



Water and Air Impacts, Marcellus Shale Gas Extraction



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Water Issues #1, Stormwater Runoff from Disturbed Areas

Figure 3 – Well Pad Showing Drilling Rig



Figure 8 – Stormwater Diversion Ditch to Collect Offsite Water



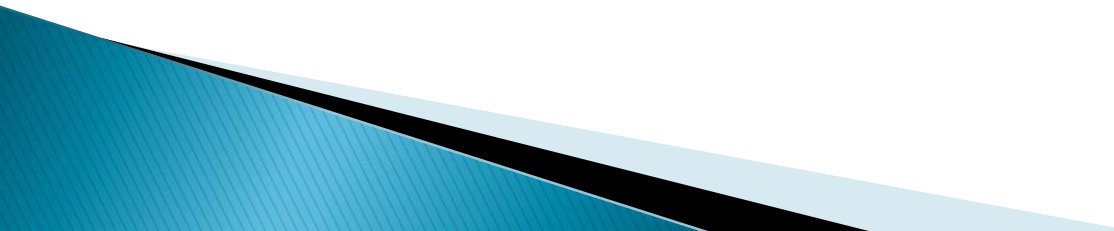
Water Management Technologies Used by Marcellus Shale Gas Producers, Veil, 2010, Argonne National Laboratory, Environmental Science Division

Water Issues, #2 Water Supply for Drilling and to Hydrofracture

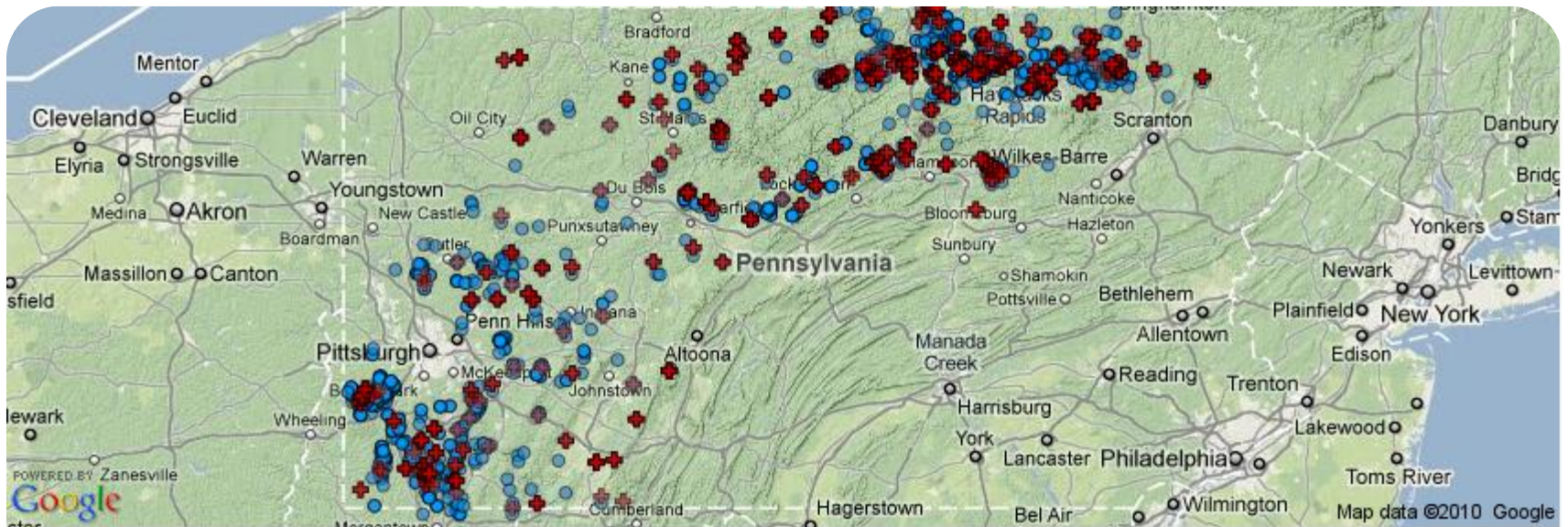


Water Issues #3, Management of Flowback and Produced Water

Options

- Inject underground through a disposal well (onsite or offsite)
 - Discharge to a nearby surface water body
 - Haul to a municipal wastewater treatment plant (often referred to as a publicly owned treatment works or POTW)
 - Haul to a commercial industrial wastewater treatment facility, and
 - Reuse for a future frac job either with or without treatment.
- 

Marcellus Wells Drilled and PA DEP Violations



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Wells Drilled and Associated Violations in PA

<http://data.fractracker.org/cbi/snapshot/page?concept=~0151a6ee0ec65e11df8d0ae894f4446c59>

Created by
Samantha Malone
on Sep 22, 2010



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<http://fractracker.org>

Permitted PA Facilities Accepting Wastewater from Oil and Gas Operations



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PA Facilities Approved to Receive Oil and Gas Wastewater

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Samantha Malone
on Aug 14, 2010

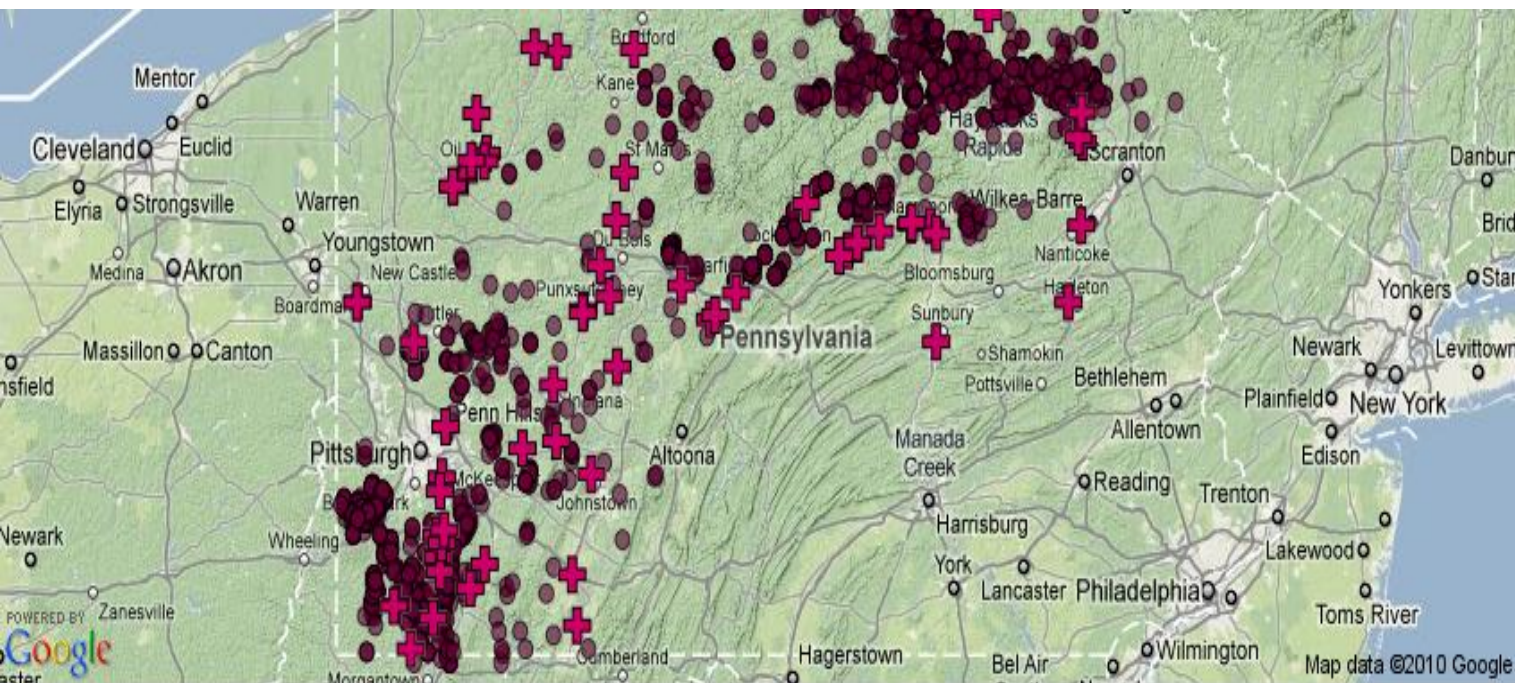
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Marcellus Wells and Wastewater Facilities in Pennsylvania



Wastewater Treatment Facilities Acc...

