Potential Impacts to Air from Marcellus Shale Gas Extraction Operations

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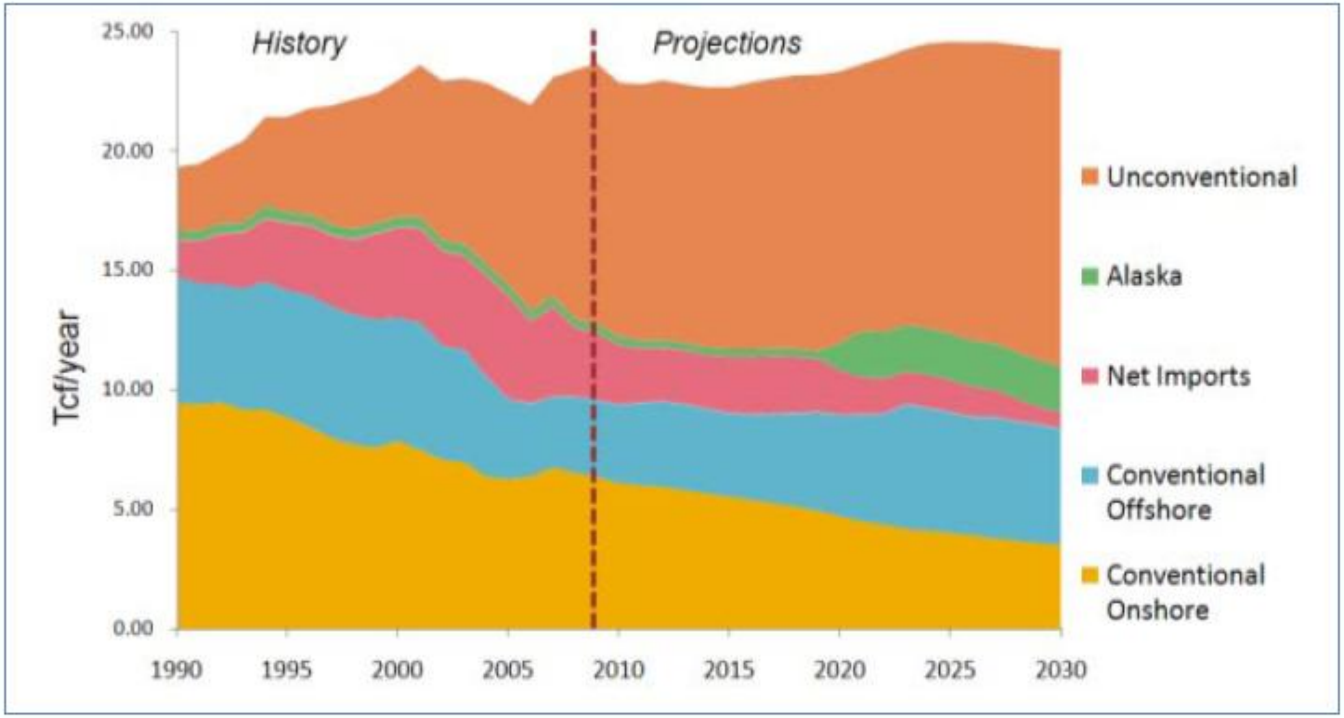
Projections of Sources of Methane Gas

