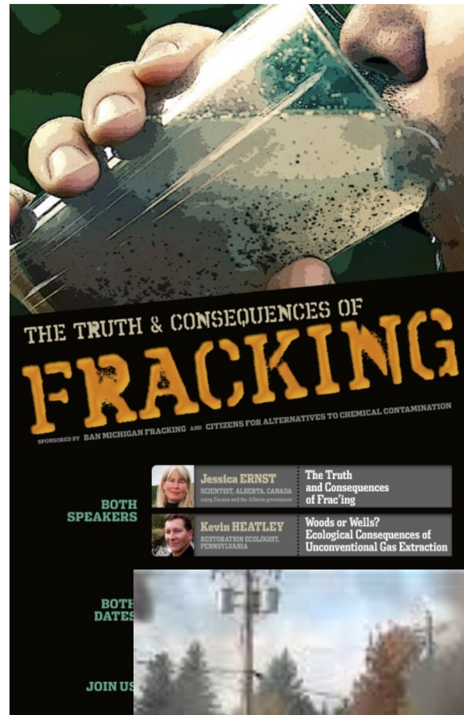
Regulatory and Public Issues

Reason	Percent (%)
Environmental Concerns	76.3
Negative Effects on Water	66.1
Negative Effects on Air	42.4
Chemicals in Water	30.5
General Health Concerns	61.0
Health Problem in Family member attributed to drilling	20.3
Personal legal rights have been infringed upon by companies	11.9
Concerns about safety of drilling operations	33.9
Concerns about lack of regulation of industry	42.4
Bias, conflict of interest, or lack of expertise in desired subject area by members of the committee	18.6
Export of domestic natural gas resources	10.2
Depreciation in property values	3.4

Adgate (2013)

Risk Information: Media





Risk Information: Science

"*Trust, but verify*"

Scientific Method:

a) Observe
b) Hypothesize
c) Test
d) Conclude
e) Replicate Results to Verify
f) **Negative results as equally-important as positive results**

Environmental Risk Assessment

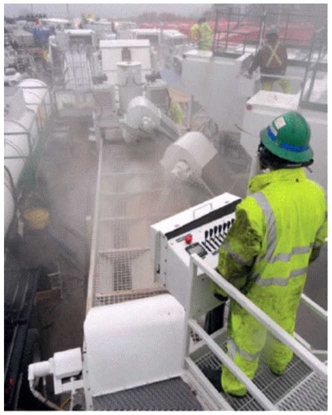
Definition:

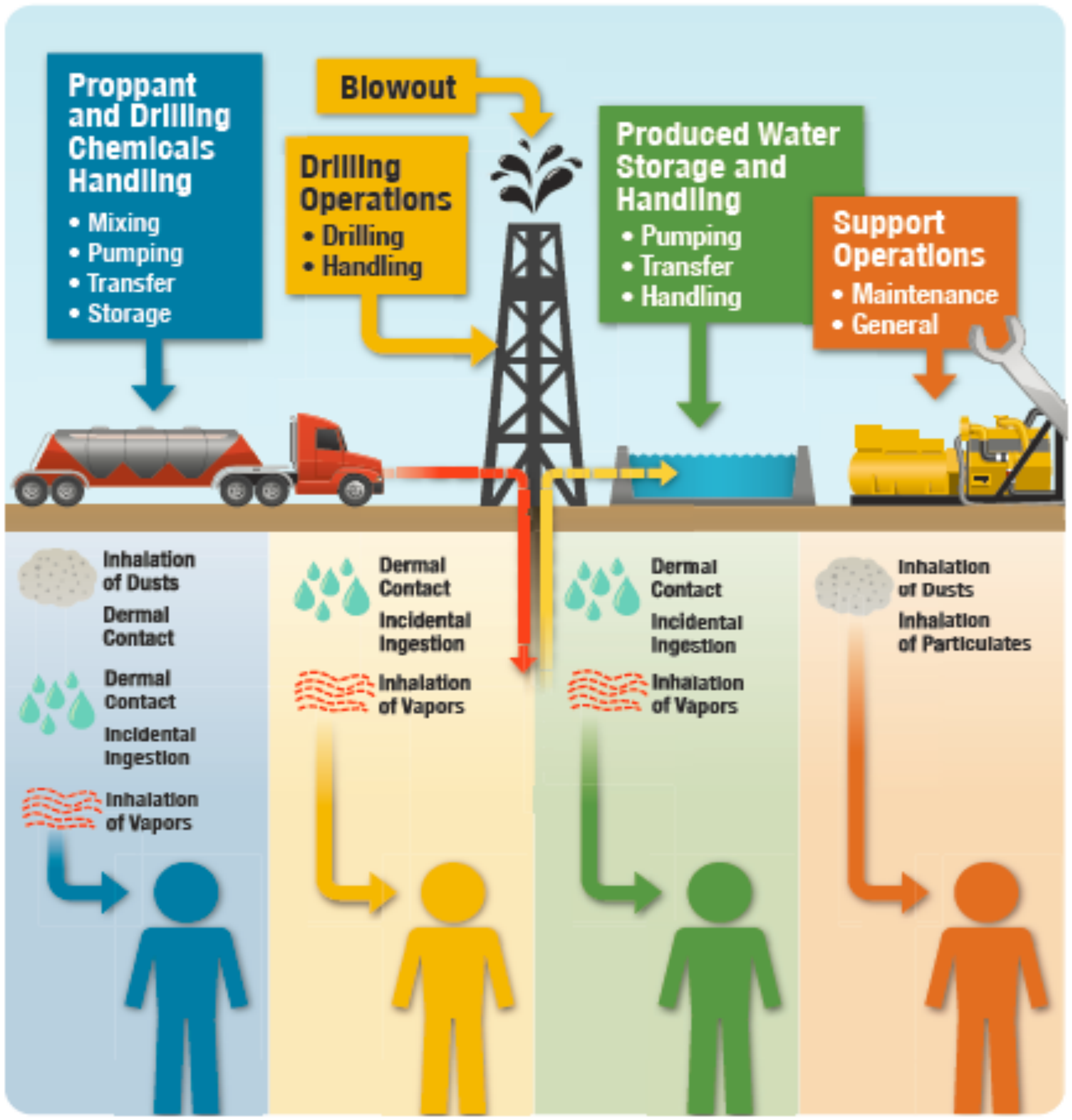
A systematic characterization of potential adverse health effects resulting from human exposure to toxic agents (chemicals)