All records

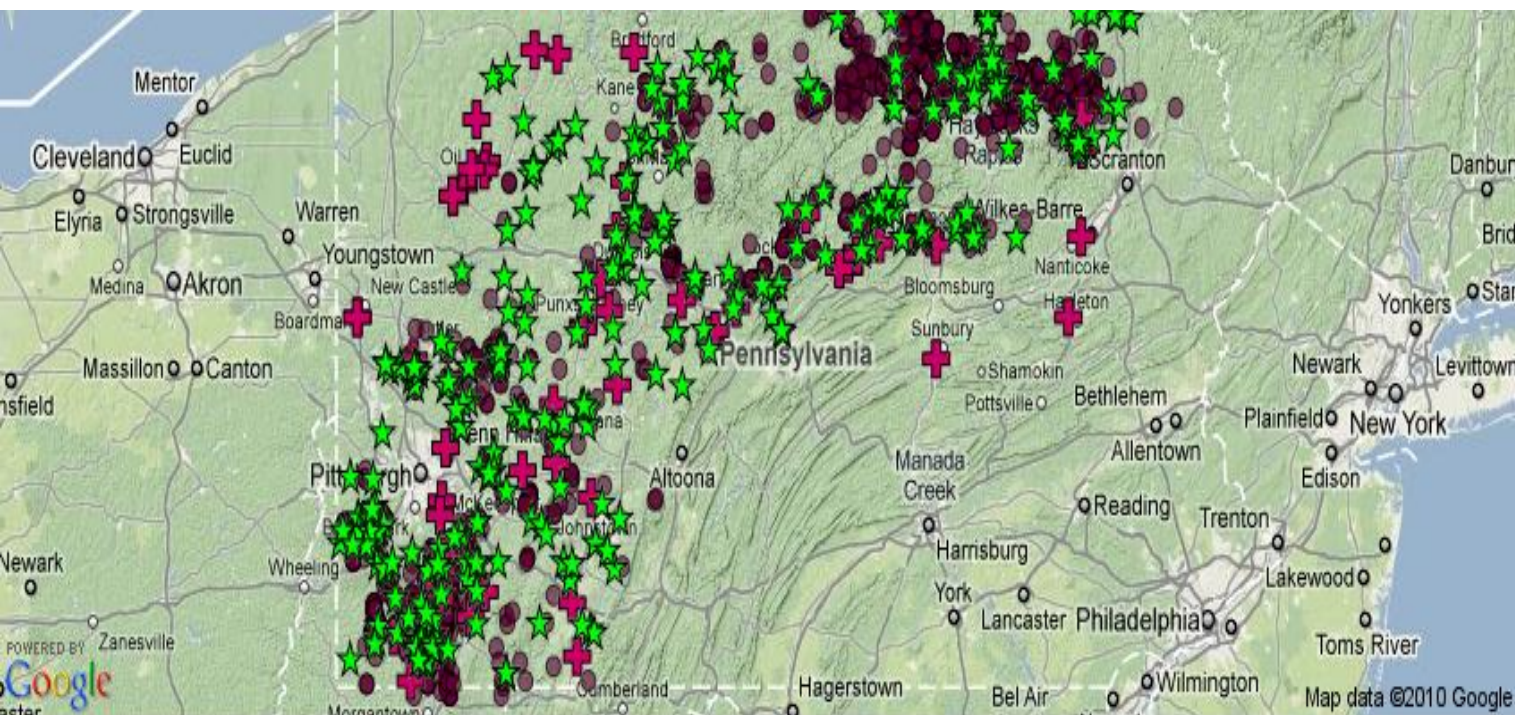


Marcellus Shale Drilled Wells in PA 20...

All records



Water Withdrawals, Wastewater Treatment Facilities and Marcellus Wells



Water Withdrawals by the Gas and Oil ...

All records



Wastewater Treatment Facilities Acce...

All records

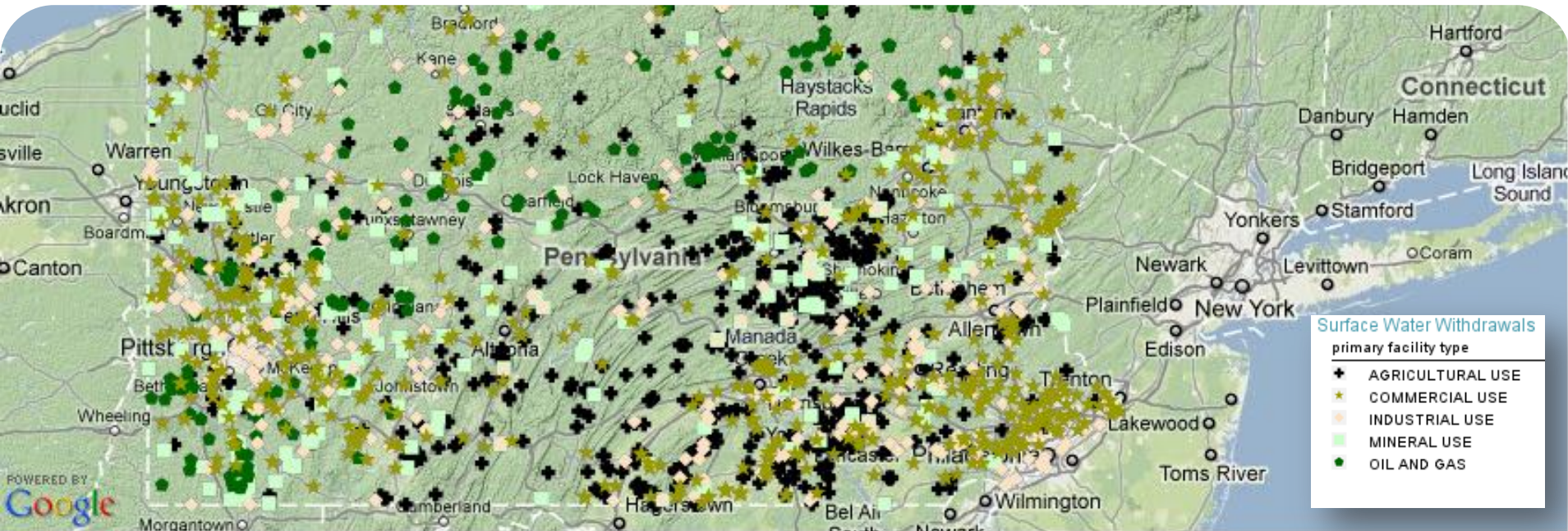


Marcellus Shale Drilled Wells in PA 20...

