Hydraulic Fracturing: Experiences with Clinical Evaluation

http://www.parrotkeyresort.com/photos

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Disclosures

I have no conflicts of interest to disclose.

All my opinions are my own based on my experience and interpretation of the available scientific and my own clinical data.
What is a medical toxicologist?

- Specialized training in:
  - Medication Overdose
  - Medication Adverse Effects
  - Medication Interaction
  - Bites, Stings, and Envenomations
  - Environmental and Occupational Exposures
Outline

- Objectives
- Case example
- The Toxicology of hydraulic fracturing
  - Water Concerns
  - Air Concerns
Objectives

- To understand the possible sources of toxicologic exposures from hydraulic fracturing.
- To review the common chemicals that are used in the UOGD
- Things that are evaluated
Case

- 67 year-old woman presents with complaints of diffuse pain, muscle weakness, dry red skin, and increasing difficulty with ambulation over the last 3-4 years.
- PMH: Diabetes, Hyperlipidemia, Hypertension, GERD, lumbar radiculopathy.
- Referred to you for an abnormal blood barium level of 150mcg/l and worsening symptoms since hydraulic fracturing began near her home.
- She underwent a blood barium test after a public hearing discussed possible barium contamination in ground water as a result of hydraulic fracturing.
- The patient states her “drinking water becomes cloudy” during periods of active “fracking.”
Case Con’t

- Water testing showed elevated sodium and barium levels.
  - Did not show any benzene, toluene, or ethylene glycol.
  - There were no other significant levels of contamination noted.
- Air testing did not show any specific levels above the normal reporting range.
- BMP, CBC, LFTs within normal limits.
- MRI of lumbar spine was unchanged from similar MRI 6 years earlier.
Physical Exam

- Only notable for mild non-pitting, bilateral lower extremity edema, seborrheic keratosis to back and chest wall, diffuse melanotic spotting and chronic skin changes consistent with aging.
- The patient’s scalp and upper extremities did show scaling diffusely consistent with dry skin, but no erythema, induration, or raised areas.
- Neurologic exam was unremarkable with 5/5 strength to all extremities, normal reflexes, and no focal deficits.
What I’ve found so far

- Very non-specific findings
- Most cases that come to me are from populations at risk
  - Multiple medical problems
  - Aged
  - Children
- Most of my high correlated cases come with mucous membrane irritation
Toxicology of Hydraulic Fracturing

#1
Water Toxicity Issues

#2
Air Toxicity Issues
Toxicology of Hydraulic Fracturing

#1
Water Toxicity Issues

#2
Air Toxicity Issues
Possible Water Contamination

- Hydraulic fracturing
  - Only approx 9-53% of fluid reclaimed
  - Migration of fluid to aquifer
  - Methane migration from drilling/fracturing
  - Tailings Ponds
- Casing failure
  - Methane contamination from drilling migration
  - Fracturing fluid migration to aquifer
- Backflow water
  - Contains metals, salts, organics, radioactivity
  - Spills/run off most common cause of contamination (Metzger 2011)
  - Improper disposal of backflow water
<table>
<thead>
<tr>
<th>Compound</th>
<th>Purpose</th>
<th>Common Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glutaraldehyde</td>
<td>Bactericide</td>
<td>Disinfectant</td>
</tr>
<tr>
<td>Sodium/Potassium Chloride</td>
<td>Delays gel polymer breakdown</td>
<td>Table salt</td>
</tr>
<tr>
<td>Ammonium bisulfate</td>
<td>Prevents pipe corrosion</td>
<td>Water treatment</td>
</tr>
<tr>
<td>N, N-Dimethyl formamide</td>
<td>Prevents pipe corrosion</td>
<td>Plastics, pharmaceuticals</td>
</tr>
<tr>
<td>Petroleum distillates</td>
<td>Minimizes friction/”slinks” water</td>
<td>Make up, laxatives</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>Prevents deposits on pipe</td>
<td>Radiator Fluid</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>Increases fluid viscosity</td>
<td>Glass cleaner</td>
</tr>
<tr>
<td>2 Butoxyethanol</td>
<td>Glycol Ether component of cleaners</td>
<td>Window cleaners</td>
</tr>
<tr>
<td>Sodium bicarbonate</td>
<td>Maintains components</td>
<td>Antacids, detergents</td>
</tr>
<tr>
<td>Modified acrylamide copolymer</td>
<td>Minimizes friction between fluid and pipe</td>
<td>Water treatment/Soil conditioner</td>
</tr>
<tr>
<td>Diethanolamine</td>
<td>Lubricant/Emulsifier</td>
<td>Liquid soaps/Shampoos</td>
</tr>
<tr>
<td>Guar gum</td>
<td>Thickens water, helps suspend sand</td>
<td>Thicken foods and cosmetics</td>
</tr>
<tr>
<td>Acids: Hydrochloric, Boric and Citric</td>
<td>Dissolve minerals &amp; initiate rock fractures</td>
<td></td>
</tr>
</tbody>
</table>
Hydraulic Fracturing Fluid