Risk $= f($ **Exposure** + **Toxicity** $)$

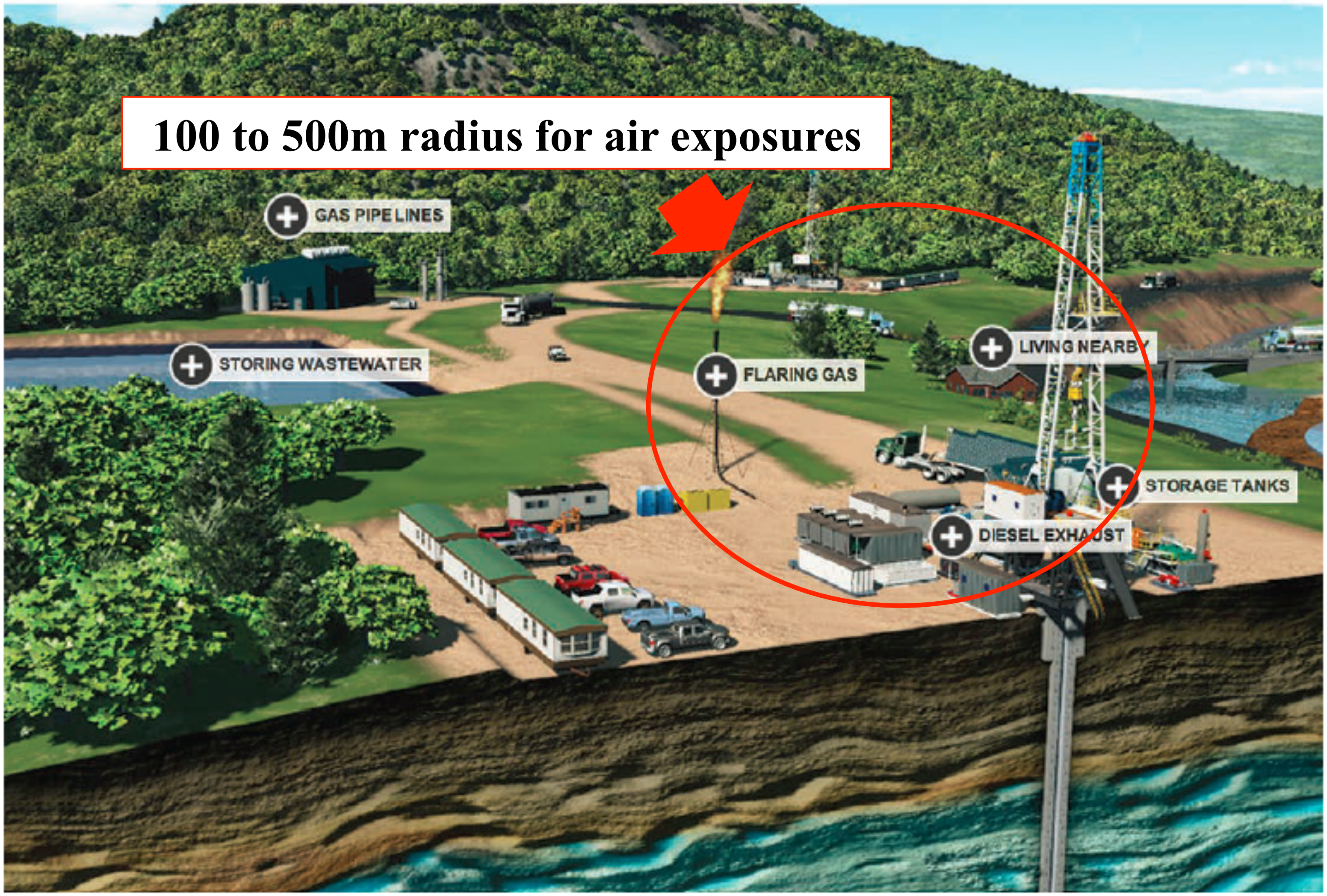
No Risk if no Exposure or Toxicity

Exposure Potential: Worker

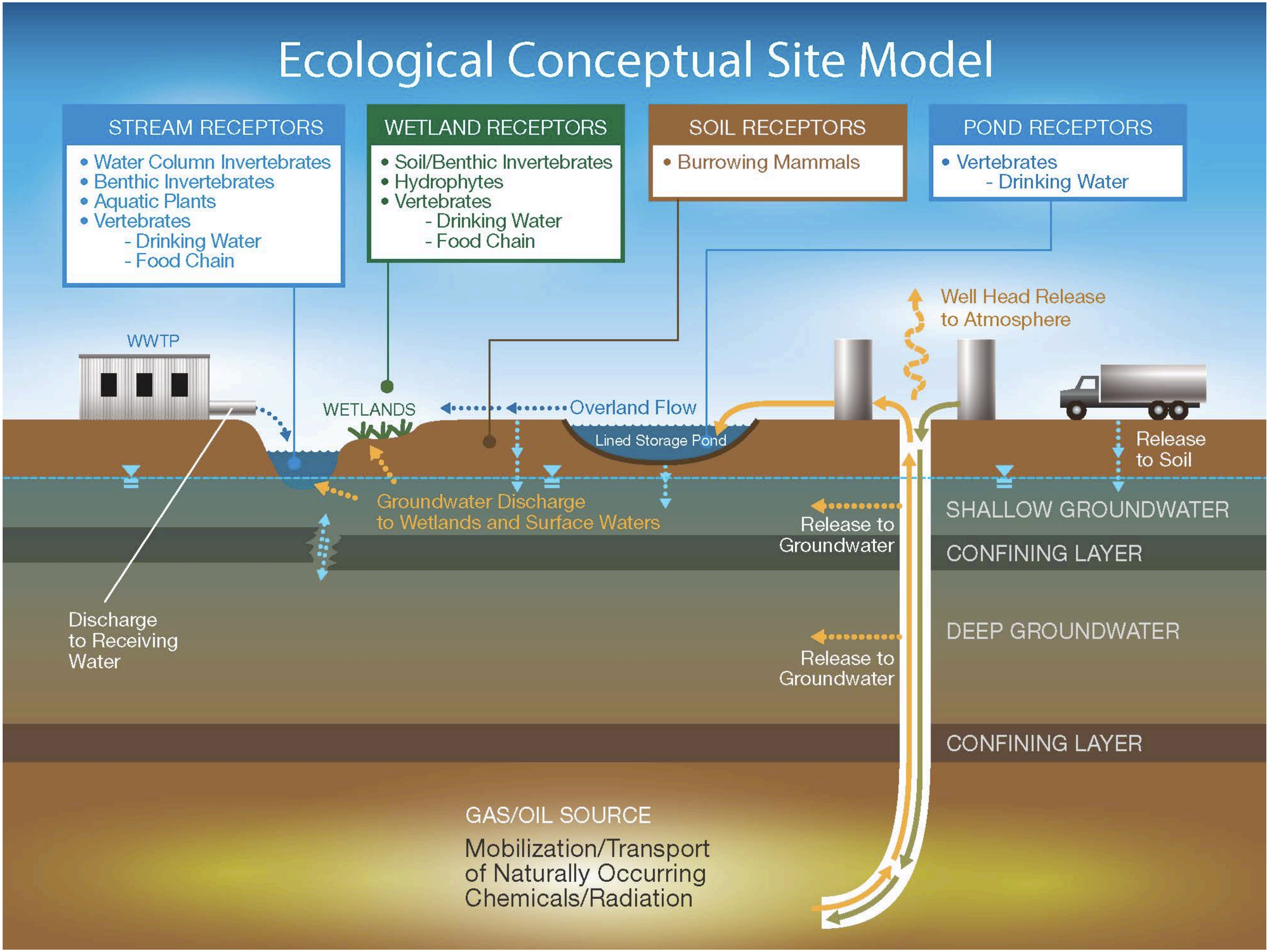




Exposure Potential: Public



This interactive graphic on NPR's website summarizes what scientists do and do not know about the risks to air, water, and public health from unconventional oil and gas development. Notably, the graphic effectively communicates uncertainty about such risks (NPR 2012).



Ecological Conceptual Site Model
STREAM RECEPTORS
• Water Column Invertebrates
• Benthic Invertebrates
• Aquatic Plants
• Vertebrates
- Drinking Water
- Food Chain
WETLAND RECEPTORS
• Soil/Benthic Invertebrates
• Hydrophytes
• Vertebrates
- Drinking Water
- Food Chain
SOIL RECEPTORS
• Burrowing Mammals
POND RECEPTORS
• Vertebrates
- Drinking Water
Well Head Release
to Atmosphere
WWTP
WETLANDS
Overland Flow
Lined Storage Pond
Release
to Soil
Groundwater Discharge
to Wetlands and Surface Waters
Release to
Groundwater
SHALLOW GROUNDWATER
CONFINING LAYER
Discharge
to Receiving
Water
DEEP GROUNDWATER
Release to
Groundwater
CONFINING LAYER
GAS/OIL SOURCE
Mobilization/Transport
of Naturally Occurring
Chemicals/Radiation

Synopsis of Reported Risks

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)

Synopsis of Reported Risks

- **Air (off-Site):**
  - Parachute, CO complaint linked to gas condensate overflow
  - CO study estimated elevated risks after 70 yrs exposure (SRI 2008)
  - CDPHE (2010) study in CO did not indicate unacceptable risks
  - Air study near CO drill rigs indicated non-CH_4 HCs (Colborn 2013)
  - WY study indicated acceptable levels of volatiles (Sierra 2011)
  - DRI (2010) study shows a steep air levels gradient (100m radius)
  - Carmichaels, PA complaint by a resident near a compressor station
  - PADEP (2011) air monitoring revealed low potential for acute risks
  - USURF (2011) low levels of benzene in air
  - Brown (2013) PA Health Project
  - Dish, TX no impacts

Symptom	Number of cases attributable to gas extraction	Plausible primary source of exposure
Dermal	7	Water
Eye irritation	4	Air
Respiratory	13	Air
Neurological	3	Air