All records



Permitted PA Surface Water Withdrawals



Surface Water Withdrawals Permitted by the PA DEP

<http://data.fractracker.org/cbi/snapshot/page?concept=~01e503b6babf7311df9d25a33e266fe72b>

<http://data.fractracker.org/cbi/snapshot/page?concept=~01e503b6babf7311df9d25a33e266fe72b>

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on Sep 13, 2010

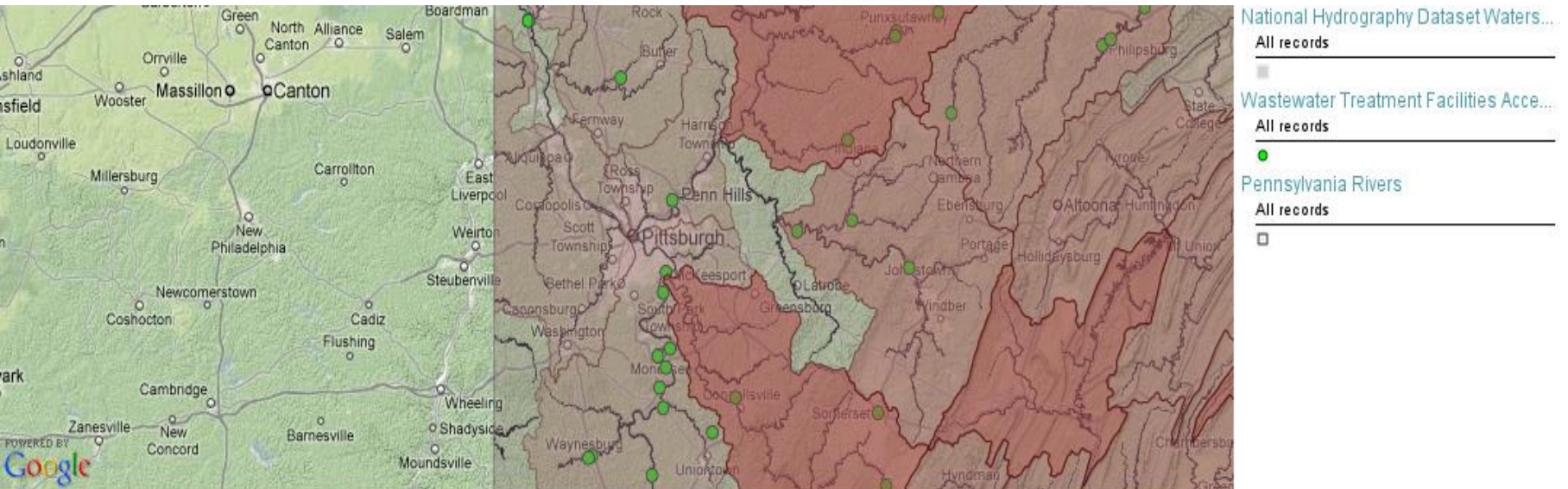
on Sep 13, 2010
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Conrad Volz



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<http://fractracker.org>

- # Permitted facilities focused on Monongahela drainage
- Rivers and watershed boundaries added to the map.
 - Total of 13 facilities located in Monongahela River drainage.



Permitted Facilities in Monongahela Drainage and Volumes Allowed Per Day

Permitted Site 1000 Gallons/Day

- 1) McKeesport – Monongahela (POTW) 115
- 2) Clariton Municipal Authority – Peters Creek (POTW) 60
- 3) Mon Valley Brine (Monongahela River) 200
- 4) Authority of Borough of Charleroi – Monongahela (POTW) 30
- 5) Municipal Authority of Belle Vernon – Monongahela (POTW) (2 permits) 10
- 6) Municipal Authority of Belle Vernon – Monongahela (POTW) 5
- 7) Borough of California – Monongahela (POTW) 10
- 8) Brownsville Municipal Authority – Dunlap Creek (POTW) 9
- 9) Franklin Township Sewer Authority – South Fork Tenmile Creek (POTW) 50
- 10) Waynesburg Borough – South Fork Tenmile Creek (POTW) 8
- 11) Shallenberger–Ronco – Monongahela (NPDES permit effective. As of 10/31/09, WQM permit in progress.) 500
- 12) Shallenberger–Rankin Run (NPDES permit effective on 11/1/2008.) 125
- 13) Shallenberger Connellsville – Youghiogheny 1,000
- 14?) Somerset Regional Water Resources (East Branch Coxes Creek) (RO and Evaporators proposed. NPDES permit granted on 12/17/2009. Amendment to the NPDES permit is pending.) ?

Range of TGD: 612 – 2,112

Concentrations of Selected Important Contaminants from Marcellus Shale Flowback Water (FBW)*

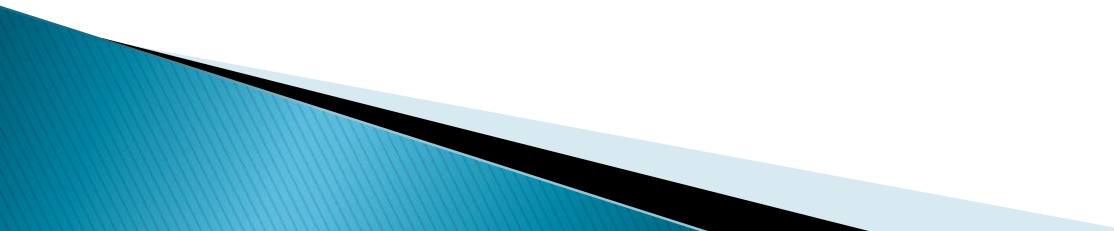
Total Dissolved Solids (TDS): 161,636 mg/L

Barium: 2,950 mg/L

Strontium: 3,280 mg/L

Chloride: 95,400 mg/L

* From Blauch, MF et al, 2009, Marcellus Shale Post-Frac Flowback Water-Where is all the Salt Coming From, SPE 125740.



Conversions to pounds of contaminant per day into Monongahela drainage

- ▶ 612,000 gallons FBW * 3.79 L/gallon* 161,636 mg/L dissolved solids* 2.2×10^{-6} pounds/mg= **824,825 lbs. of TDS**
- ▶ 612,000 gallons FBW * 3.79 L/gallon* 2,950mg/L Barium* 2.2×10^{-6} pounds/mg= **15,053 lbs. of barium**
- ▶ 612,000 gallons FBW * 3.79 L/gallon* 3,280mg/L Strontium* 2.2×10^{-6} pounds/mg= **16,737 lbs. of strontium**
- ▶ 612,000 gallons FBW * 3.79 L/gallon* 95,400 mg/L chloride* 2.2×10^{-6} pounds/mg= **486,812 lbs. of chloride**