- Chemicals vary by company
- Proprietary mixtures
  - Not required to disclose publically.
  - 2010 study showed 632 different chemical products compiled from information from various companies.
- However, some of the oil/gas companies have released lists of their fracturing chemicals.
Methane

- Methane migration
  - From casing failure (~3% fail; 219/6466 wells) 
    (PA DEP Oil and Gas Compliance Report 2013)
  - Migration from deep sources
    - 48 wells in PA within 2500 ft of drilling show no difference in pre and post drilling [methane]
      (Center for Rural PA, PA General Assembly. 2011)
Methane

- A cause for concern in both air and water
- PA Wells frequently contaminated with methane
  - Contaminations known to predate drilling
  - ~350,000 wells drilled in PA
  - ~100,000 well location is unknown
Toxic Alcohol and Related

- All rapidly absorbed GI
- All metabolized by alcohol dehydrogenase
- All parent compounds/metabolites renal excretion
Toxicology

- Metabolites
  - Ethylene Glycol: Glycolic/Oxalic Acid
  - Methanol: Formic Acid
  - Isopropanol: Acetone
# Clinical Manifestations

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>GI</th>
<th>CNS</th>
<th>CV/MSK</th>
<th>Renal</th>
<th>Ophthalmologic</th>
<th>Metabolic Acidosis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene Glycol</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+ ATN</td>
<td>+</td>
<td>+++</td>
</tr>
<tr>
<td>Methanol</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+++</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>‘Blind drunk’</td>
<td></td>
</tr>
<tr>
<td>Isopropanol</td>
<td>+</td>
<td>+++</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Most inebriating</td>
<td>-</td>
<td>-</td>
<td>Ketosis</td>
</tr>
</tbody>
</table>

**Note:**
- **GI** refers to gastrointestinal symptoms.
- **CNS** refers to central nervous system symptoms.
- **CV/MSK** refers to cardiovascular and musculoskeletal symptoms.
- **Renal** refers to renal symptoms.
- **Ophthalmologic** refers to ophthalmologic symptoms.
- **Metabolic Acidosis** refers to metabolic acidosis symptoms.

**Explanation:**
- Ethylene Glycol can cause gastrointestinal symptoms, central nervous system symptoms, and renal symptoms, leading to metabolic acidosis.
- Methanol can cause gastrointestinal symptoms and cardiovascular symptoms, leading to metabolic acidosis.
- Isopropanol can cause most inebriating symptoms, leading to metabolic acidosis.

**Additional Notes:**
- **Pancreatitis** is mentioned in the context of methanol, indicating potential pancreatitis complications.
- **‘Blind drunk’** indicates a specific symptom complex associated with methanol's effects.
- **Ketosis** is a metabolically significant side effect related to isopropanol's ingestion.
Metal Contamination

- Largest reason for Toxicology Clinic visits
Mercury

Forms - Occupational Exposures

- Elemental ($\text{Hg}^0$, quicksilver) - Dentists, Jewelers, Thermometers

- Inorganic ($\text{Hg}^+$, $\text{HgCl}_2$, mercuric chloride) - Explosives, Dye makers, Taxidermists

- Organic (methylmercury) - Drug makers, farmers, Embalmers
Mercury

- Clinical Presentation
  - Inorganic
    - Acute
      - Corrosive
      - Renal failure
      - Shock/CV collapse
    - Chronic
      - Acrodynia
      - Tremor
      - Erethism
      - Renal insufficiency
Mercury

- Clinical Presentation
  - Organic
    - Long chain (phenylmercury)
      - Tremor
      - Erethism
      - Renal insufficiency
    - Short chain (methylmercury)
      - CNS dysfunction
      - Prenatal (Minimata Bay)
Arsenic - Overview

