Hydraulic Fracturing: Experiences with Clinical Evaluation

http://www.parrotkeyresort.com/photos

Dr. Michael Gary Abesamis, MD
UPMC Department of Emergency Medicine
Division of Medical Toxicology - Out-patient Clinic Director
University of Pittsburgh School of Medicine
ACMT Medical Toxicology Clinic Network Chair
West Virginia Poison Center Medical Director

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

Chemical Additives

Compound	Purpose	Common Use
Glutaraldehyde	Bactericide	Disinfectant
Sodium/Potassium Chloride	Delays gel polymer breakdown	Table salt
Ammonium bisulfate	Prevents pipe corrosion	Water treatment
N, N-Dimethyl formamide	Prevents pipe corrosion	Plastics, pharmaceuticals
Petroleum distillates	Minimizes friction/"slicks" water	Make up, laxatives
Ethylene glycol	Prevents deposits on pipe	Radiator Fluid
Isopropanol	Increases fluid viscosity	Glass cleaner
2 Butoxyethanol	Glycol Ether component of cleaners	Window cleaners
Sodium bicarbonate	Maintains components	Antacids, detergents
Modified acrylamide copolymer	Minimizes friction between fluid and pipe	Water treatment/Soil conditioner
Diethanolamine	Lubricant/Emulsifier	Liquid soaps/Shampoos
Guar gum	Thickens water, helps suspend sand	Thicken foods and cosmetics
Acids: Hydrochloric, Boric and Citric	Dissolve minerals & initiate rock fractures	

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

Alcohol	GI	CNS	CV/MSK	Renal	Ophthalmologic	Metabolic Acidosis
Ethylene Glycol	+	+	+	+ ATN	+ CN palsy	+++
Methanol	+ Pancreatitis	+	-	-	+ 'Blind drunk'	+++
Isopropanol	+ Bleeding	+++ Most inebriating	-	-	-	- Ketosis

Metal Contamination

- Largest reason for Toxicology Clinic visits

Mercury

- Forms-Occupational Exposures
  - Elemental (Hg^o, quicksilver)- Dentists, Jewelers, Thermometers
  - Inorganic (Hg^+, $HgCl_2$, mercuric chloride)- Explosives, Dye makers, Taxidermists
  - Organic (methylmercury)- Drug makers, farmers, Embalmers

Mercury

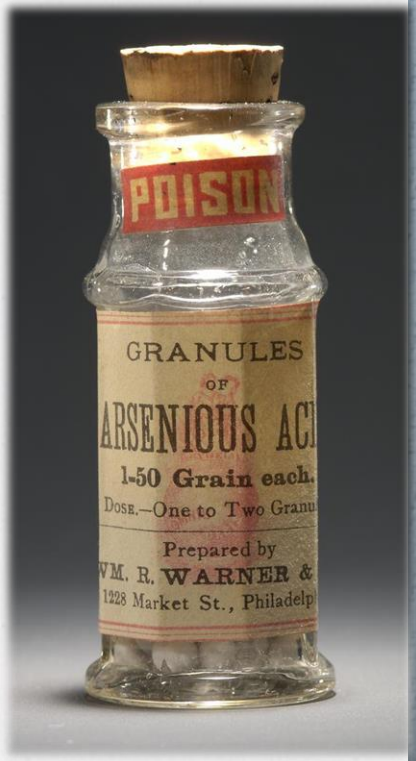
- Clinical Presentation
  - Inorganic
    - Acute
      - Corrosive
      - Renal failure
      - Shock/CV collapse
    - Chronic
      - Acrodynia
      - Tremor
      - Erethism
      - Renal insufficiency

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-protien 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