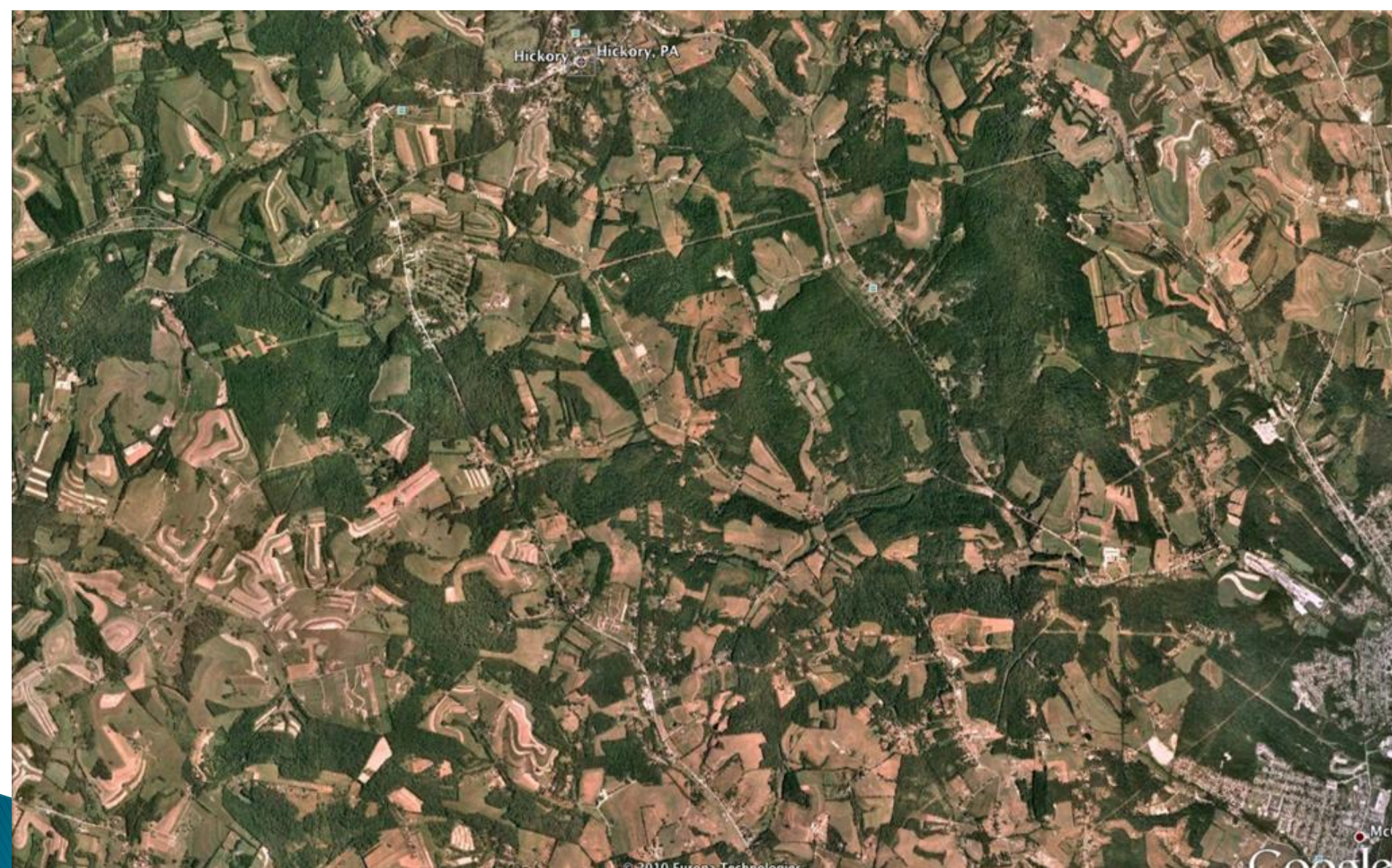
Potential Impacts to Air from Marcellus Shale Gas Extraction Operations

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Health

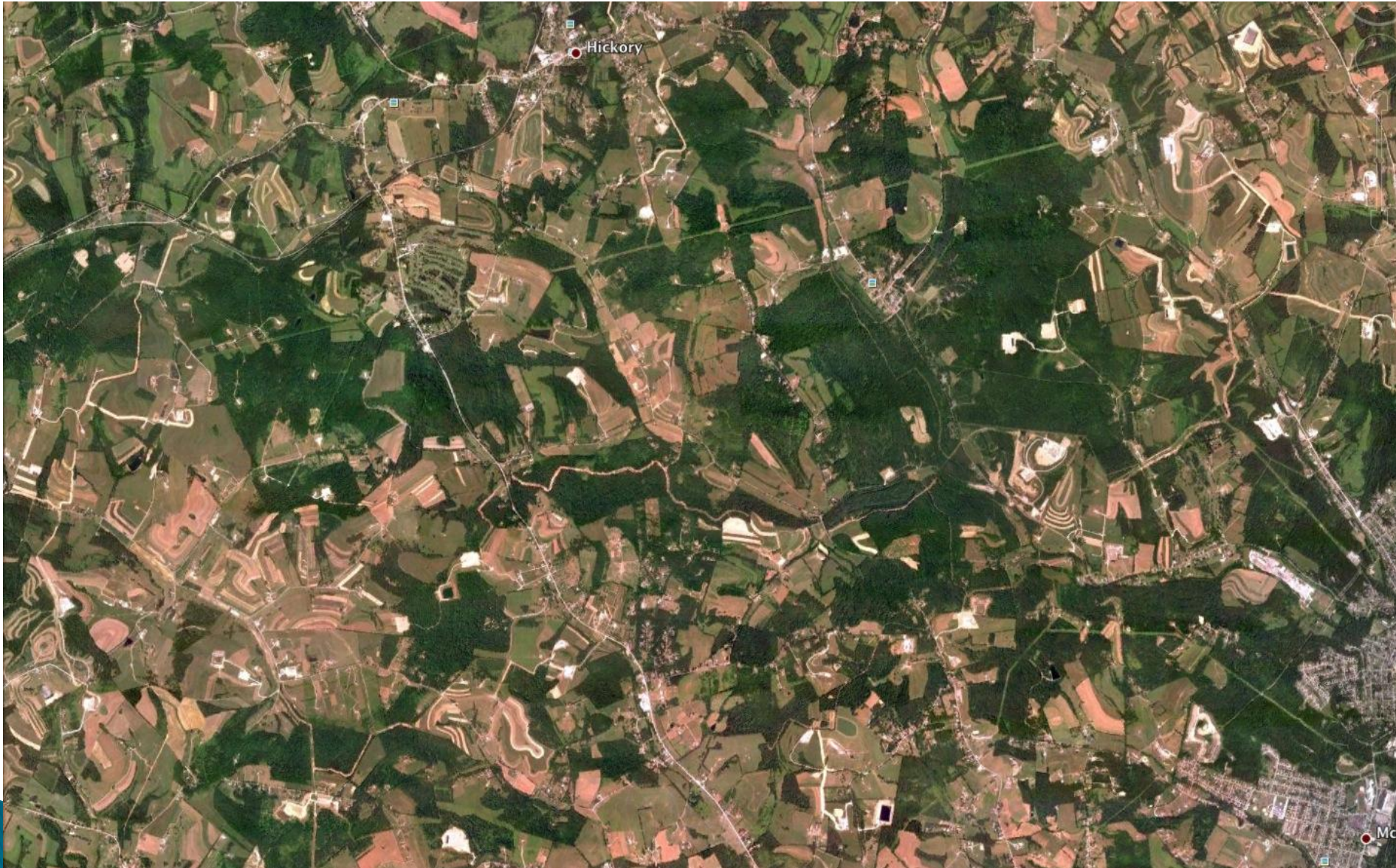
Director—Center for Healthy Environments and Communities (CHEC)