- Arsenic has been reviewed in the medical community for over 2000 years.
  - Hippocrates used arsenic sulfides for topical treatment of ulcers
  - 15-17 century gained fame as a homicidal agent in Europe
  - Potassium arsenite was used to treat fevers in the late 18th century.
  - 19th century-arsenic compounds made up pigments for “Scheele’s green.”
Toxicity

- Trivalent arsenic
  - binds sulfhydryl groups
  - inhibits conversion of pyruvate to acetyl CoA
  - inhibits thiolase and glutathione synthetase
  - induces DNA-protein cross linkage
  - interferes with microtubule assembly
- Pentavalent arsenate
  - mistaken for phosphate
  - uncouples oxidative phosphorylation

- Issues with energy production
Chronic Illness

- Has multiple effects on the body
- Associated with
  - Increased fetal loss and premature delivery
  - Liver steatosis, fibrosis and cellular hypertrophy
  - Neurobehavioral changes and memory problems
  - Hearing loss, and neuropathy.
  - CVD, Ischemic HD, and athresclerosis
  - Colicy abdominal pain
  - Chronic Bronchitis
  - DM-II
  - Cancers
  - Skin Lesions (hyperpigmentation), Contact dermititis.
  - Anemia and Agranulocytosis.
Arsenicosis

- AKA arsenicalism, arseniasis
Blackfoot disease

- Peripheral Vascular disease with associated gangrene.
- Thought to be related to obliteratorive arterial disease of the lower extremity.
Peripheral neuropathy

- Many times mistaken for Guillain-Barre Syndrome
- Presents with mostly sensory deficit with some muscle weakness in the caudal to rostral pattern.
- Deficit is greater to the sensory than the motor.
- Generally begins weeks after exposure
Trivalent arsenic is used in treatment of refractory APML.

Arsenic is a Class I IARC substance.

Positive relationships have been established with the following cancers:

- Skin: Bowen’s disease, Squamous Cell, Basal Cell.
- Lung: Appears to have a synergistic effect with smoking.
- Urinary tract cancers: Also increased significantly with smoking.
Monitoring for Arsenic Exposure

- Toenails (Mees lines) and hair
- Blood: ICP-MS
- Urine: AA, AF, ICP-MS
- Speciation is essential for determining disease risk.
Metals in Backflow Water

Many metals are naturally found in backflow water:

- Sodium
- Chloride
- Calcium
- Magnesium
- Strontium
- Barium
- Bromide
- Etc.
Barium

- Common contaminant in drinking water
  - Very common in many private wells
  - Typical US levels ~30mg/Liter.
  - Regions such as Kentucky, Illinois, New Mexico and Pennsylvania have been measured as high as 300mg/Liter.
    - Very common in soil around Marcellus Shale
  - Only soluble forms of barium are poisonous
    (For example, barium sulfate is insoluble)
Barium Levels

- Levels on tested individuals vary greatly
  - Generally do not correlate with toxicity
  - Not clear how to interpret low-level exposures
- Review of multiple laboratory studies:
  - Wide range of levels in tested population
  - Many labs report levels greater than 11mcg/liter
  - Normal blood concentrations range from 10mcg/liter to 400mcg/liter seen with no effects
Barium Toxicity

- Severe hypokalemia and kidney injury
- Abdominal pain
- Nausea, vomiting, diarrhea
- Esophageal injury and hemorrhagic gastritis
- Weakness
- Arrhythmias

Chronic exposures: Kidney injury, numbness, tingling, paralysis, and associated increase in hypertension and cardiovascular disease.
Lead

- Occupational exposure
  - Welders, painters, construction workers, battery manufacturers, radiator repair
- Exposure is most likely occupational inhalation, although groundwater contamination is possible if drilling pipe contains lead
- Possible hand to mouth exposure for workers using lead threading compounds for the drilling pipe
- Poor occupational hygiene - Workers may also bring lead home which can be concern for other home occupants (i.e. children).
Lead Toxicity

- Toxic effects are dose dependent.
  - Acute
    - Abdominal pain
    - Ataxia
    - Encephalopathy
    - Seizures
    - Nerve palsy
    - Neurocognitive changes
  - Chronic
    - Anemia
    - Neurocognitive deficits
      - Main Concern with low dose environmental exposure
    - Hypertension
    - Renal insufficiency
    - Encephalopathy
    - Peripheral Neuropathy and wrist or foot drop.
    - Reproductive effects
      - Increased rate of spontaneous abortion
      - Reduced birth weight
      - Male infertility
Radioactivity

