Shale Gas Production via Hydraulic Fracturing

AOSC / CHEM 433 & CHEM 633

Ross Salawitch & Walt Tribett

Class Web Site: http://www.atmos.umd.edu/~rjs/class/spr2019

- Overview of shale gas production via horizontal drilling and hydraulic fracturing (aka fracking)
- Concerns about shale gas production:
  - Earthquakes
  - Contamination of ground water
  - Air quality (surface O_3 precursors)
  - Climate (fugitive release of CH_4)

Lecture 21

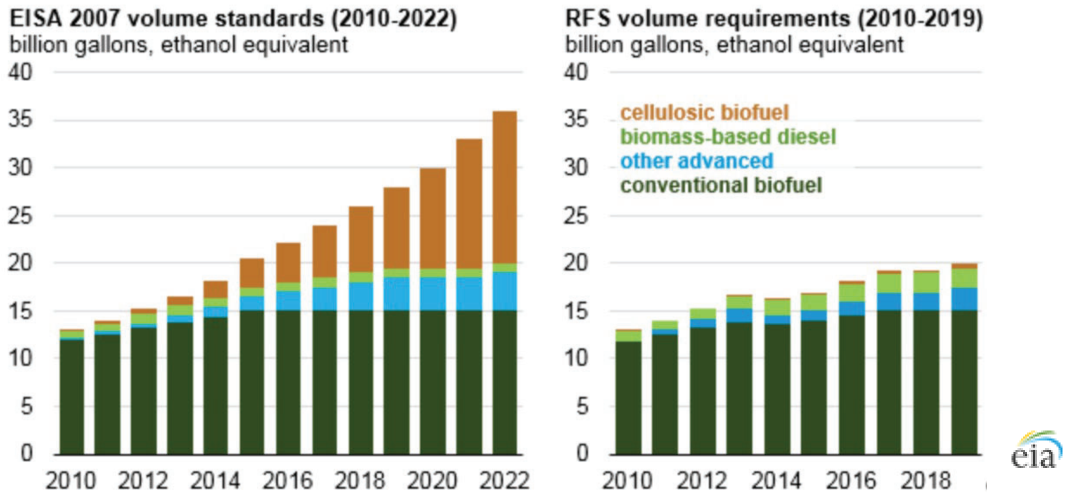
2 May 2019

Course Logistics

- Problem Set #4 has been posted
  - Due Tues, 7 May
  - Review will be held on Mon, 13 May, 6:30 pm
- Energy Plan (assigned only to 433 students) has also been posted
  - Due Thurs, 9 May (one week from today)
  - Several will be selected for presentation in class on 14 May
- Presentations/Paper (assigned to 633 students; 433 students can participate)
  - Mon, 13 May, 2 pm
- Final Exam
  - Mon, 20 May, 10:30 am to 12:30 pm
  - Please return *Chemistry in Context* to receive refund of your $20

U.S. Renewable Fuel Standard

EISA: Energy Independence and Security Act of 2007

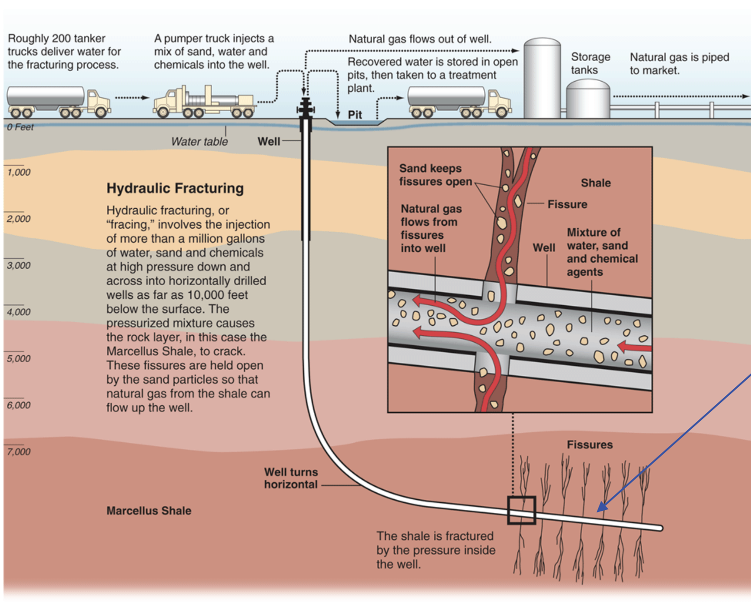


On November 30, 2018, the U.S. Environmental Protection Agency (EPA) issued a final rule for the 2019 Renewable Fuel Standard (RFS) program, with the total U.S. renewable fuel volume requirement set 3% higher than the 2018 mandate, but nearly 30% lower than the statutory volume standards set forth by the Energy Independence and Security Act of 2007 (EISA 2007). Similar to previous years, EPA exercised its cellulosic waiver authority to decrease volume standards for cellulosic biofuels because growth has been slower than Congress had envisioned in EISA, passed more than a decade ago.

https://www.eia.gov/todayinenergy/detail.php?id=37712

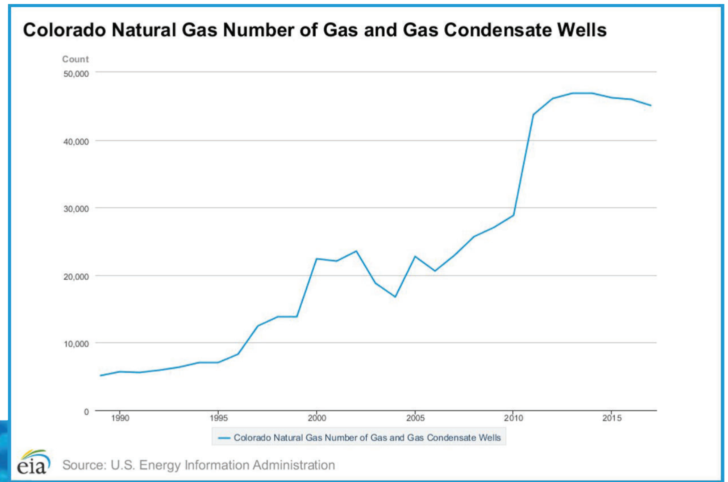
Hydraulic Fracturing

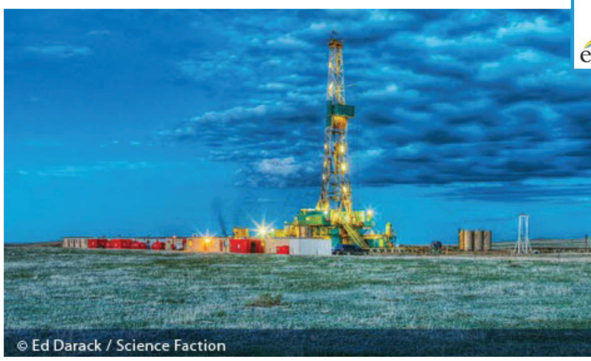
- Pumping of chemical brine to loosen deposits of natural gas from shale
- Extraction of CH_4 from shale gas became commercially viable in 2002/2003 when two mature technologies were combined: horizontal drilling and hydraulic fracturing
- High-pressure fluid is injected into bore of the well at a pressure that fractures the rock



Shale gas fracturing of 2 mile long laterals has been done only in the past decade