Hickory and Houston, Washington County, PA September 20, 2005

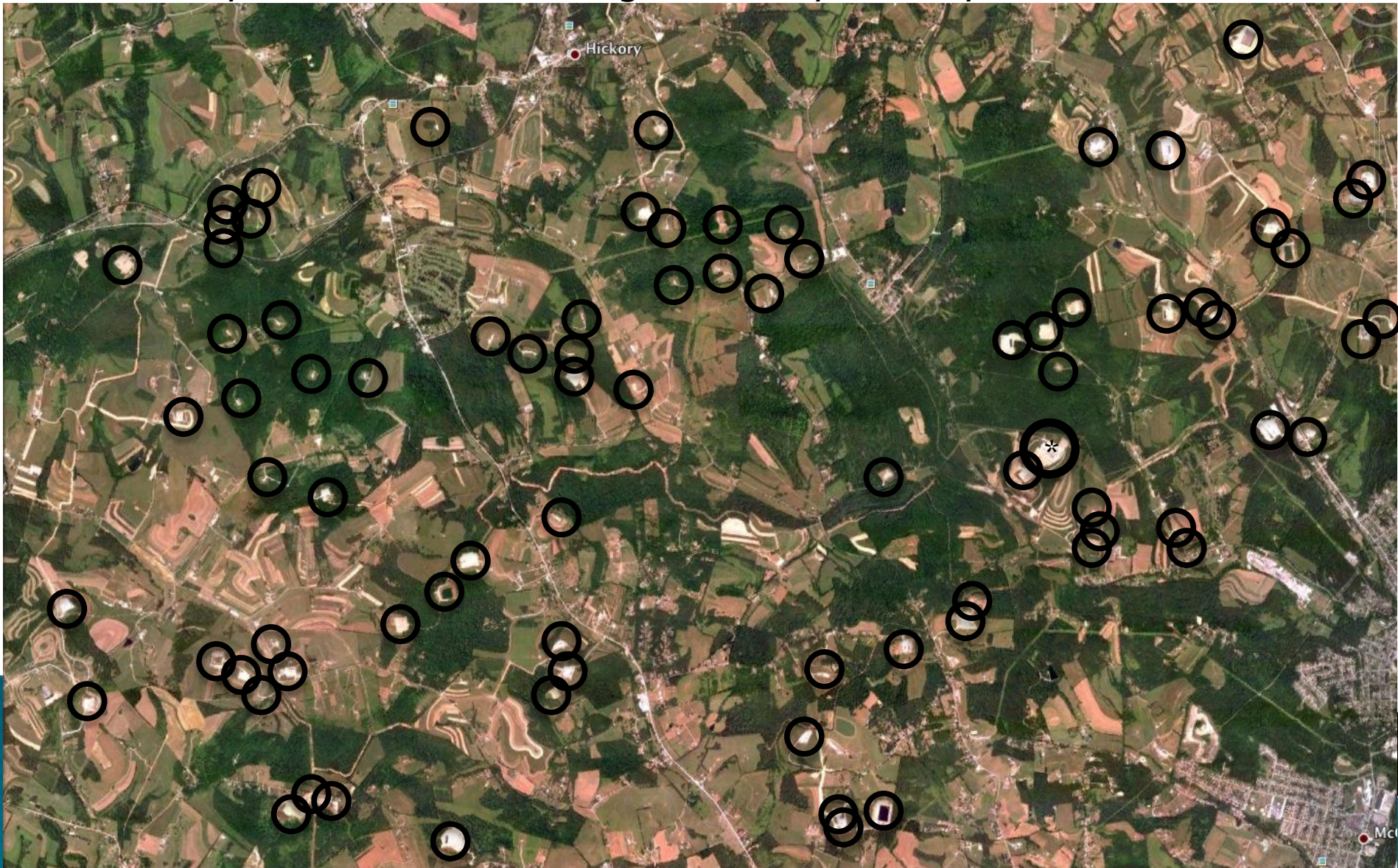


Courtesy of John Stoltz, PhD

Hickory and Houston, Washington County, PA, July 2, 2010



Hickory and Houston, Washington County, PA, July 2, 2010



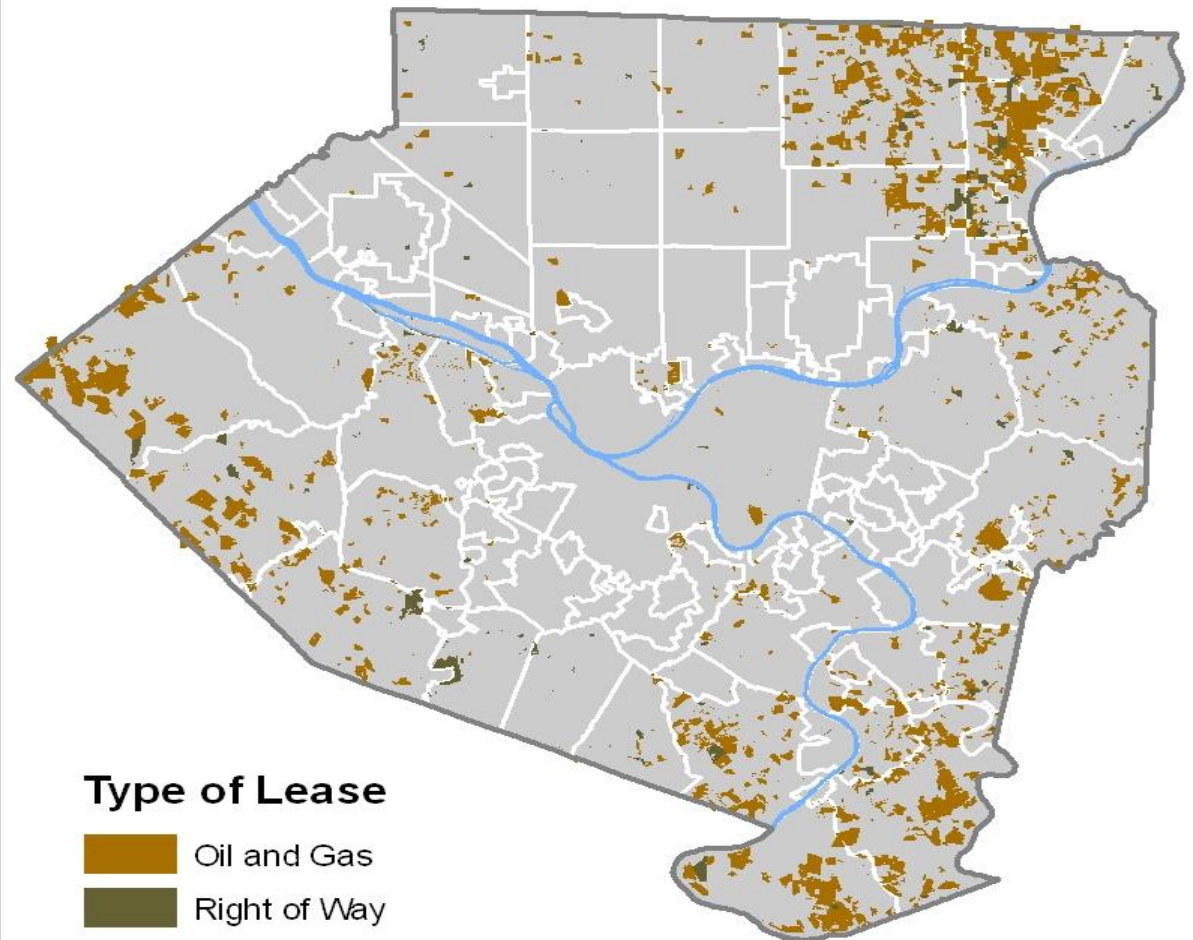
* MarkWest Refinery ○ Well pad or Compressor Station