Symptom	% of Individuals
Skin rash or irritation	48%
Nausea or vomiting	45%
Abdominal pain	38%
Breathing difficulties or cough	41%
Nosebleeds	21%

Synopsis of Reported Risks

- **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)
  - Transportation accidents (King 2012)
  - Blow-outs (DC 2013)

Synopsis of Reported Risks

- **Groundwater:**
  - Barnett Shale private wells show As, Se, and Sr above drinking water criteria near gas wells (Fontenot 2013)
  - Frac fluids not commonly detected (Howarth 2011)
  - Many may pre-date frac operations, non-baseline data
  - Most focus on methane (Osborn 2011)
  - Published events allegedly tied to fracking:
    - Dimock, PA (StateImpact 2013)
    - Pavillon, WY (PADEP 2009)
  - Rare occurrences caused by non-standard conditions
  - Boyer (2012) PA GW study on 233 DW wells indicates no impacts
  - Warner (2012) PA GW study suggest natural links to formations
  - GW impacts likely prevented by adhering to design specifications and BMPs (e.g., green completions by 2015)

Synopsis of Reported Risks

- A properly designed, installed, and operated gas well does not have inherent features that cause groundwater pollution
- Nevertheless, apart from external factors such as transportation accidents and spills, *well design and construction are potentially the next highest causes of environmental malfunctions affecting groundwater quality* (King 2011)
- As any engineered system, one cannot expect 100% trouble-free well design and construction

Synopsis of Reported Risks

- 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)

Reported Incidents

- **Groundwater:**
  - 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
  - Published events allegedly tied to fracking:
    - Dimock, PA (StateImpact 2013)
    - Pavillon, WY (PADEP 2009)
  - Barnett Shale study on private wells show As, Se, and Sr above drinking water criteria near gas wells (Fontenot 2013)

Synopsis of Reported Risks

- **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

Chemical Identity

- USEPA identified 1,000 chemicals (USEPA 2012)
- 347 unique CAS entries (8 states require listing on fracfocus.org)
- Trade Secret constituents generally exempt from public disclosure
- Frac fluid 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

Chemical Identity

- Fluid Additives (CEC 2011):
  - Methanol
  - Glycols
  - Diesel
  - Naphthalene
  - BTEX
  - **Aldehydes (e.g., glutaraldehyde)**
- Formation Elements Detected in Exposure Media:
  - Benzene
  - Radium
  - Boron
  - Strontium

Chemical Identity

- Colorado Baseline Sampling Rule:
  - Major cations and anions (e.g., Ca, Na, Cl)
  - TDS
  - Metals (Ba, B, Se, Sr)
  - Nutrients (N and P)
  - Dissolved gases (Methane, Ethane, Propane)
  - pH
  - Conductivity
  - Alkalinity
  - Bacteria
  - TPH
  - BTEX
- Need to capture operation constituents
  - Inbound and outbound
- Support data for a risk/impact assessment

Analytical Methods

- Proposed Analytical Methods (USEPA 2012):

Alcohols:	SW-846 Methods 5030 and 8260C
Aldehydes:	SW-846 Method 8315
Alkylphenols:	No standard method
Alkylphenol ethoxylates:	No standard method
Amides:	SW-846 Methods 8032A and 8316
Amines (alcohols):	No standard method
Hydrocarbons:	SW- 846 Methods 5030 and 8260C
Carbohydrates:	No standard method
Ethoxylated alcohols:	ASTM D7485-09
Glycols:	Region 3 Draft SOP
Halogens:	SW-846 Method 9056A
Inorganics:	SW-846 Methods 3015A and 6020A
Radionuclides:	SW-846 Method 9310

Environmental Monitoring Points

- Monitoring strategy applicable to:
  - Surface releases/spills
  - Groundwater impacts
  - Blow-outs (air and other exposure media)
  - Storage pond testing
  - Soil and sediment testing
  - Waste characterization
  - Forensic/culpability investigations
  - Wastewater treatment systems