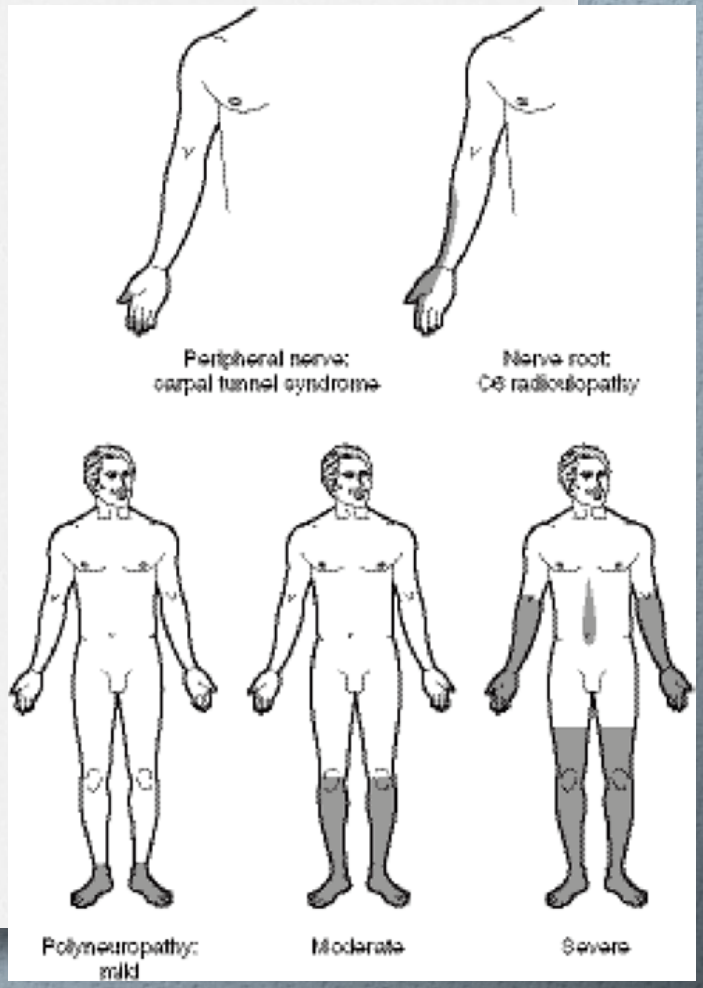
- AKA arsenicalism, arseniasis

Blackfoot disease

- Peripheral Vascular disease with associated gangrene.
- Thought to be related to obliterative 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



Cancers

- 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.

Highest

Lowest

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


marcellus-shale.us

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

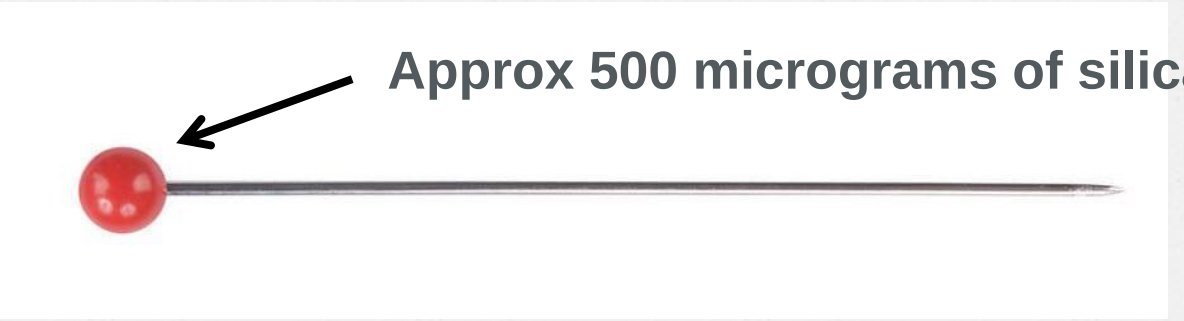
Silica

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.



Back to case

- 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

Patient Data Base

- Geisenger Health System in Central and Eastern Pennsylvania is creating a data base to monitor patients living in fracking zones.
- Provide large population to track effects longitudinally.

References

- Brikskin, J (2012). " February Update:EPA's Study of Potential Impacts of Hydraulic Fracturing on Drinking Water Rescources: Wastewater Source Appointment Project." www.epa.gov/hfstudy. Accessed 7/20/2012.
- Chapman, EC et al (2012). "Geochemical and Strontium Isotope Characterization of Produced Waters from Marcellus Shale Natural Gas Extraction." Environ Sci Technol 46:3545-3553.
- DiGuilio, EC et all (2011). Drft: investigation of ground water contamination near Pavillion, Wyoming. EPA 600/R-00/000
- Finkel ML, & Law A (2011). "The Rush to Drill for Natural Gas: A Public Health Cautionary Tale." American J of Public Health 101(5) 784-785.
- Fryzek, J et al (2013) Childhood Cancer Incidence in Pennsylvania Counties in Relation to Living in Counties with Hydraulic Fracturing Sites JOEM 55:7 (796-801)
- Gooddy W, et al (1975). "Spark-Source Mass Spectrometry in the investigation of neurological disease. Brain 98:65-70.
- Metzger, M (2011). Hydrofracking and the Environmetn. Water Quality Products 16(11) 14-15.

References

- McLernon, S (2012). EPA to run test in Wyo Fracking contamination row March 9. www.law360.com .
- Nicot, JP & Scanlon BR. (2012). “Water use for Shale-Gas Production in Texas, U.S.” Environ Sci Technol 46:3580-3586.
- Osborn SG et al (2012). “ Methane Contamination of Drinking Water accompanying gas-well Drilling and Hydraulic Fracturing.” PNAS 108(20) 8172-8176.
- Schmidt, CW Estimating wasewater impacts from fracking. Envir Health Perspect (121.4.pA117).
- Santos JS, Ballestero TP & Pitombeira E (2011) “An analytical Model for Hydraulic Fracturing in Shallow Bedrock Formations.” Groundwater 49(3) 415-425.
- Warner NR, et al (2012). “Geochemical evidence for possible natural migration of Marcellus Formation brine to shallow aquifers in Pennsylvania.” PNAS 109(30) 11961-11966.
- EPA Hydraulic Fracturing Study Plan (2011) “Impacts of Hydraulic Fracturing on Drinking Water Rescources.” EPA/600/R-11/122. November 2011.