2600 Parcels (May 2010)

217 (2008)

1,102 (2009)

Energy-Related Leasing Activity by Parcel, Allegheny County, 2003 - 2010*



* January - May 2010

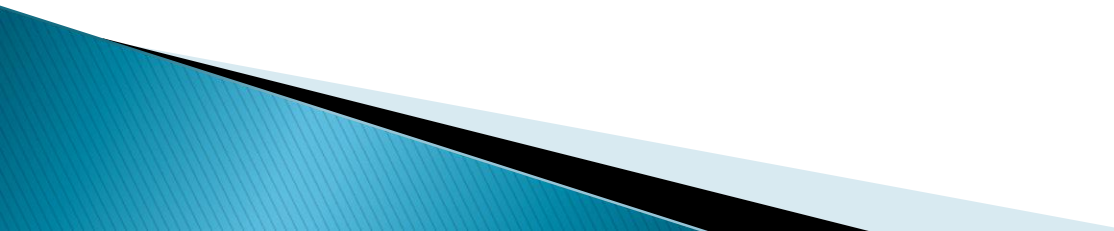
Source: Allegheny County Department of Real Estate
University Center for Social and Urban Research
University of Pittsburgh

Potential Shale Gas Extraction Air Pollution Impacts

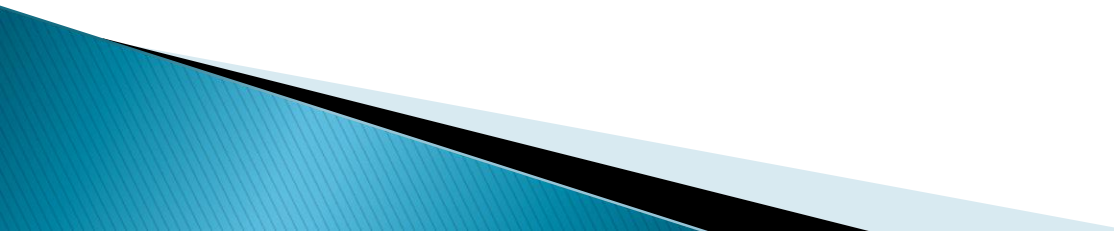
1. How organic compounds in the shale layer enter air and become Hazardous Air Pollutants

- ▶ good evidence that flowback and produced water from shale layers themselves contain organic compounds that could volatilize into the environment when brought to the surface

1. How organic compounds in the shale layer can enter air and become Hazardous Air Pollutants

- ▶ Gas is of thermogenic or biogenic origin and stored as sorbed hydrocarbons, as free gas in fracture and intergranular porosity, and as gas dissolved in kerogen and bitumen (Schettler and Parmely, 1990; Martini et al., 1998).
 - ▶ Kerogen and bitumen are extremely large molecular weight and a diverse group of organic compounds.
- 

1. How organic compounds in the shale layer can enter air and become Hazardous Air Pollutants

- ▶ The [USGS factsheet 2009-3032](#) states clearly that hydrofrac water “in close contact with the rock during the course of the stimulation treatment, and when recovered may contain a variety of formation materials, including brines, heavy metals, radionuclides, and organics that can make wastewater treatment difficult and expensive” to dispose of.
- 

Organic Compounds Come From the Shale Layer Itself

- ▶ Certainly gas shales contain numerous organic hydrocarbons; we know, for example, that the Marcellus contains from 3–12% organic carbon (OC), the Barnett: 4.5% OC, and the Fayetteville: 4–9.8% OC (Arthur et al, 2008).
- ▶ Volatile hydrocarbons occur naturally in produced water and that produced water from gas–condensate–producing platforms contains higher concentrations of organic compounds than from oil–producing platforms (Veil et al., 2004).

Organic Compounds Come From the Shale Layer Itself

- ▶ Produced waters from gas production have higher contents of low molecular-weight aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylene than those from oil operations.
- ▶ Produced water contains: aliphatic and aromatic carboxylic acids, phenols, and aliphatic and aromatic hydrocarbons. They are not easily removed from produced water and are generally discharged directly into fracing ponds.

Organic Chemicals in Flowback and Produced Water May Also Come From Chemical Additives

- ▶ Chemicals added to produced water or put into a producing well – such as corrosion and scale inhibitors, scale solvents, biocides, antifreeze, and oil and grease, and impurities in the chemicals used.
- ▶ Further, some paraffin's and aromatics have moderate solubility in water; as long as oil-gas and water flow upward together these can become dissolved in water. The longer the transit time (as in deep Marcellus wells) the more hydrocarbon can dissolve into water. This paper reports finding toluene, ethylbenzene, [phenol](#), [naphthalene](#) and [2,4-dimethylphenol](#) in produced water and states that [bis\(2-ethyl-hexyl\) phthalate](#), [di-n-butyl phthalate](#), [fluorine](#) and [diethyl phthalate](#) have been found in produced water by the EPA.

Fang CS, 1990, [Petroleum drilling and production operations in the Gulf of Mexico. Estuaries](#), Vol 13, No 1, pp. 89–97.

How do organic compounds in gas extraction waters enter air?

First a review of Henry's Law

Henry's Law states that the solubility of a gas in a liquid is a function of the partial pressure of the gas above that liquid.

The concentration of the gas in the liquid is proportional to its concentration in the atmosphere with the Henry's Law Constant describing the relationship.

Every organic compound has a unique Henry's Law constant, m (dimensionless), or K_h (pressure-mass per volume) at a specific temperature and pressure (remember $PV=nRT$) so this constant is critical to predicting volatilization of organic chemical from the water phase into the air phase.

The equations corresponding to the above two constants are;

$$C_{air} = m * C_{water}$$

$$P_v = K_h * C_{water}$$

where;

C_{air} : concentration in headspace, (mass/volume)

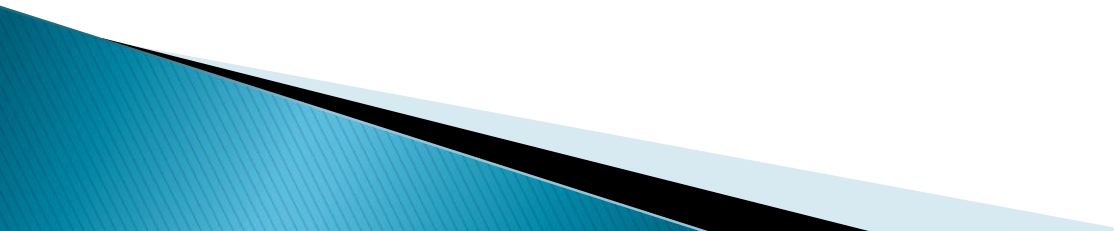
C_{water} : concentration in water, (mass/volume)