- Marcellus backflow water is most radiogenic
  Average ~5000 pCi/L
- Soils have high amounts of naturally occurring radioactive metals (NORMs):
  - Uranium
  - Radon
  - Strontium
  - Cesium
New York Times, Feb 2011

- Radiation contamination in water?
  - High levels of radon, uranium, alpha emitters, and benzene found in the surrounding river waters
  - Mapped the area around 149 wells
  - Claimed link to fracking from waste water treated at sewage plants

- Article was criticized:
  - No baseline levels
  - Possible other contamination from old mines
  - Presented to seem very high, when the calculated exposure was very low
Radiation concerns

- Most concerns of contamination due to storage and transport of water
- Contamination due to leaking liners
  - Ponds are buried after use
Toxicology of Hydraulic Fracturing

#1
Water Toxicity Issues

#2
Air Toxicity Issues
Possible Air Quality Contamination

- Hydraulic fracturing
  - Diesel particulates at compressor stations
  - Hydrogen sulfide exposure
  - Methane and other VOC’s during drilling
  - Leaking storage containers

- Casing production
  - Silica exposure from concrete mixing stations

- Backflow water
  - VOC’s at retention ponds
  - Radioactivity at retention ponds
VOCs

- Volatile Organic Compounds
  - High vapor pressure at room temperature.
  - Most frequently encountered VOCs:
    - Methane
    - Benzene
    - Methyl Mercaptan
  - Exposures largely:
    - Backflow water
    - Drilling site
PA Dept of Environmental Protection

- 3 testing periods
  - Monitoring for
    - VOC’s
    - BTEX
    - Carbon monoxide
    - Nitrogen dioxide
    - Ozone
Diesel Particulate Matter

- As many as 20 x 200 or more hp diesel engines running at one time during pumping
- Particulates and gases from engines
  - Aldehydes
  - Nitrogen oxides
  - Carbon monoxide
  - Plus, particulates
Hydrogen Sulfide

- Possible exposure
  - From gas release while drilling
  - Formed in situ by bacterial metabolism in “fracking” tanks, pond sediments, etc.
- Clinically
  - “Knock-Down” agent by binding cytochrome oxidase on electron transport chain
  - Mucous membrane irritant
Exposure concerns

- Toxicity may be linked to:
  - Chronic lung disease
  - Lung cancer?
  - Also likely adding to odors noticed by public
- Significant research currently in this area
Silica

- Silicon dioxide, silica, quartz
- Creates fine respirable crystalline dusts
- Causes silicosis and lung cancer
- Used on site as proppant and component of cement
  - Remember: ~10% of fracking fluid is sand
- Most workers exposed during sand transfer operations
Respirable Crystalline Silica

Photos courtesy of NIOSH
Silica

- NIOSH (2011) collected 116 air samples from 11 drilling sites
  - 54/116 (47%) exceeded OSHA PEL
  - 92/116 (79%) exceeded NIOSH REL and ACGIH TLV
  - 35/116 (31%) exceeded REL by more than 10x

Filtering half-face respirators have max use concentration to 10x NIOSH REL
Silica

How Much Silica Is In NIOSH REL?

- REL = 0.05 mg/m$^3$
- Average worker inhales 10 m$^3$ air in 1 work day.
  Therefore...
- 500 micrograms of inhaled silica exceeds REL.

Approx 500 micrograms of silica
You reassure the patient and on follow-up 6 months later barium level is 400 then 135 on repeat. She tells you on this visit she feels “normal.”

She admits she was concerned because she heard there had been spraying at the local waste site about a mile from her house of fracking wastewater for dust control, but that it was recently paved over.
Toxicology of Hydraulic Fracturing

#1 Water Toxicity Issues

#2 Air Toxicity Issues

#3 Stress related illness
Problems with evaluation

- No clear case definition
- No objective laboratory findings
- Most data used to evaluate these exposures are based on occupational exposures
- No data on possible synergistic effects
Future work
Geisenger Health System in Central and Eastern Pennsylvania is creating a database to monitor patients living in fracking zones.

- Provide large population to track effects longitudinally.
References


O DiGuilio, EC et al (2011). Drft: investigation of ground water contamination near Pavillion, Wyoming. EPA 600/R-00/000


References

- Schmidt, CW Estimating wastewater impacts from fracking. Envir Health Perspect (121.4.pA117).