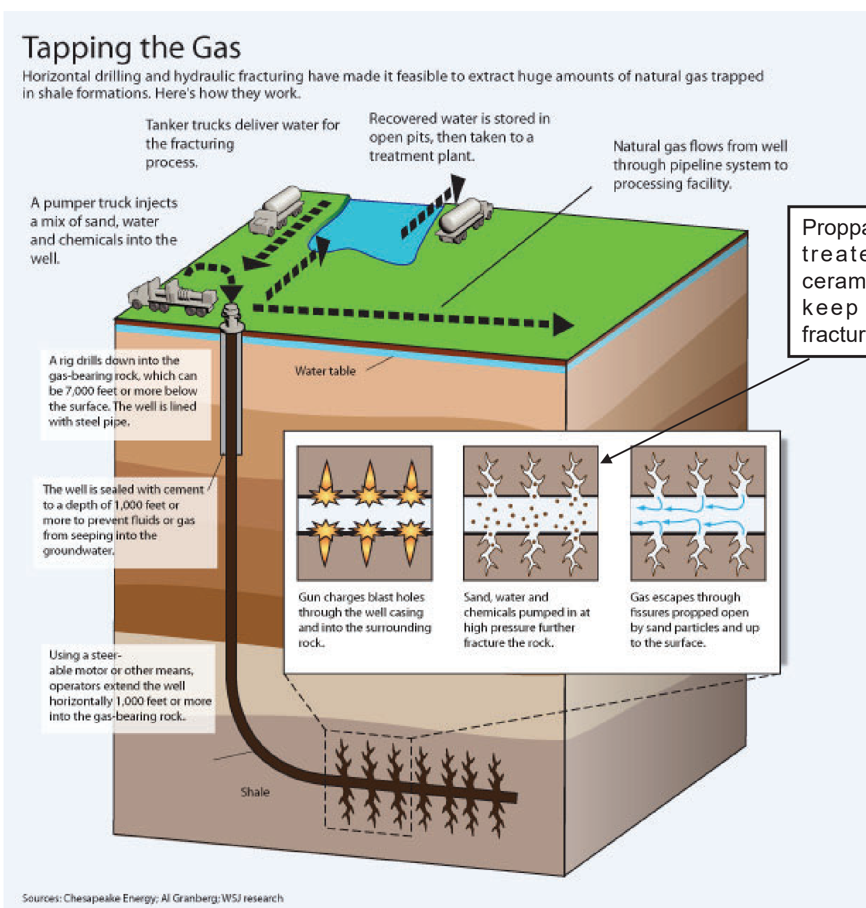
Image: https://assets.propublica.org/legacy/images/articles/natural_gas/marcellus_hydraulic_graphic_090514.gif





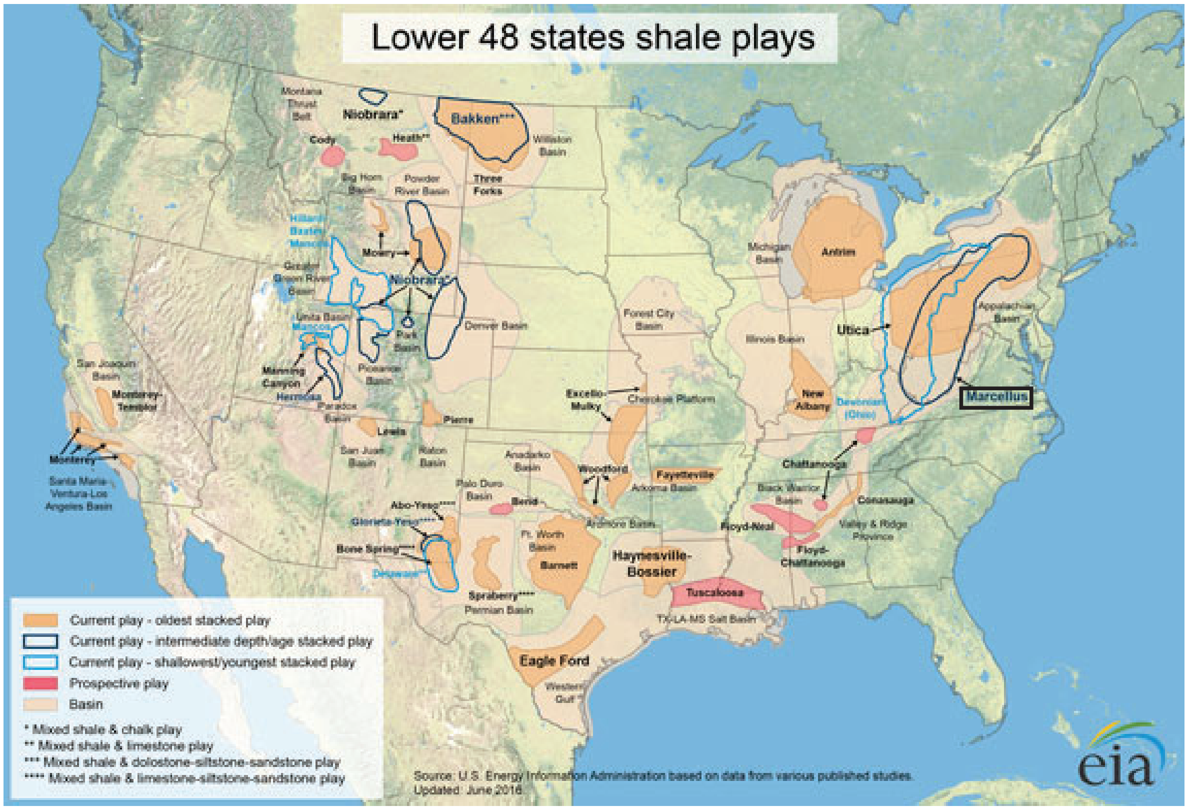
A hydraulic fracturing natural gas drilling rig on the Eastern Colorado plains.
In 2017, there were more than 45,00 natural gas wells in the state of Colorado.

Weinhold, Envir. Health Perspective, 2012: http://ehp.niehs.nih.gov/120-a272/
http://www.eia.gov/dnav/ng/ng_prod_wells_s1_a.htm



Proppant: solid material, typically treated sand or man-made ceramic materials, designed to keep an induced hydraulic fracture open

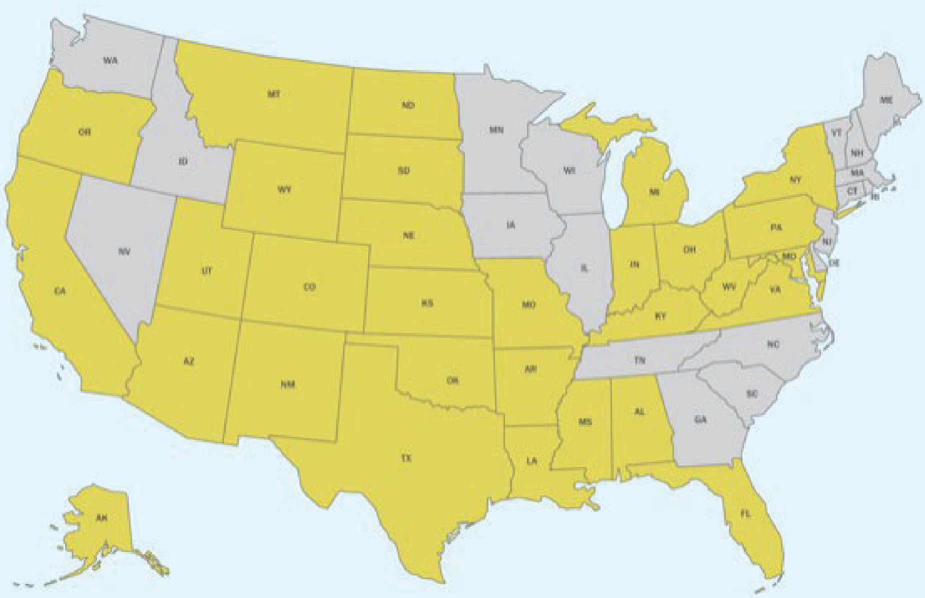
Image: http://online.wsj.com/article/SB10001424052702303491304575187880596301668.html



https://www.eia.gov/energyexplained/index.cfm?page=natural_gas_where

States with Active Natural Gas Production

as of 2009 (most states)



States with Active Natural Gas Production

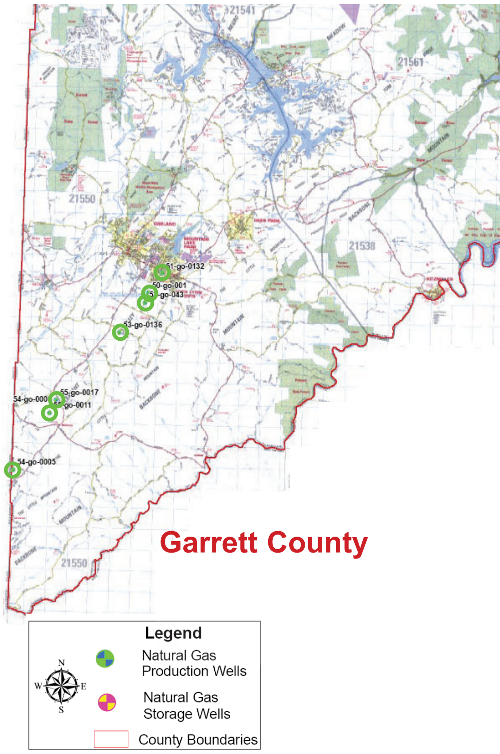
For most states these figures reflect the number of wells as of 2009. At the time this census was published, three states had not yet reported 2009 data. The number reported for Kentucky is for 2008, the number for Pennsylvania is for 2004, and the number for Tennessee is for 2006.