P_v : partial pressure in vapor phase

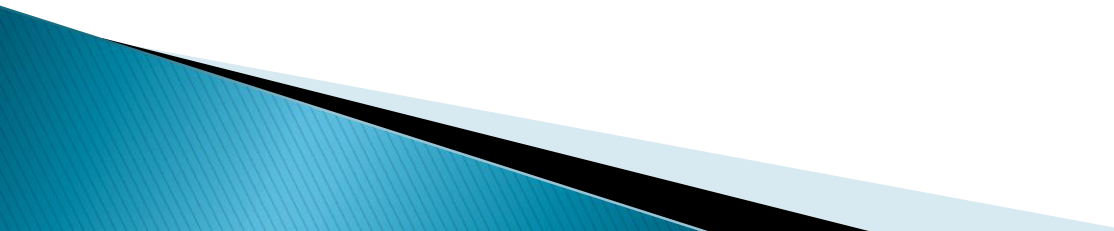
K_h : Henry's Law constant

m : dimensionless Henry's Law constant

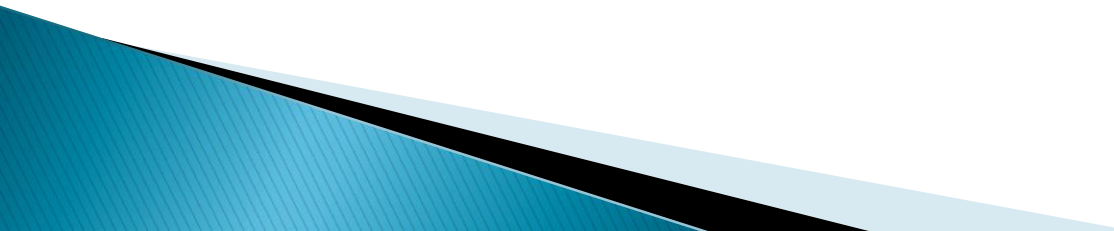
How do organic compounds in gas extraction waters enter air?

- ▶ Flowback or produced water that returns to the surface and goes into a frac pond-pit or impoundment will offgas (become a vapor in air) its organic compounds into the air.
 - ▶ Each organic compound enters air according to its Henry's Law constant, its concentration in the water and its partial pressure in air.
 - ▶ This is dependant on T and P—all things being equal more volatilization will occur on hot sunny days with low humidity.
 - ▶ This conceptually becomes an air pollution problem, and the organic compounds are now termed Hazardous Air Pollutants (HAP's).
 - ▶ We have little data now on species of organic chemicals in air as a result of this process—research needs to be done.
 - ▶ Indications from other shale plays are that there are contributions from the processes to air— but there is controversy regarding if these levels can produce health effects.
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How do organic compounds in gas extraction waters enter air?

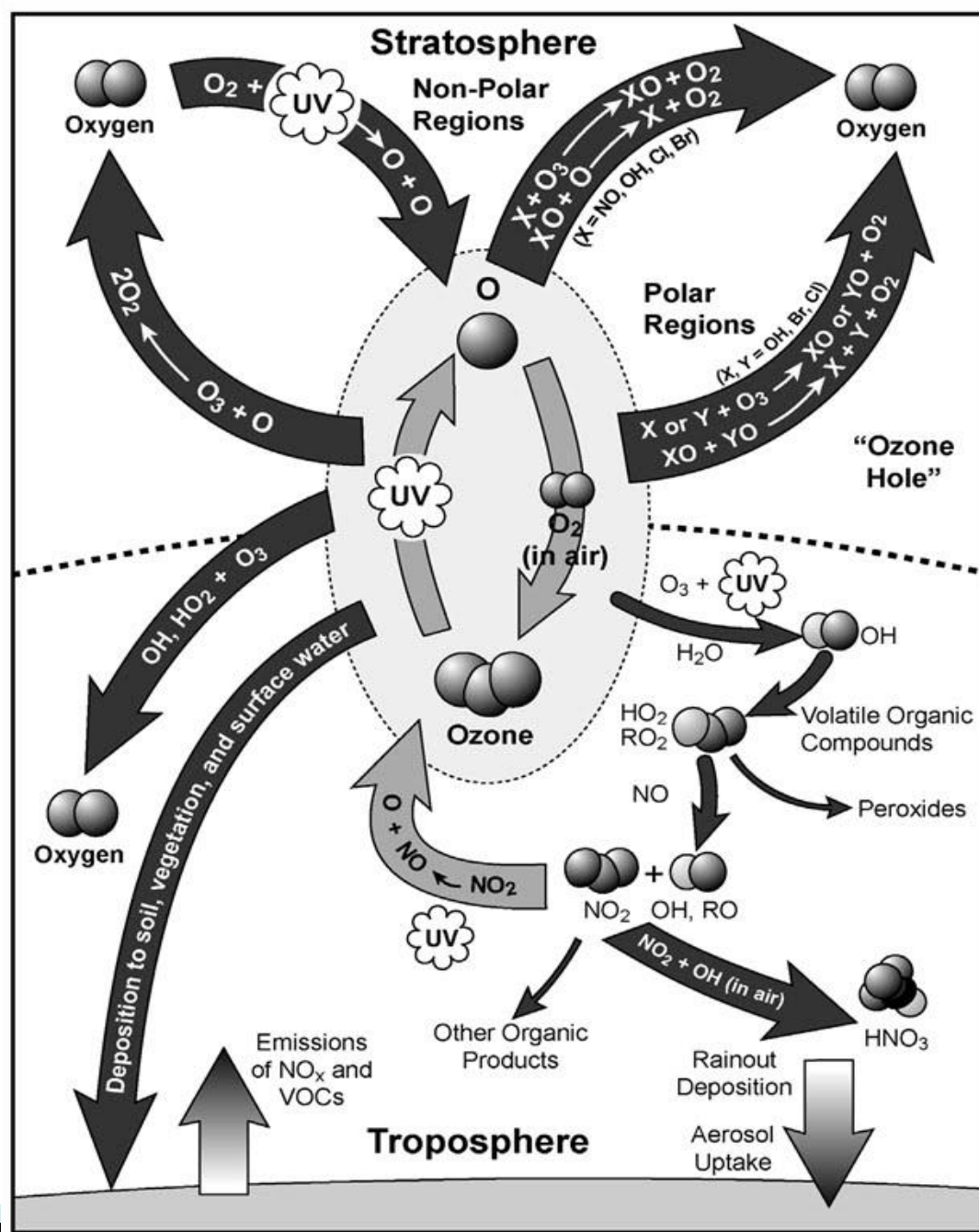
- ▶ Additionally, separators, condensers, cryo plants and compressors can leak causing some volatile organic compounds to enter air. Incomplete combustion in flaring also adds VOC's to air.
 - ▶ CHEC is right now doing UV-DOAS spectrophotometry of gas extraction processes in the Marcellus to determine the concentrations and species of organic chemicals that may be given off by these processes.
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How volatile organic compounds can act as precursor chemicals for the formation of ozone