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

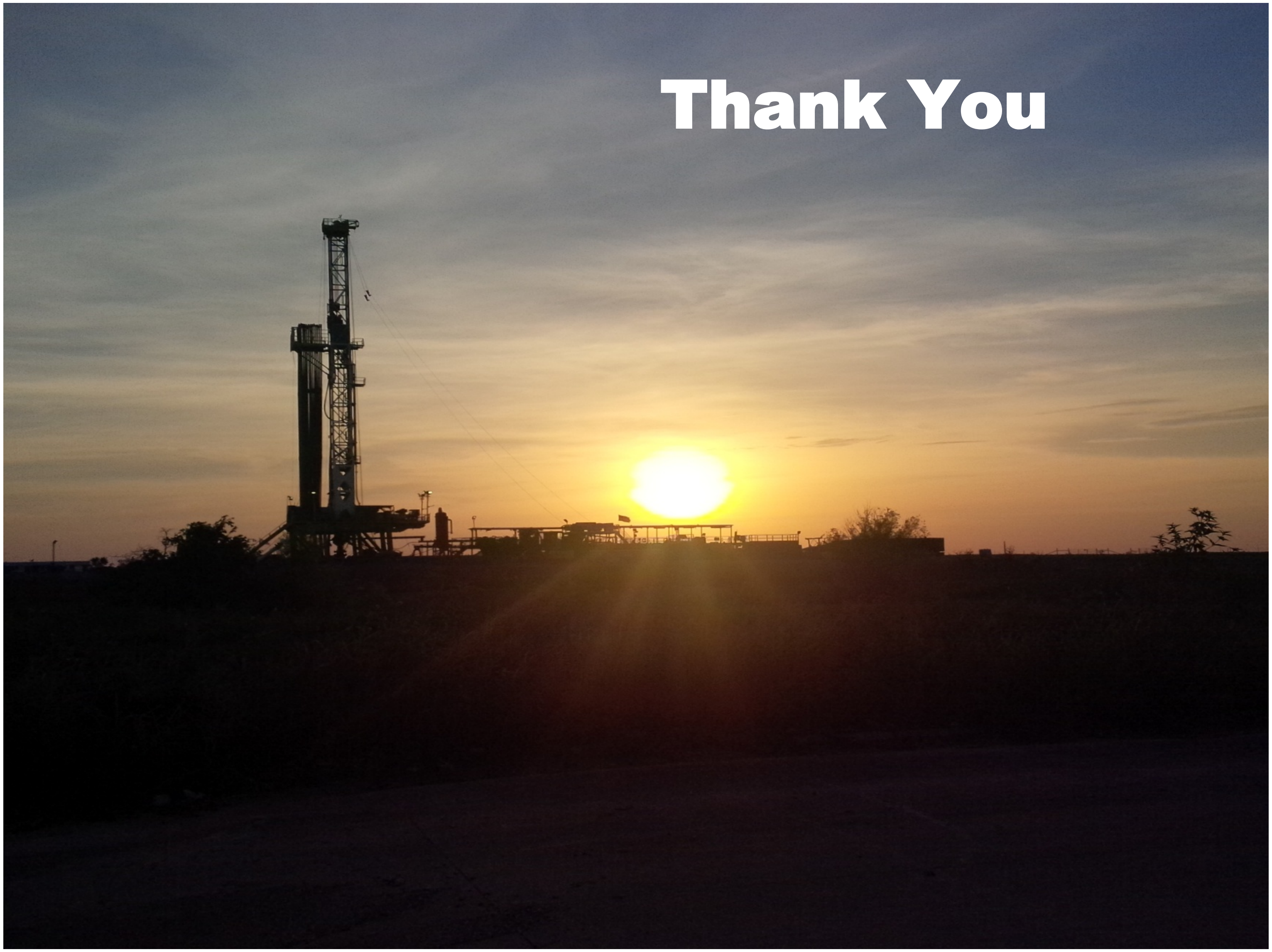
Chemical Name	Reference Dose (mg/kg BW-day)	Reference Concentration (mg/m^3)
Tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione	1.20E-01	8.40E+00
Alkyl dimethyl benzyl ammonium chloride	4.26E-01	Not Available
Phosphonium, tetrakis(hydroxymethly)-sulfate	2.48E-01	9.17E-01
2,2-Dibromo-3-nitrilopropionamide	1.18E-01	5.33E-02
Dipropylene glycol monomethyl ether	7.50E+00	3.03E+00
5-Chloro-2-methyl-4-isothiazolin-3-one	2.10E-01	Not Available
Methylene bis(thiocyanate)	5.50E-02	Not Available
Magnesium chloride	2.80E+00	Not Available
Ethoxylated nonylphenol	1.31E+00	2.10E-01
2-(2-Methoxyethoxy)ethanol	4.16E+00	2.00E+00
Oxydiethylene bis(alkyl dimethyl ammonium chloride)	5.63E+00	1.39E+01
Polyethylene glycol	1.40E+01	Not Available
Diatomaceous earth, calcined	Not Toxic	Not Toxic
Ammonium lauryl sulfate	Not Toxic	Not Toxic
Ethanol	3.00E+00	2.00E+01
2-Bromo-3-nitrilopropionamide	1.78E-01	5.33E+01
Didecyl dimethyl ammonium chloride	8.40E-02	NA
2-(Thiocyanomethylthio)benzothiazole	3.00E-02	1.70E-01
1,2-Bromo-2-nitropropane-1,3-diol	1.80E-01	5.00E+00
Dialkyl dimethyl ammonium chloride	2.00E+00	Not Available
Heavy aromatic petroleum naphtha	6.00E+00	6.25E+01
Glutaraldehyde	5.00E-02	8.00E-05