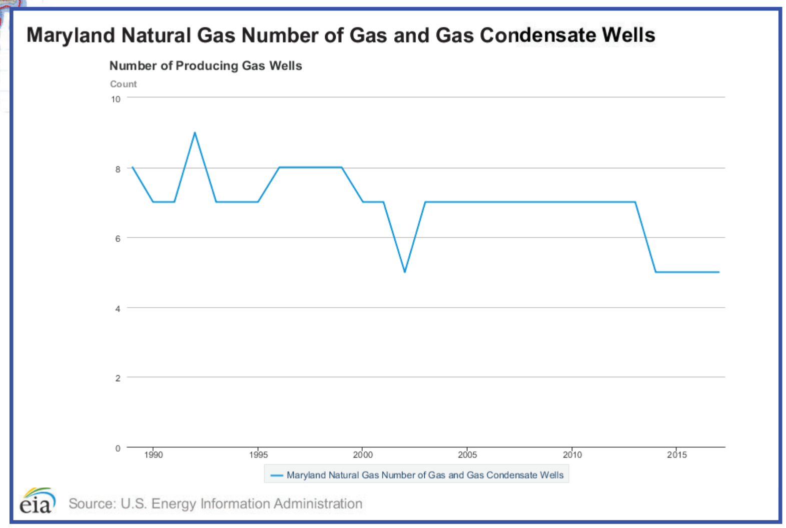
States	No. of Wells
Texas	121,534
Oklahoma	52,287
West Virginia	42,645
New Mexico	39,497
Colorado	38,278
Pennsylvania	35,928
Wyoming	32,617
Ohio	28,181
Kansas	26,025
Louisiana	18,519
Kentucky	13,330
Michigan	10,462
Virginia	7,078
New York	6,995
Utah	6,860
Arkansas	6,859
Montana	6,760
Alabama	6,157
California	4,142
Mississippi	1,734
Alaska	1,046
Indiana	620
North Dakota	509
Nebraska	354
South Dakota	137
Oregon	23
Arizona	6
Maryland	4
Florida	4
Missouri	2

Source: U.S. Energy Information Administration[22]

Weinhold, Envir. Health Perspective, 2012: http://ehp.niehs.nih.gov/120-a272/

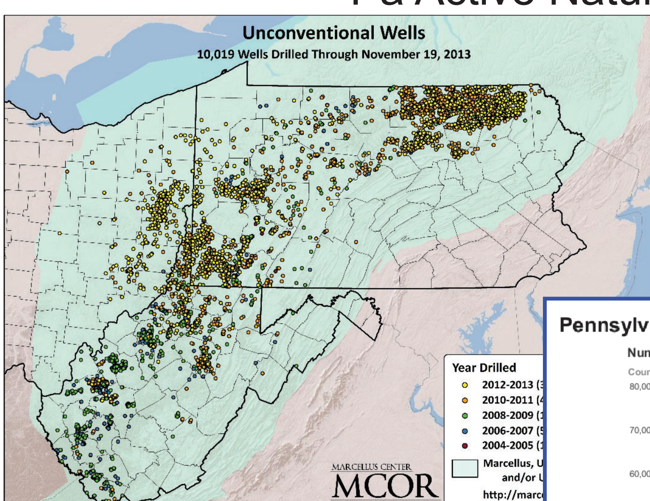
Md Active Natural Gas Production

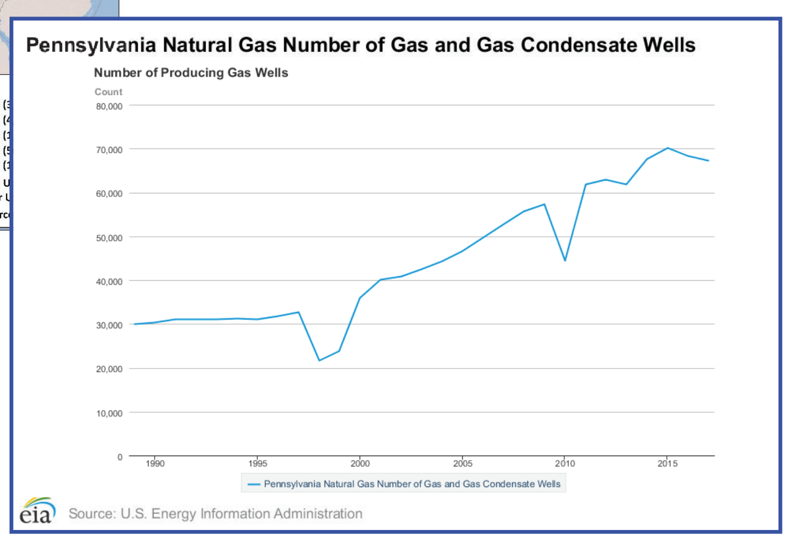




Map: www.mde.state.md.us/programs/Land/mining/Non%20Coal%20Mining/Documents/www.mde.state.md.us/assets/document/mining/NaturalGasWellLocationMap.pdf
Chart: http://www.eia.gov/dnav/ng/hist/na1170_smd_8a.htm

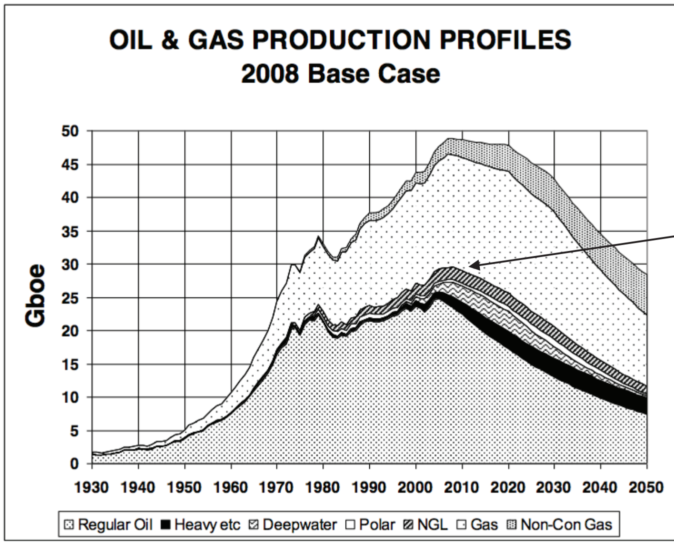
Pa Active Natural Gas Production





Map: http://www.marcellus.psu.edu/images/Spud%20Map%20All%2011.19.13.jpg
Chart: http://www.eia.gov/dnav/ng/hist/na1170_spa_8a.htm

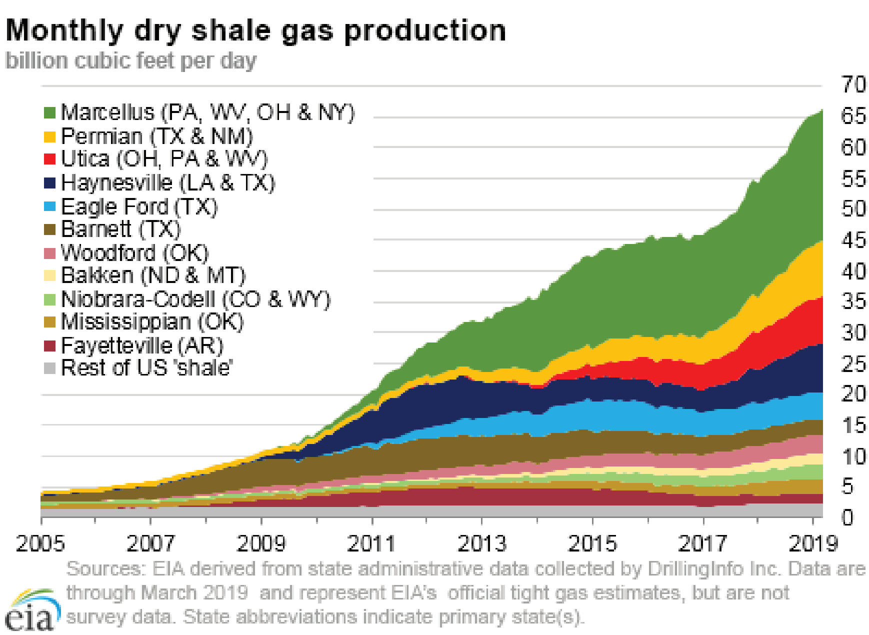
Natural Gas



- Most reserves in Middle East & Russia.
- Hubbert analysis had indicated peak of natural gas production around 2020

http://gailtheactuary.files.wordpress.com/2010/11/colin-campbell-april-2009-forecast.png