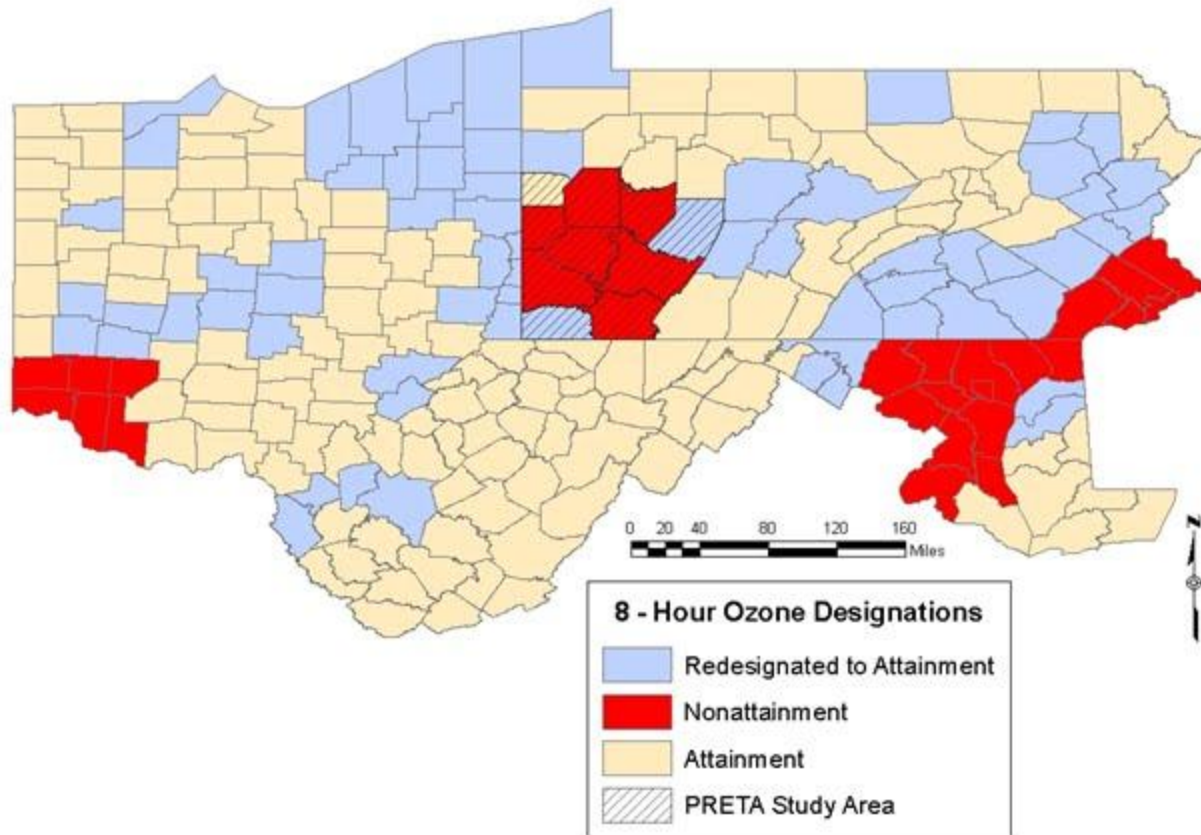
- ▶ Ozone is a secondary pollutant that is formed in polluted areas by atmospheric reactions involving two main types of precursor pollutants volatile organic compounds (VOC's) and nitrogen oxides (NO_x).
 - ▶ Carbon monoxide (CO) from incomplete combustion of fuels is also an important precursor for ozone formation.
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How volatile organic compounds can act as precursor chemicals for the formation of ozone

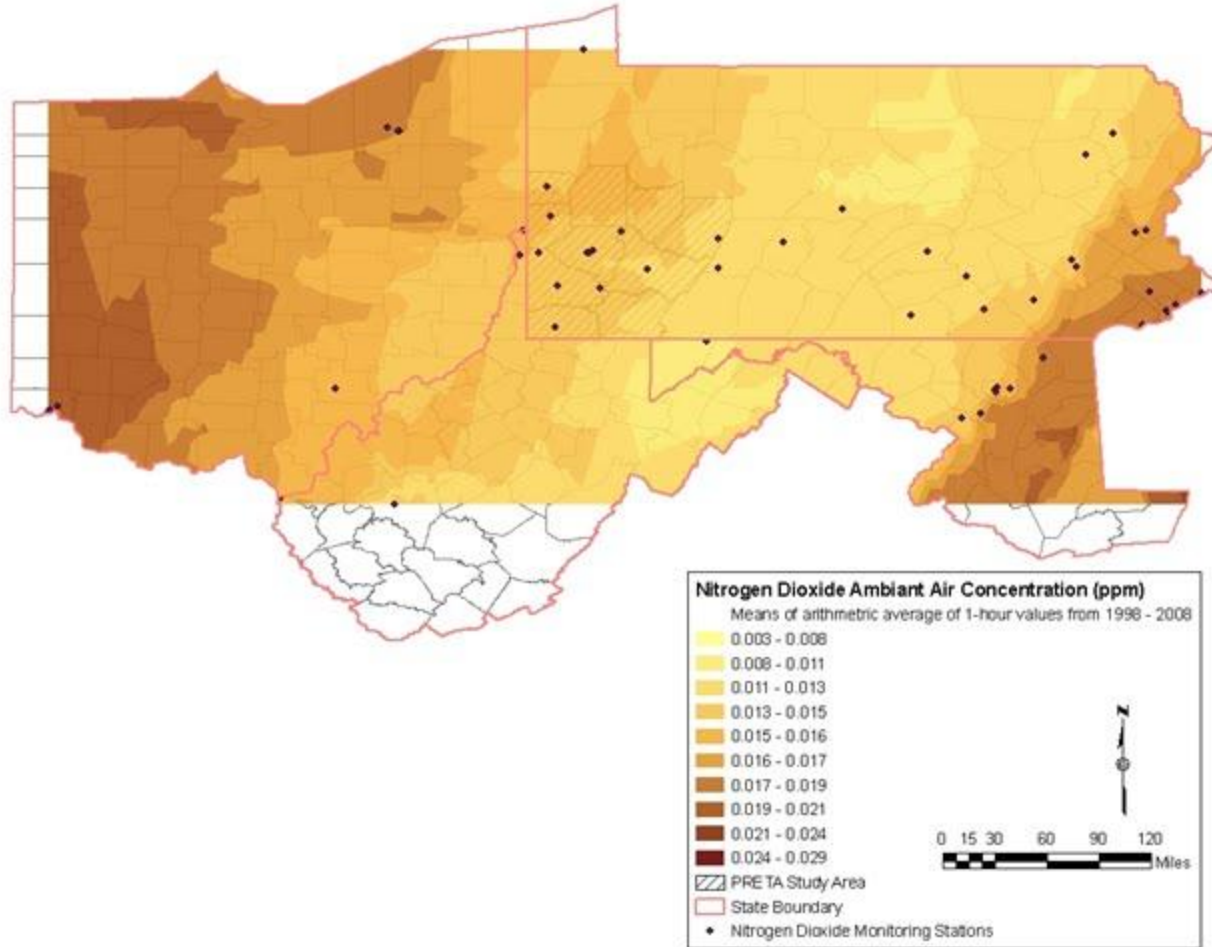
- ▶ The formation of ozone and other oxidation products (like peroxyacyl nitrates and hydrogen peroxide), including oxidation products of the precursor chemicals, is a an extremely complex reaction that depends on the intensity and wavelength of sunlight, atmospheric mixing and interactions with cloud and other aerosol particulates, the concentrations of the VOC's and NO_x in the air, and the rates of all the chemical reactions.



Existing Ozone Problems in 4 state area-pr-Marcellus Extraction



Existing NO₂ Concentrations Over 4 State Area—Means of 1–Hour Values Over 1998–2008 (influence of Marcellus Shale would not be significant yet—data given to get approximation of NO₂ that is available to react with volatile organics from gas operations)



Emitters of NO₂ in 2002 by Tonnage Category (Does not include mobile sources of NO₂ but does give major sources of NO₂ that are available to react with volatile organics from gas operations—to form ozone)