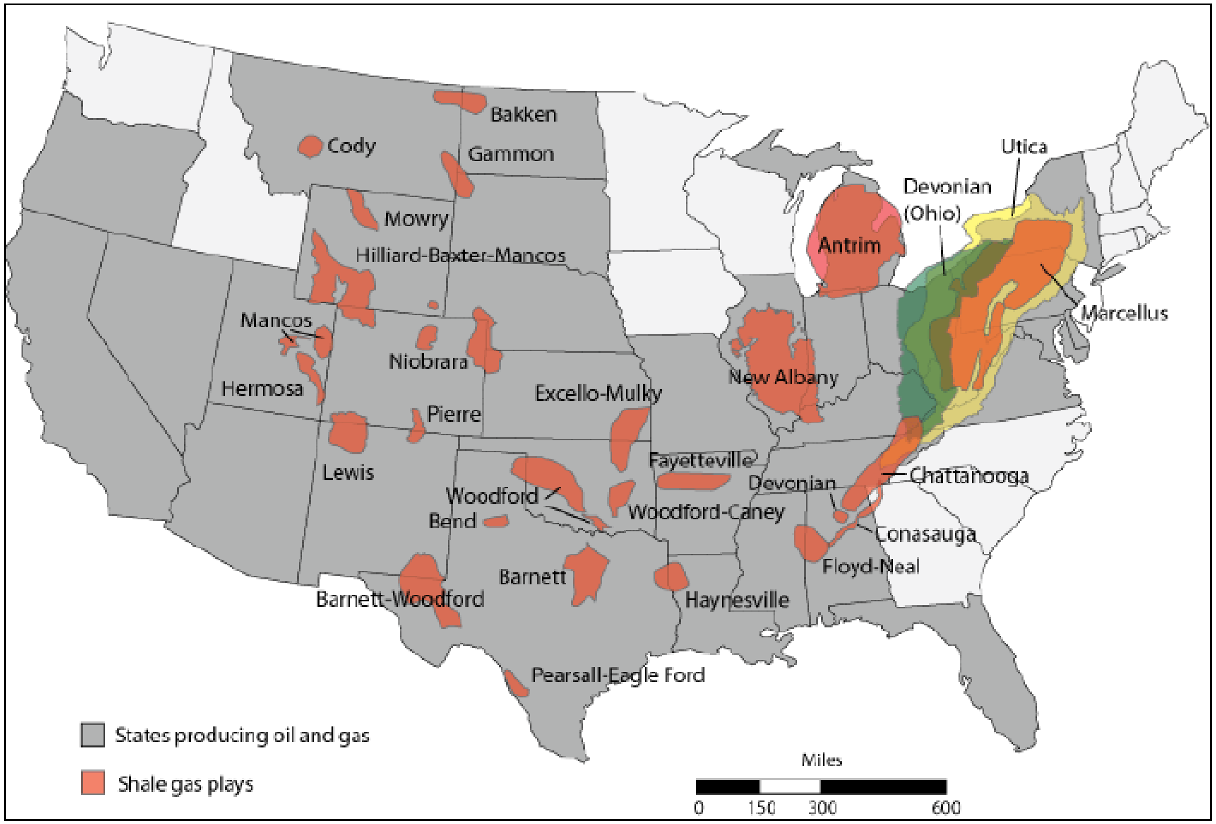
Figure 1 – U.S. Natural Gas Supply by Source



Source: DOE/EIA Annual Energy Outlook 2009. Note that Tcf refers to trillion cubic feet.