Monthly US natural gas production

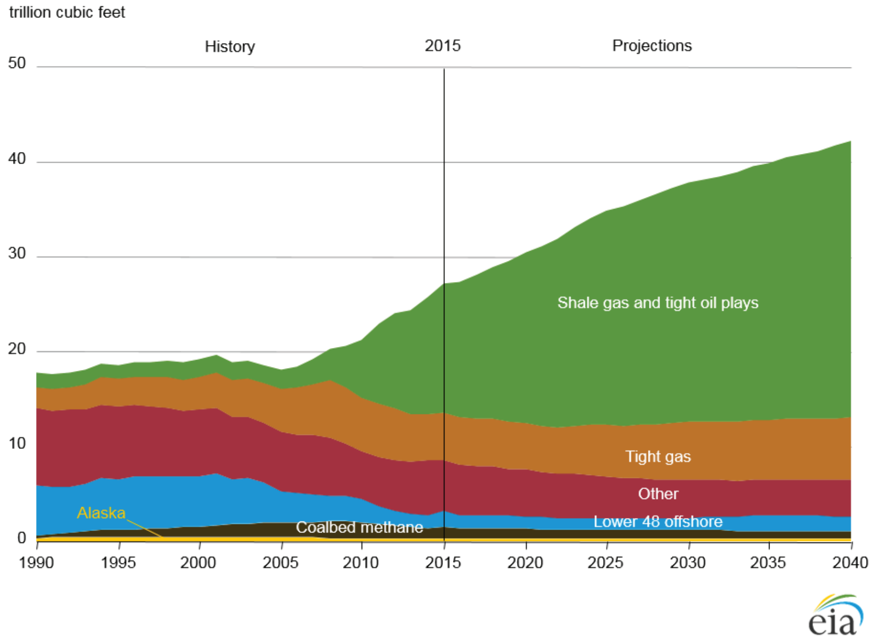


Marcellus accounts for ~ 30% of U.S. shale gas production

https://www.eia.gov/energyexplained/index.php?page=natural_gas_where

U.S. Shale Gas Production

Figure MT-46. U.S. dry natural gas production by source in the Reference case, 1990–2040

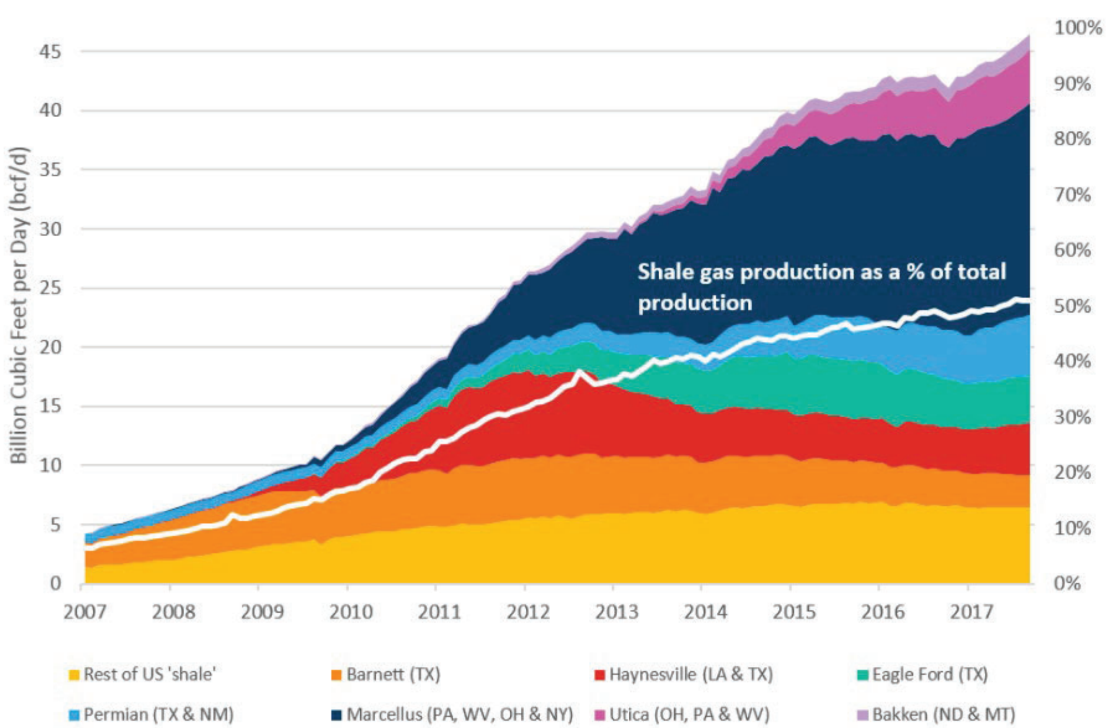


Year	% of US Total CH_4 Production Via Fracking
2001	2
2006	6
2008	12
2011	29
2013	40
2014	44
2015	48
2016	55
2017	57

https://www.eia.gov/energyexplained/index.php?page=natural_gas_where

Production numbers from https://www.eia.gov/dnav/ng/ng_prod_sum_dc_NUS_mmcf_a.htm

U.S. Shale Gas Production

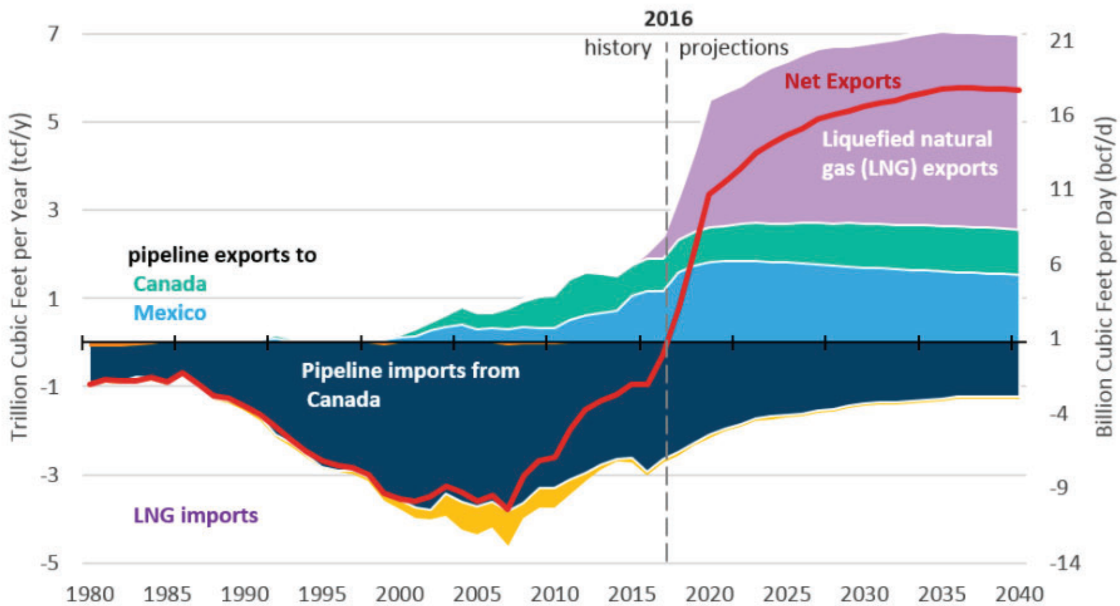


Center for Strategic and International Studies | Energy and National Security Program
Source: Adapted from U.S. Energy Information Administration Data (October 2017).