Biocidal Agents - Risk

Chemical Name	Hydraulic Fracturing Fluid Concentration (mg/L)	Incidental Consumption Exposure (mg/kg-day)	Incidental Contact Exposure (mg/kg BW-day)	Total PEQ
Tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione	1.90E+01	9.30E-03	2.68E-02	3.01E-01
Alkyl dimethyl benzyl ammonium chloride	2.54E+01	1.24E-02	3.59E-02	1.13E-01
Phosphonium, tetrakis(hydroxymethly)-sulfate	9.10E+00	4.45E-03	1.29E-02	6.98E-02
2,2-Dibromo-3-nitrilopropionamide	**6.85E+01**	**3.35E-02**	**9.68E-02**	**1.10E+00**
Dipropylene glycol monomethyl ether	NA	NC	NC	NC
5-Chloro-2-methyl-4-isothiazolin-3-one	1.91E+01	9.34E-03	2.70E-02	1.73E-01
Methylene bis(thiocyanate)	NA	NC	NC	NC
Magnesium chloride	3.90E+00	1.91E-03	5.51E-03	2.65E-03
Ethoxylated nonylphenol	NA	NC	NC	NC
2-(2-Methoxyethoxy)ethanol	NA	NC	NC	NC
Oxydiethylene bis(alkyl dimethyl ammonium chloride)	NA	NC	NC	NC
Polyethylene glycol	4.20E+02	2.05E-01	5.93E-01	5.71E-02
Diatomaceous earth, calcined	3.28E+02	NC	NC	NC
Ammonium lauryl sulfate	NA	NC	NC	NC
Ethanol	1.88E+02	9.19E-02	2.65E-01	1.19E-01
2-Bromo-3-nitrilopropionamide	3.00E-01	1.47E-04	4.24E-04	3.21E-03
Didecyl dimethyl ammonium chloride	9.80E+00	4.79E-03	1.38E-02	2.22E-01
2-(Thiocyanomethylthio)benzothiazole	NA	NC	NC	NC
1,2-Bromo-2-nitropropane-1,3-diol	3.80E+00	1.86E-03	5.37E-03	4.02E-02
Dialkyl dimethyl ammonium chloride	NA	NC	NC	NC
Heavy aromatic petroleum naphtha	NA	NC	NC	NC
Glutaraldehyde	**1.29E+02**	**6.33E-02**	**1.83E-01**	**4.92E+00**

Summary

- Growth in gas play exploration to continue globally
- Stakeholder pressure to ensure no impacts on environment
- Need analytical methods for risky biocides (e.g., 2,2-dibromo-3-nitrilopropionamide and glutaraldehyde)
- Estimated concentrations in frac fluid in ppm range
- Potentially found in various aqueous media (groundwater, surface water, wastewater, etc)
- Media concentration far lower (depends on release scenario)
- Data needed to support hypothetical, yet realistic human and ecological risk assessments


Thank You