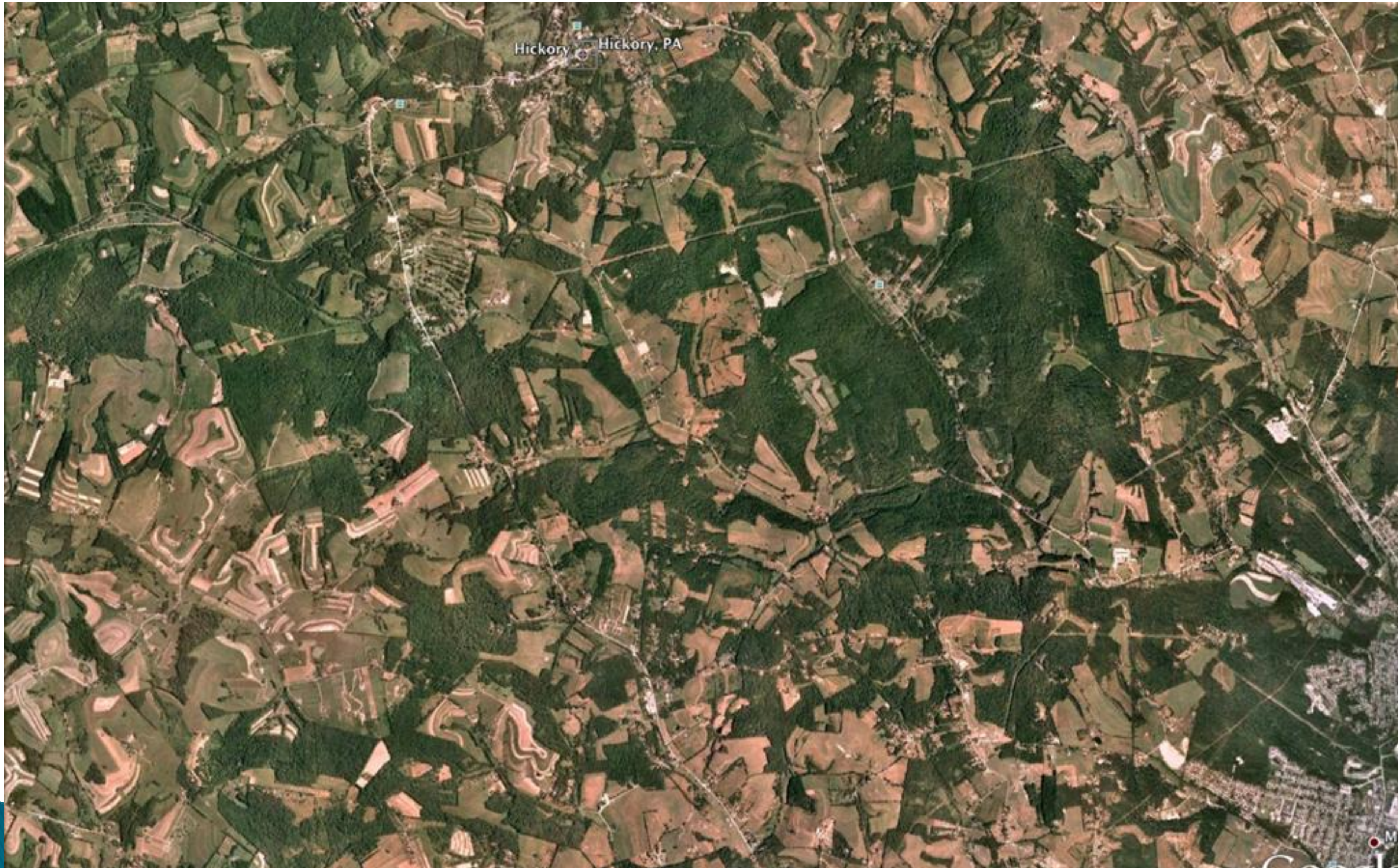
US SHALE GAS PLAYS

Figure 2 – U.S. Shale Gas Plays



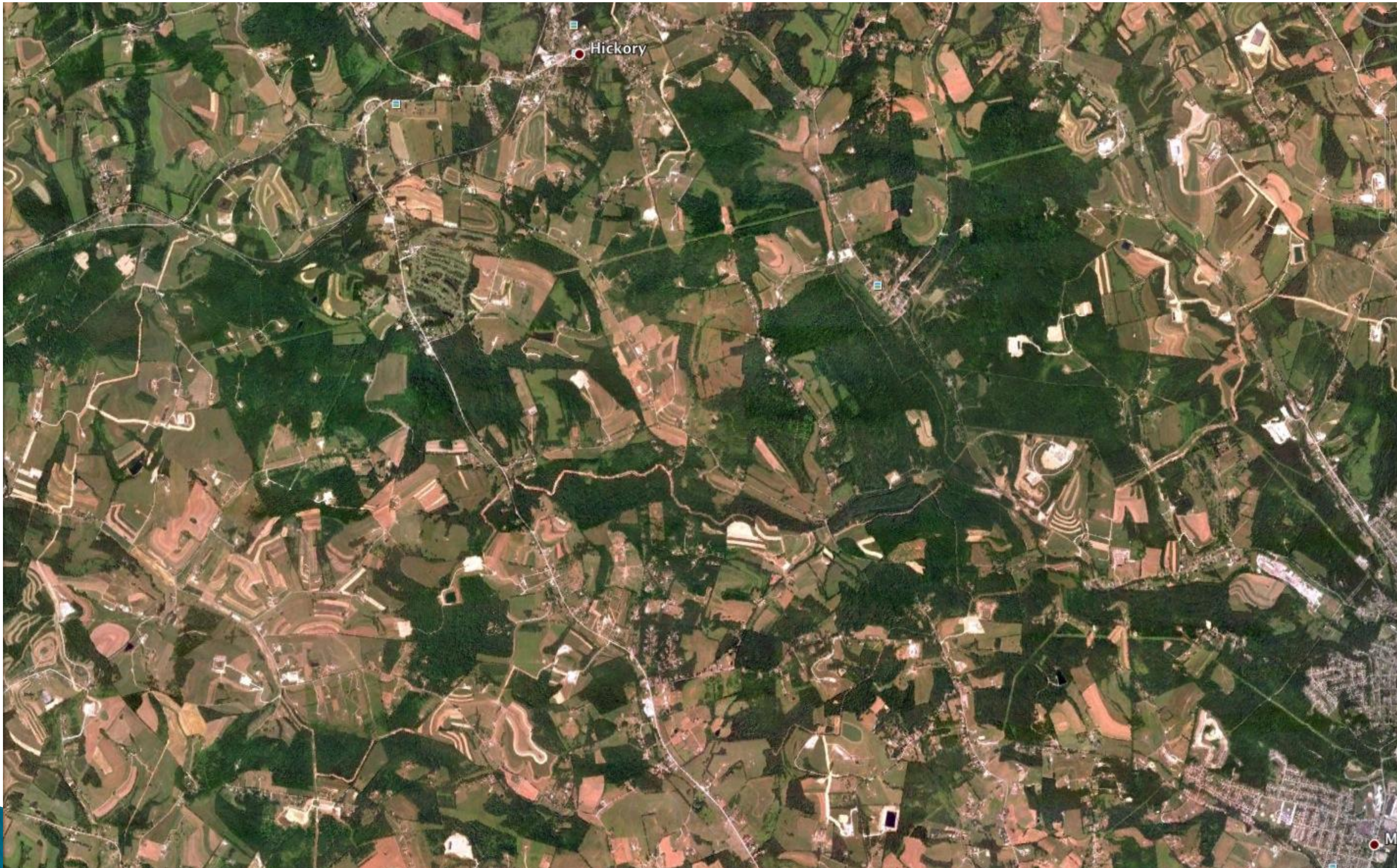
Source: Provided by staff from DOE's Office of Fossil Energy.