https://www.csis.org/features/us-natural-gas-global-economy

Shale Gas provides domestic source to meet U.S. consumer needs

U.S. Natural Gas Exports and Imports



Center for Strategic and International Studies | Energy and National Security Program
Source: Adapted from U.S. Energy Information Administration data (October 2017).

https://www.csis.org/features/us-natural-gas-global-economy

Tight Gas and Shale Gas

Tight gas: CH_4 dispersed within low porosity silt or sand that create "tight fitting" environment; has been extracted for many years using hydraulic fracturing

Shale gas: CH_4 accumulated in small bubble like pockets within layers sedimentary rock such as shale, like tiny air pockets trapped in baked bread

Image:
http://www.wintershall.com/en/different-types-of-reserves-tight-gas-and-shale-gas.html

Shale Gas Production & Public Policy

- U.S. imports very little CH_4 (some imports from Canada)
- Price of CH_4 has fallen by a factor of 2 since 2008
- Concerns about shale gas production fall into four categories:
  - **Earthquakes**
  - **Contamination of ground water**
  - **Air quality (surface O_3 precursors)**
  - **Climate (fugitive release of CH_4)**
- Former U.S. Dept of Energy Secretary David Chu (served 21 Jan 2009 to 22 April 2013) commissioned two reports from the Shale Gas Subcommittee of the Secretary of Energy Advisory Board (SEAB) to “identify measures that can be taken to reduce the environmental impact and to help assure the safety of shale gas production”
- First report (11 Aug 2011) identified 20 action items (see table, next slide)
- Second report (18 Nov 2011) outlined recommendations for implementation of action items
- EPA issued new standards for the oil and natural gas industry on 14 Jan 2015
- Notably absent is extended discussion of earthquake issue

https://www.epa.gov/controlling-air-pollution-oil-and-natural-gas-industry

Shale Gas Production & Public Policy

- First report (11 Aug 2011) identified 20 action items

1. Improve public information about shale gas operations
2. Improve communication among state and federal regulators
3. Improve air quality: 4. Industry to measure CH_4 & other air pollutants 5. Launch federal interagency effort to establish GHG footprint over shale gas extraction life cycle 6. Encourage companies & regulators to reduce emissions using proven technologies & best practices
7. Protect water quality: 8. Measure and report composition of water stock 9. Manifest all transfers of water among different locations 10. Adopt best practices for well casing, cementing, etc & conduct micro-seismic surveys to “assure that hydraulic growth is limited to gas producing formations” 11. Field studies of possible CH4 leakage from shale gas wells to water reservoirs 12. Obtain background water quality measurements (i.e., CH_4 levels in nearby waters prior to drilling)

Protect water quality (cont.): 13. Measure and report composition of water stock
14. Disclosure of fracking fluid composition
15. Reduce use of diesel fuel for surface power
16. Manage short-term & cumulative impacts on communities & wild life: sensitive areas can be deemed off-limit to drilling and support infrastructure through an appropriate science based process
17. Create shale gas industry organiz. to promote best practice, giving priority attention to: 18. Air: emission measurement & reporting at various points in production chain 19. Water: Pressure testing of cement casing & state-of-the-art technology to confirm formation isolation
20. Increase R & D support from Administration & Congress to promote technical advances such as the move from single well to multiple-well pad drilling

https://www.edf.org/sites/default/files/11903_Embargoed_Final_90_day_Report%20.pdf

Concern #1: Earthquakes

2012 Seismological Society of America meeting

ARE SEISMICITY RATE CHANGES IN THE MIDCONTINENT NATURAL OR MANMADE?

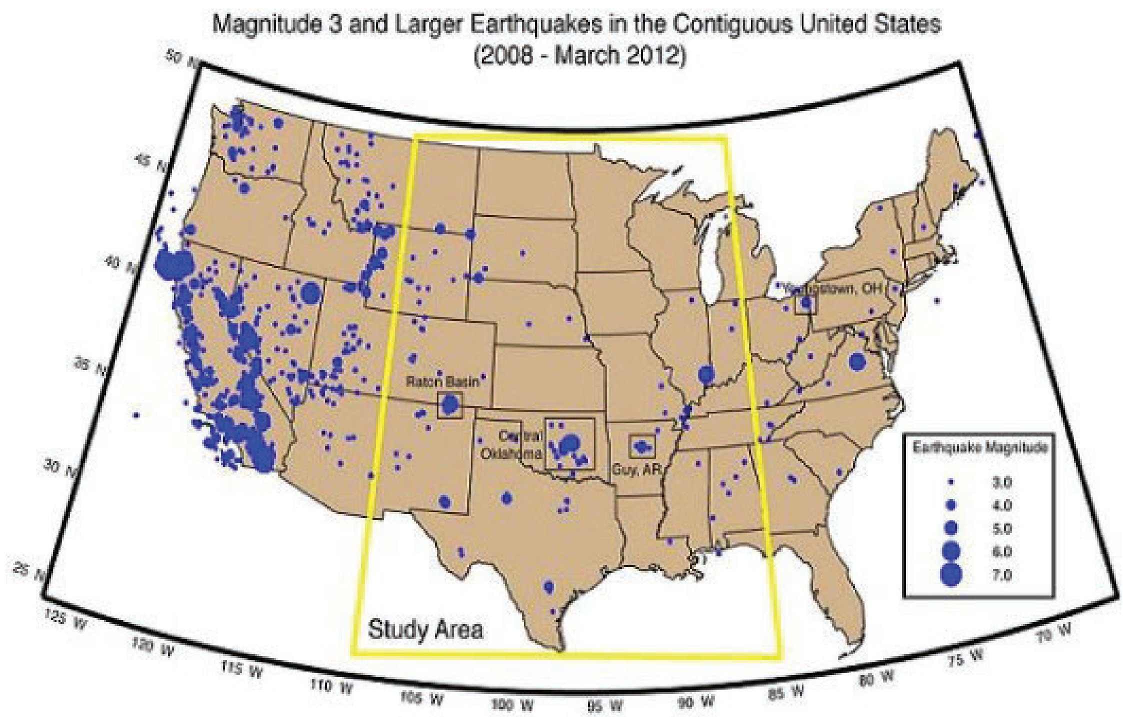
ELLSWORTH, W. L., US Geological Survey, Menlo Park, CA; HICKMAN, S. H., US Geological Survey, Menlo Park, CA; LLEONS, A. L., US Geological Survey, Menlo Park, CA; MCGARR, A., US Geological Survey, Menlo Park, CA; MICHAEL, A. J., US Geological Survey, Menlo Park, CA; RUBINSTEIN, J. L., US Geological Survey, Menlo Park, CA

A remarkable increase in the rate of M 3 and greater earthquakes is currently in progress in the US midcontinent. The average number of M >= 3 earthquakes/year increased starting in 2001, culminating in a six-fold increase over 20th century levels in 2011. Is this increase natural or manmade? To address this question, we take a regional approach to explore changes in the rate of earthquake occurrence in the midcontinent (defined here as 85° to 108° West, 25° to 50° North) using the USGS Preliminary Determination of Epicenters and National Seismic Hazard Map catalogs. These catalogs appear to be complete for M >= 3 since 1970. From 1970 through 2000, the rate of M >= 3 events averaged 21 +- 7.6/year in the entire region. This rate increased to 29 +- 3.5 from 2001 through 2008. In 2009, 2010 and 2011, 50, 87 and 134 events occurred, respectively. The modest increase that began in 2001 is due to increased seismicity in the coal bed methane field of the Raton Basin along the Colorado-New Mexico border west of Trinidad, CO. The acceleration in activity that began in 2009 appears to involve a combination of source regions of oil and gas production, including the Guy, Arkansas region, and in central and southern Oklahoma. Horton, et al. (2012) provided strong evidence linking the Guy, AR activity to deep waste water injection wells. In Oklahoma, the rate of M >= 3 events abruptly increased in 2009 from 1.2/year in the previous half-century to over 25/year. This rate increase is exclusive of the November 2011 M 5.6 earthquake and its aftershocks. A naturally-occurring rate change of this magnitude is unprecedented outside of volcanic settings or in the absence of a main shock, of which there were neither in this region. While the seismicity rate changes described here are almost certainly manmade, it remains to be determined how they are related to either changes in extraction methodologies or the rate of oil and gas production.

