# Hydraulic Fracturing: Experiences with Clinical Evaluation

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.
- 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.
- 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

- 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 had diffusely 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

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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 | |

# 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 ($Hg^0$, quicksilver)- Dentists, Jewelers, Thermometers
  - Inorganic ($Hg^+$, $HgCl_2$, mercuric chloride)- Explosives, Dye makers, Taxidermists
  - Organic (methylmercury)- Drug makers, farmers, Embalmers

# Mercury

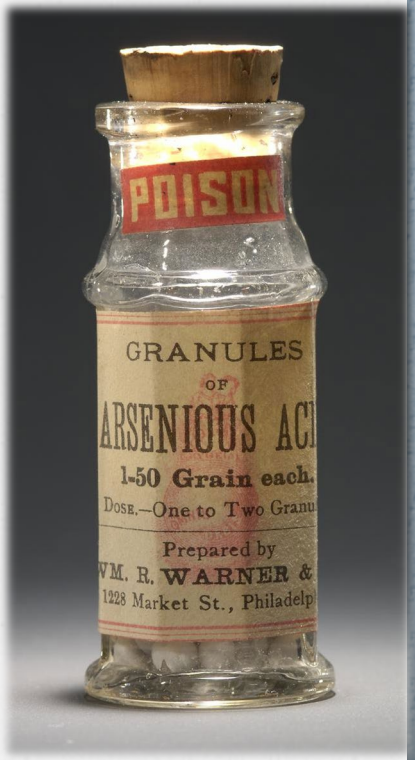
- Clinical Presentation
  - Inorganic
    - Acute
      - Corrosive
      - Renal failure
      - Shock/CV collapse
    - Chronic
      - Acrodynia
      - Tremor
      - Erethism
      - Renal insufficiency

# 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

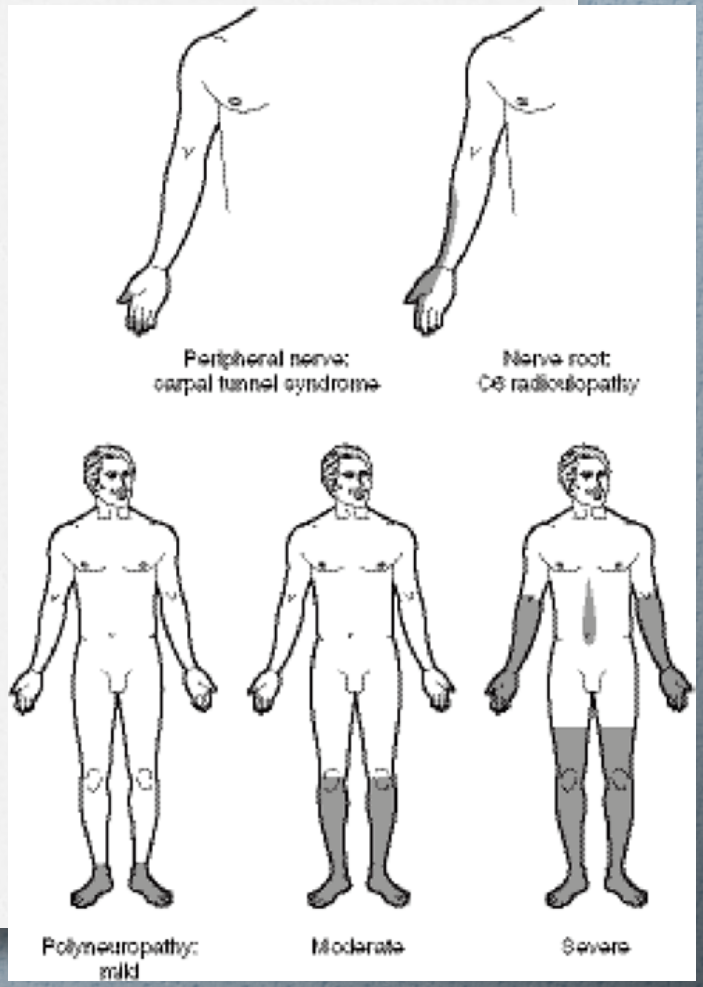
- AKA arsenicalism, arseniasis

# 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

# Radiation concerns

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

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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**

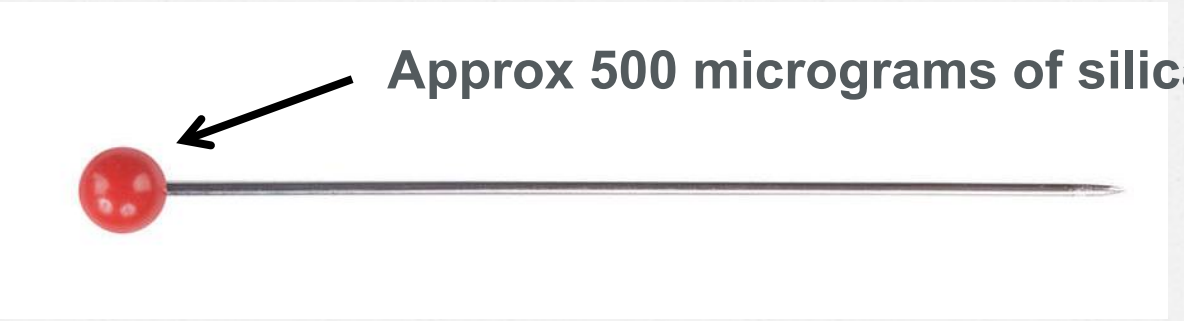
# Silica

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.



# 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.

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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