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

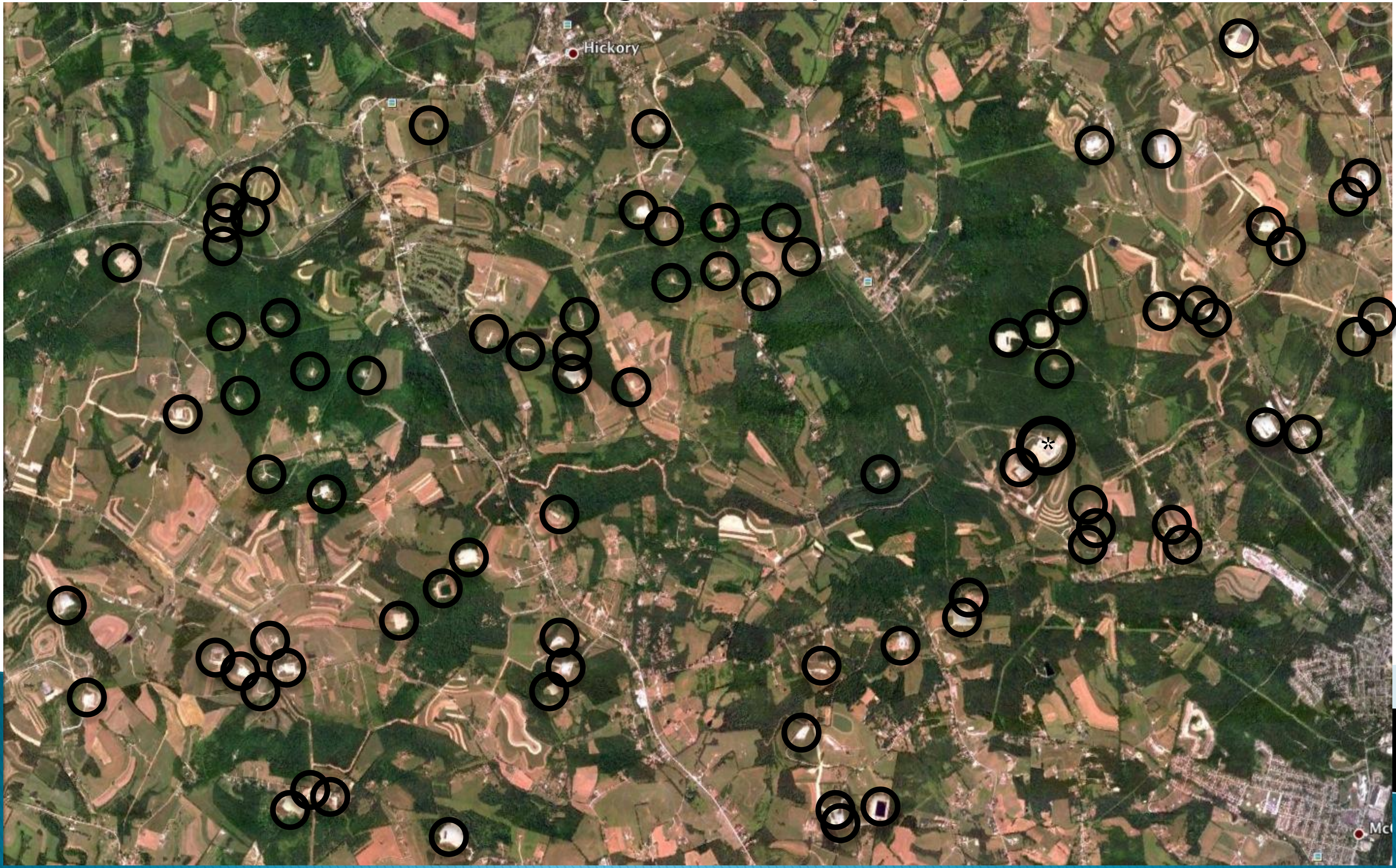


Courtesy of John Stoltz, PhD

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



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

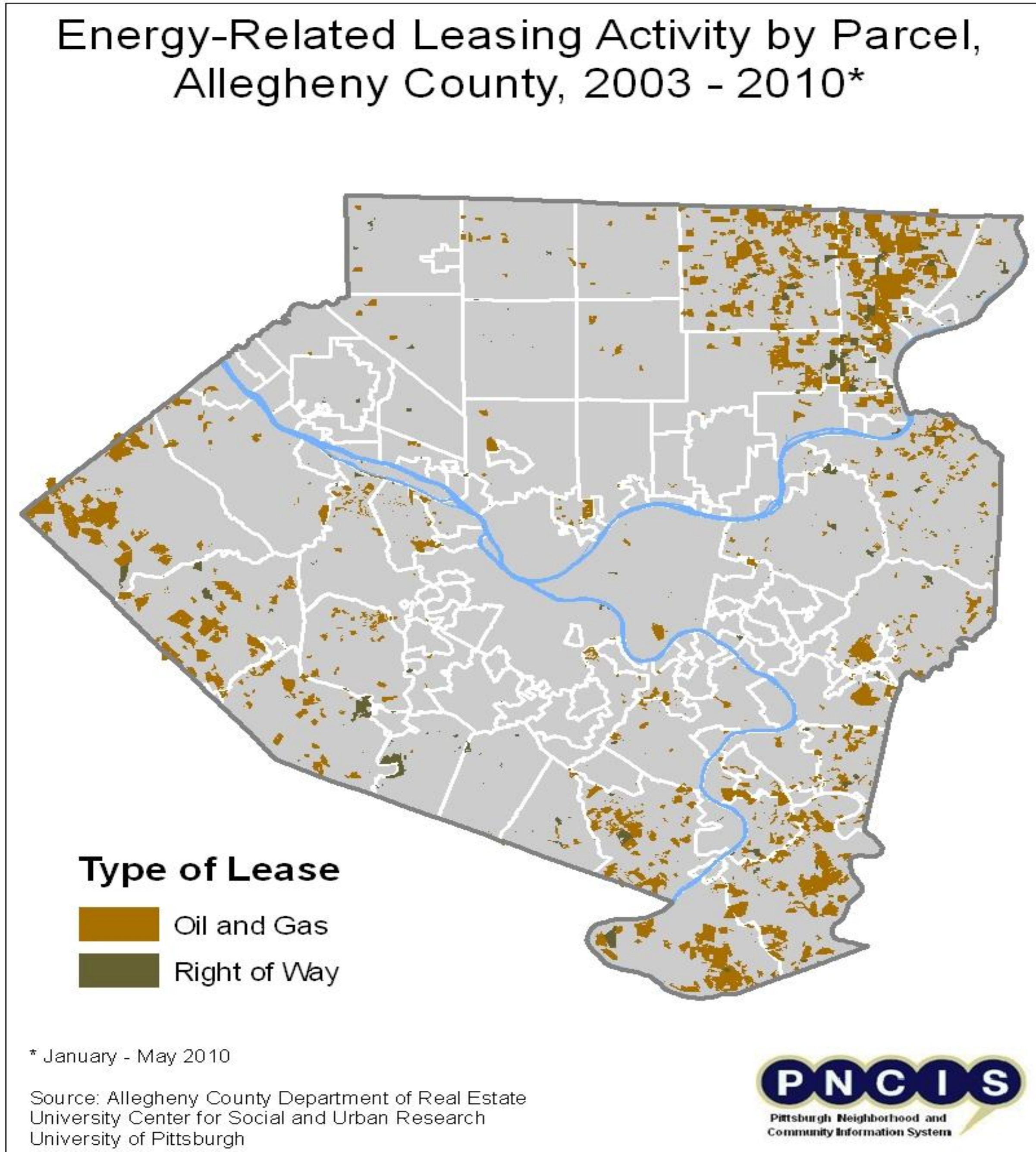


* MarkWest Refinery ○ Well pad or Compressor Station

2600 Parcels (May 2010)

217 (2008)

1,102 (2009)