Wednesday, April 18th / 3:45 PM Oral / Pacific Salon 4 & 5

Concern #1: Earthquakes

Ellsworth's study area:



http://www.esa.org/esablog/ecology-in-the-news/increase-in-magnitude-3-earthquakes-likely-caused-by-oil-and-gas-production-but-not-fracking

Concern #1: Earthquakes

Ellsworth's study suggests:

- Deep waste water injection wells are the culprit, especially if in the vicinity of a fault
- Increased fluid pressure in pores of the rock can reduce the slippage strain between rock layers
- Speed of pumping is important (slow better than fast)

USGS testimony:

- On 19 June 2012, Dr. William Leath of the U.S. Geological Survey testified before the U.S. Senate Committee on Energy and Natural Resources, stating:

> The injection and production practices employed in these technologies have, to varying degrees, the potential to introduce earthquake hazards
>
> Since the beginning of 2011 the central and eastern portions of the United States have experienced a number of moderately strong earthquakes in areas of historically low earthquake hazard. These include M4.7 in central Arkansas on Feb27, 2011; M5.3 near Trinidad, Colorado on Aug 23, 2011; M5.8 in central Virginia also on Aug 23, 2011; … M5.6 in central Oklahoma on Nov 6, 2011 … and M4.8 in east Texas on May 17, 2012. Of these *only the central Virginia earthquake is unequivocally a natural tectonic earthquake.*
>
> In all other cases, there is scientific evidence to at least raise the possibility that the earthquakes were induced by wastewater disposal or other oil- and gas-related activities.
>
> USGS scientists documented a seven-fold increase since 2008 in the seismicity of the central U.S., an increase largely associated with areas of wastewater disposal from oil, gas & coalbed methane production

First three bullets:
http://www.esa.org/esablog/ecology-in-the-news/increase-in-magnitude-3-earthquakes-likely-caused-by-oil-and-gas-production-but-not-fracking
USGS testimony:
http://www.usgs.gov/congressional/hearings/docs/leith_19june2012.DOCX

Concern #1: Earthquakes

28 Jan 2015 Washington Post

The Washington Post

Search

Economy

Oklahoma worries over swarm of earthquakes and connection to oil industry

GUTHRIE, Okla. – The earthquakes come nearly every day now, cracking drywall, popping floor tiles and rattling kitchen cabinets. On Monday, three quakes hit this historic land-rush town in 24 hours, booming and rumbling like the end of the world.

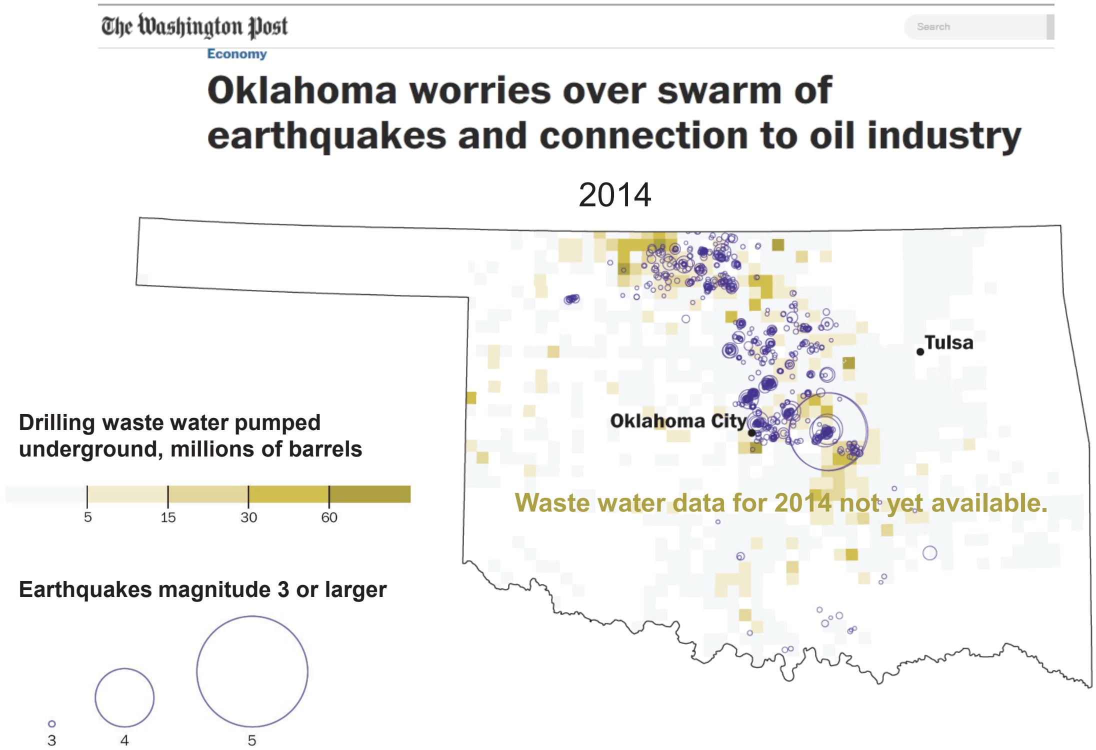
"After a while, you can't even tell what's a pre-shock or an after-shock. The ground just keeps moving," said Jason Murphey, 37, a Web developer who represents Guthrie in the state legislature. "People are so frustrated and scared. They want to know the state is doing something."

What to do about the plague of earthquakes is, however, very much an open question in Oklahoma. Last year, 567 quakes of at least 3.0 magnitude rocked a swath of counties from the state capital to the Kansas line, alarming a populace long accustomed to fewer than two quakes a year.

Scientists implicated the oil and gas industry — in particular, the deep wastewater disposal wells that have been linked to a dramatic increase in seismic activity across the central United States. But in a state founded on oil wealth, officials have been reluctant to crack down on an industry that accounts for a third of the economy and one in five jobs.

Concern #1: Earthquakes

28 Jan 2015 Washington Post



http://www.washingtonpost.com/graphics/national/oklahoma-earthquakes/

Concern #1: Earthquakes

7 Nov 2016 USA Today

USA TODAY

Search

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Oklahoma earthquake reignites concerns that fracking wells may be the cause

Rick Jervis, USA TODAY 5:34 p.m. ET Nov. 7, 2016

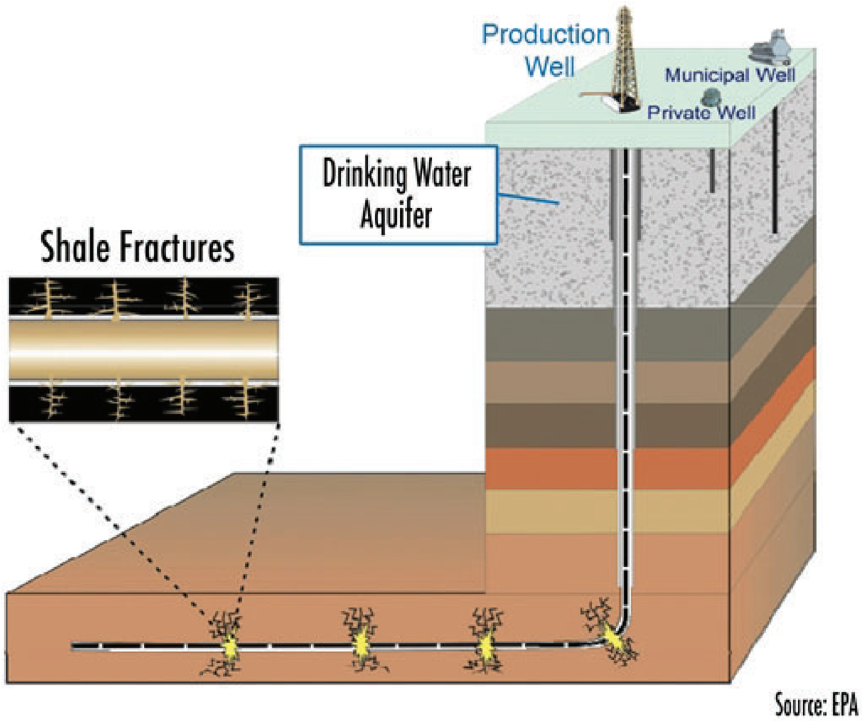
(Photo: Jim Beckel, AP)

A 5.0 magnitude earthquake that rattled north-central Oklahoma Sunday was only the sixth of that strength in state history and has reawakened concerns that oil and gas activity could be causing the tremors.