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 then 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 Kh (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;

Cair = m * Cwater

Pv = Kh * Cwater

where;

Cair: concentration in headspace, (mass/volume)

Cwater: concentration in water, (mass/volume)

Pv: partial pressure in vapor phase

Kh: 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.

How do organic compounds in gas extraction waters enter air?

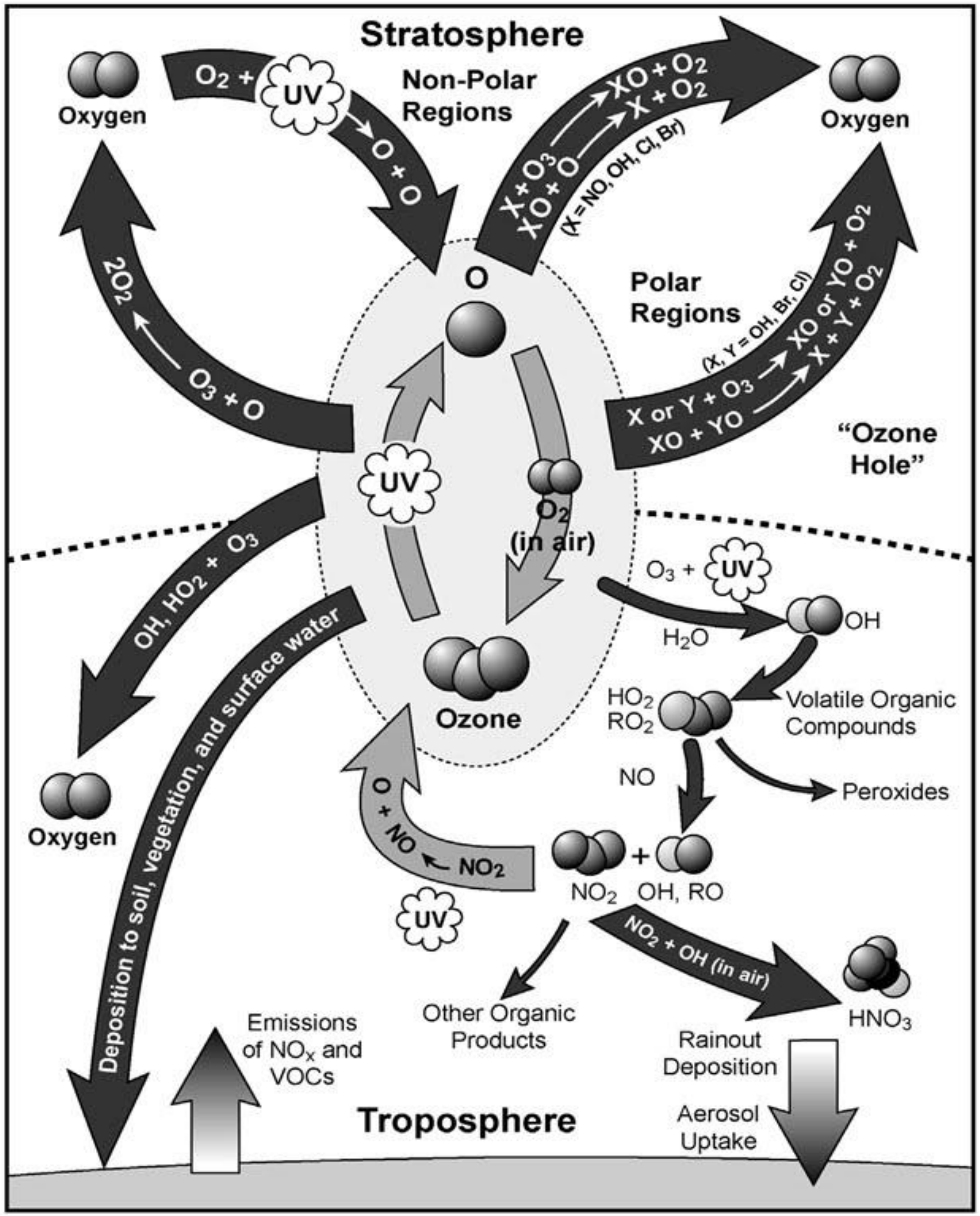
- Additionally, separators, condensers, cryo plants and compressors can leak causing some volatile organic compounds to enter air. Incomplete combustion in flaring also adds VOC's to air.
- CHEC is right now doing UV-DOAS spectrophotometry of gas extraction processes in the Marcellus to determine the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