The temblor, which occurred around 7:44 p.m. Sunday about a mile west of Cushing, Okla., sheared bricks off buildings, caused structural damage to homes and forced local schools to close Monday. Around 40 residents were evacuated from a retirement home and sheltered at a local gymnasium.

It was only the sixth 5.0 magnitude or higher to strike Oklahoma since 1882, said George Choy, a geophysicist with the U.S. Geological Survey in Boulder, Colo. Three of those larger quakes occurred this year. The strongest ever recorded in Oklahoma

Concern #2: Water Quality



http://savethewater.org/wp-content/uploads/2013/02/Stock-Save-the-water-New-Study-Predicts-Fracking-Fluids-Will-Seep-Into-Aquifers-Within-Years.jpg

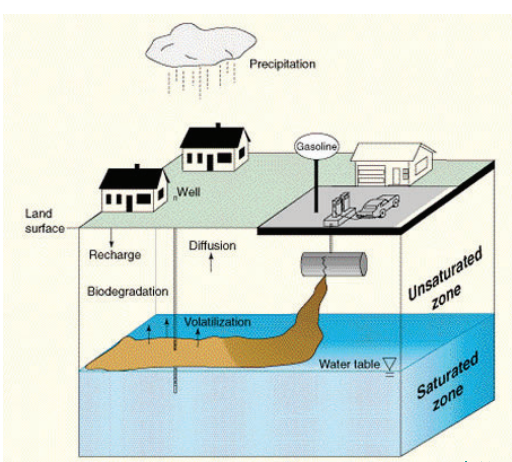
Concern #2: Water Quality

Spread of contaminants in ground water determined by

Dispersion – differential flow of water through small openings (pores) in soil

Diffusion – random molecular (Brownian) motion of molecules in water

Sorption – some chemicals may be *absorbed by soil* while others are *adsorbed* (adhere to surfaces)



Highly diffusive chemicals (such as MTBE) can spread quickly even though ground water is relatively motionless.

MTBE: Methyl tert-butyl ether; $(CH_3)_3COCH_3$

https://www.cancer.org/cancer/cancer-causes/mtbe.html

http://toxics.usgs.gov/topics/gwcontam_transport.html

Concern #2: Water Quality

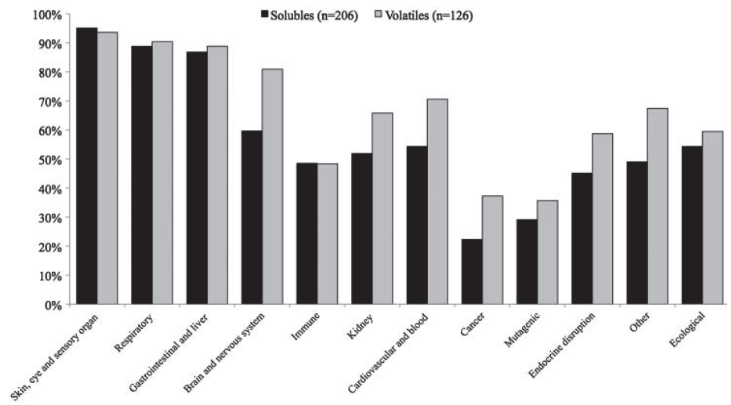
Typical Chemical Additives Used in Frac Water

Compound	Purpose	Common application
Acids	Helps dissolve minerals and initiate fissure in rock (pre-fracture)	Swimming pool cleaner
Sodium Chloride	Allows a delayed breakdown of the gel polymer chains	Table salt
Polyacrylamide	Minimizes the friction between fluid and pipe	Water treatment, soil conditioner
Ethylene Glycol	Prevents scale deposits in the pipe	Automotive anti-freeze, deicing agent, household cleaners
Borate Salts	Maintains fluid viscosity as temperature increases	Laundry detergent, hand soap, cosmetics
Sodium/Potassium Carbonate	Maintains effectiveness of other components, such as crosslinkers	Washing soda, detergent, soap, water softener, glass, ceramics
Glutaraldehyde	Eliminates bacteria in the water	Disinfectant, sterilization of medical and dental equipment
Guar Gum	Thickens the water to suspend the sand	Thickener in cosmetics, baked goods, ice cream, toothpaste, sauces
Citric Acid	Prevents precipitation of metal oxides	Food additive; food and beverages; lemon juice
Isopropanol	Used to increase the viscosity of the fracture fluid	Glass cleaner, antiperspirant, hair coloring

Source: DOE, GWPC: Modern Gas Shale Development in the United States: A Primer (2009).

http://www.exxonmobilperspectives.com/2011/08/25/fracking-fluid-disclosure-why-its-important/

% of the 632 disclosed chemicals that are either water soluble (206) or volatize (126)

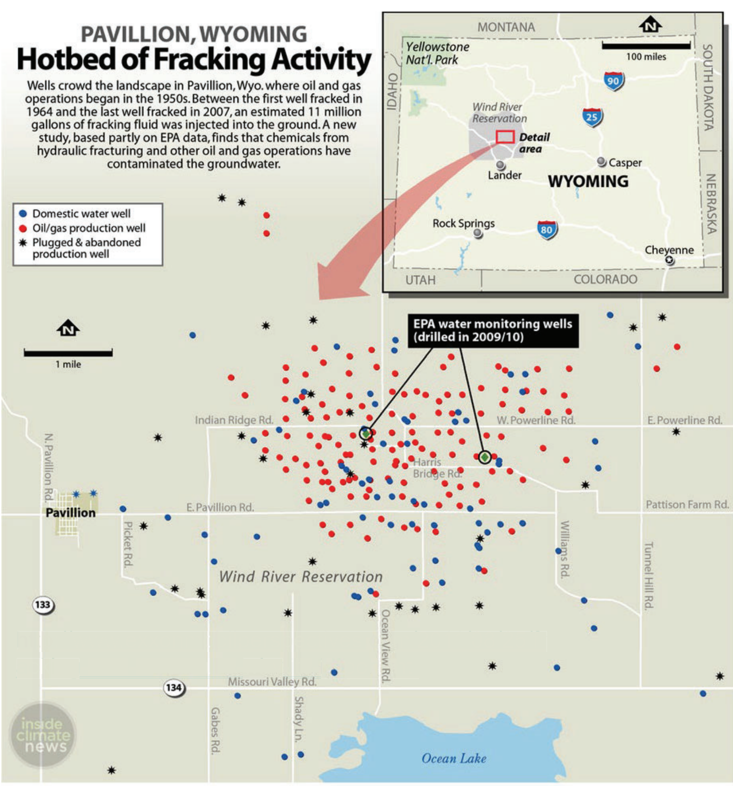


http://www.tandfonline.com/doi/pdf/10.1080/10807039.2011.605662

Many chemicals used in fracking have "everyday" uses …

We control how chemicals are used in homes, not the case for fracking

Concern #2: Water Quality



SOURCE: *Environmental Science & Technology*, March 18, 2016 PAUL HORN / InsideClimate News

Wyoming:

- 25000 wells
- Study area:
  - 11 million gallons of various fluids including hydrochloric acid and methanol, many of which are neurotoxins and carcinogens, pumped into the ground
  - Companies frequently fracked at much shallower depths than previously thought, sometimes very close to wells
  - High levels of diesel-related organic compounds & acids were found... "it seems implausible this is due to natural conditions," DiGiulio said. "When you look at the compounds, it's a virtual fingerprint of chemicals used in the field."

https://insideclimatenews.org/news/29032016/fracking-study-pavillion-wyoming-drinking-water-contamination-epa

Fluid composition: Concern #2: Water Quality

April 2011: www.fracfocus.org created as central disclosure registry for industry use

Currently, 26 states require drillers to report to FracFocus

Searchable database & Google map interface allow user to obtain info for individual wells

http://fracfocus.org/welcome

Fluid composition: Concern #2: Water Quality

April 2011: www.fracfocus.org created as central disclosure registry for industry use

As of January 2016, 28 states require the disclosure of some, but not all, chemicals used during fracking & 23 use Frac Focus

Searchable database & Google map interface allow user to obtain info for individual wells

Harvard Law School study highlights flaws in this system:

1) **Timing of Disclosures: Site does not notify States if company submits late**
2) **Substance of Disclosure: Site does not provide state specific forms, no minimum reporting standards**
3) **Nondisclosures: Companies not required to disclose chemicals if they are considered a "trade secret"**

~20% of all chemicals not reported.

http://www.eenews.net/assets/2013/04/23/document_ew_01.pdf

See also http://www.factcheck.org/2017/04/facts-fracking-chemical-disclosure

Fluid composition: Concern #2: Water Quality

http://fracfocus.org/welcome

Fluid composition: Concern #2: Water Quality

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ECONOMY

March 15, 2017 9:55 PM
Associated Press

Trump Administration Halts Obama-Era Rule on Fracking on Public Land

WASHINGTON — The Trump administration is rolling back an Obama administration rule requiring companies that drill for oil and natural gas on federal lands to disclose chemicals used in hydraulic fracturing, better known as fracking.