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 (NOx).
- Carbon monoxide (CO) from incomplete combustion of fuels is also an important precursor for ozone formation.

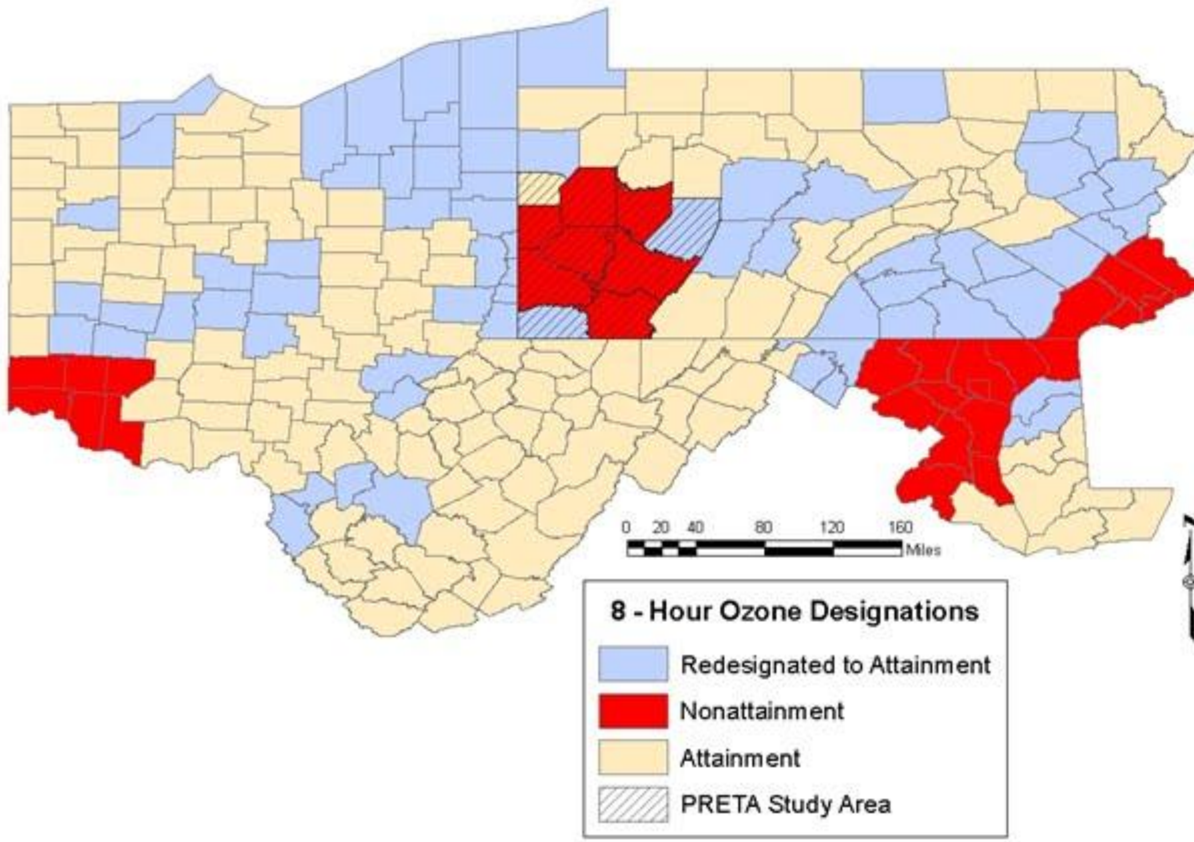
How volatile organic compounds can act as precursor chemicals for the formation of ozone

- 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 NOx in the air, and the rates of all the chemical reactions.

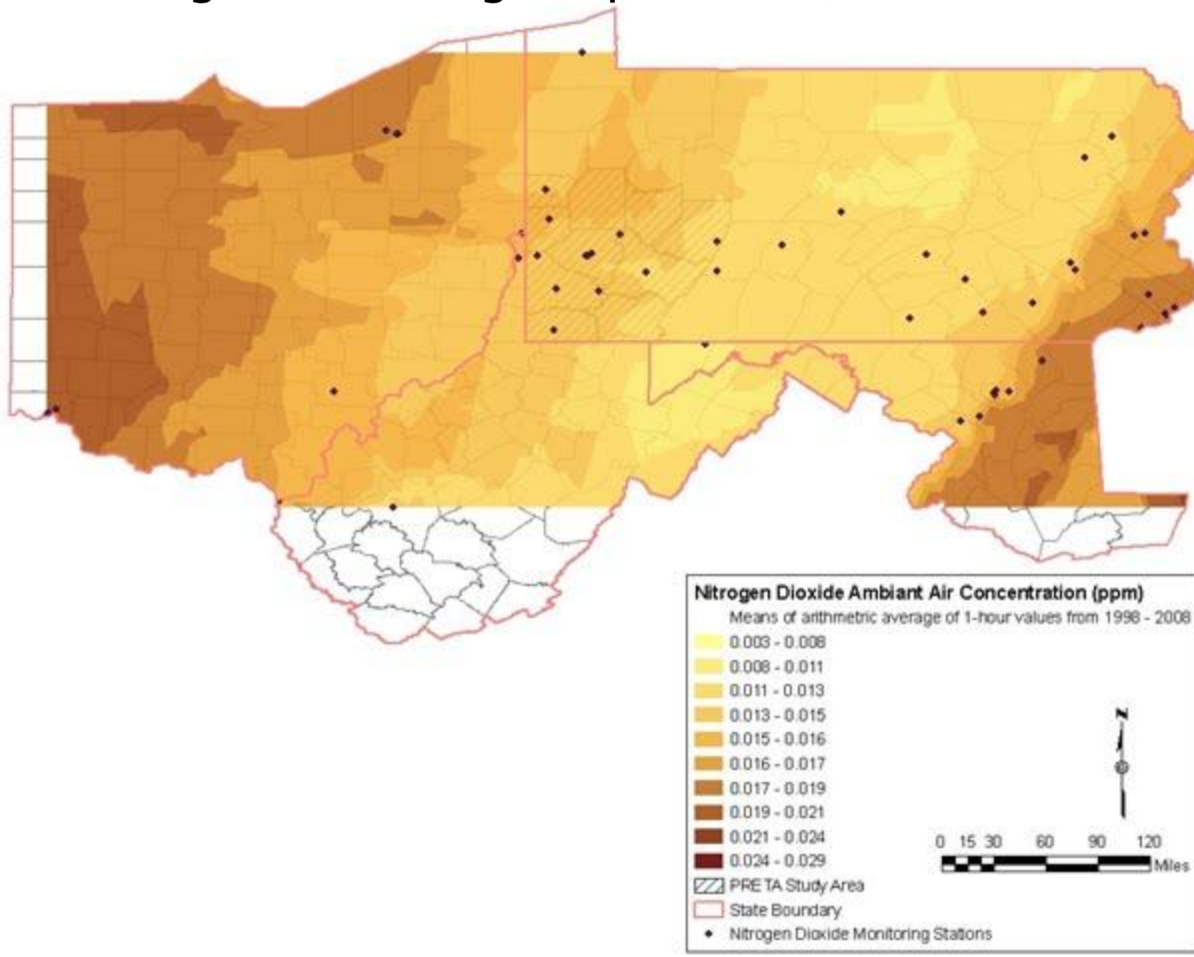


[2008 EPA Air Quality Criteria for Ozone and Related Photochemical Oxidants]()

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)