The administration said in court papers Wednesday that it is withdrawing from a lawsuit challenging the Obama-era rule and will begin a new rule-making process later this year.

The Interior Department issued the rule in March 2015, the first major federal regulation of fracking, the controversial drilling technique that has sparked an ongoing boom in natural gas production but raised widespread concerns about possible groundwater contamination and even earthquakes.

The rule has been on hold since last year after a judge in Wyoming ruled that federal regulators lack congressional authority to set rules for fracking.

FracFocus.org started in 2011

The rule relies on an online database used by at least 16 states to track the chemicals used in fracking operations. The website, FracFocus.org, was formed by industry and intergovernmental groups in 2011 and allows users to gather well-specific data on tens of thousands of drilling sites across the country.

Companies would have had to disclose the chemicals they use within 30 days of the fracking operation.

Fracking involves pumping huge volumes of water, sand and chemicals underground to split open rocks to allow oil and gas to flow.

http://www.voanews.com/a/trump-administration-halts-obama-era-rule-on-racking-on-public-land/3768474.html

The Show Must Go On

The New York Times

By Eric Lipton and Hiroko Tabuchi

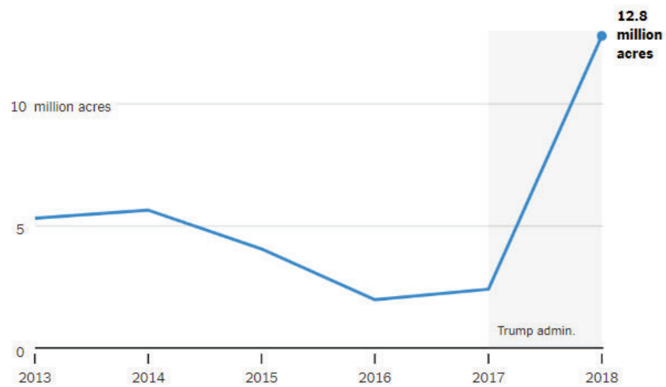
Oct. 27, 2018

Driven by Trump Policy Changes, Fracking Booms on Public Lands

The administration is auctioning off millions of acres of drilling rights and rolling back regulations, raising environmental concerns in states like Wyoming.

Federal Land For Sale

The amount of federal land offered at oil and gas lease sales has greatly increased under the Trump administration.



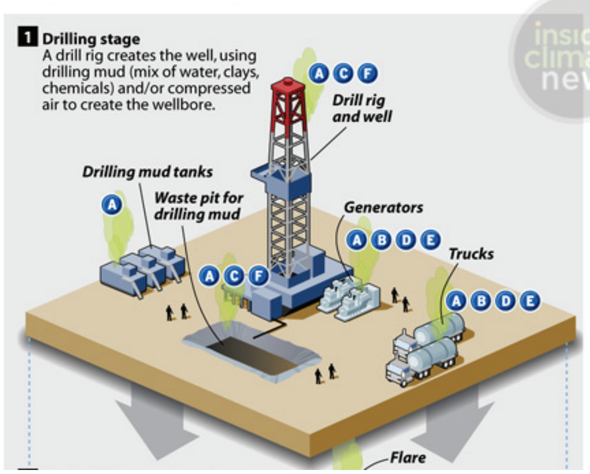
https://www.nytimes.com/2018/10/27/climate/trump-fracking-drilling-oil-gas.html

Concern #3: Air Quality

- Fracking releases a lovely mixture of air pollutants

Air Emissions from Oil and Gas Development in the Eagle Ford

There are more than 7,000 oil and gas wells in the Eagle Ford Shale, and Texas regulators have approved another 5,500. Most of them, like the one shown here, are oil wells that also produce condensate and natural gas. Developing these resources releases various air pollutants, some of which are shown in this simplified diagram.



Emission Sources

The pollutants come from a number of sources, including the diesel- or natural gas-fueled equipment, the oil and gas itself, and leaks from storage devices. The emissions' actual and relative amounts vary widely based on operator practices and local geology. The emissions occur regularly in some cases, but are intermittent in others.

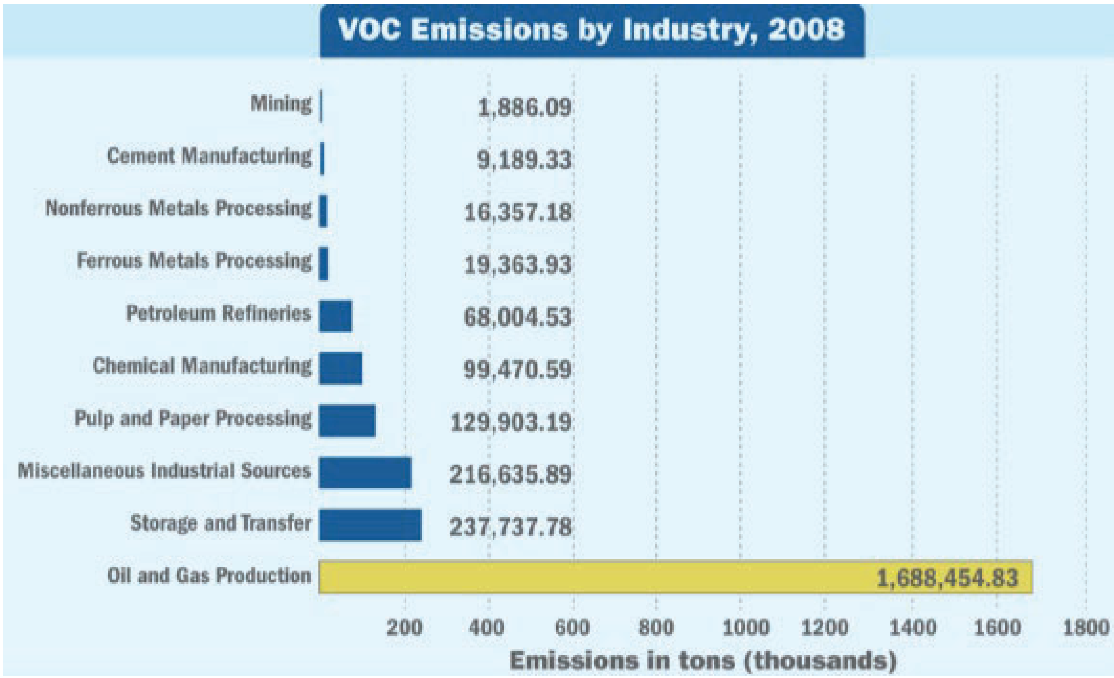
CHEMICAL	WHAT IT IS	WHAT IT DOES
A VOCs	Volatile organic compounds including benzene, formaldehyde	There are dozens of VOCs that make people sick. Some can cause cancer. VOCs react with NOx to form ozone, a respiratory irritant and greenhouse gas.
B PM	Particulate matter	Affects the heart and lungs.
C CH_4	Methane	Main component of natural gas. Much more powerful than CO_2 as a greenhouse gas.
D CO_2	Carbon dioxide	Major greenhouse gas.
E NOx	Nitrogen oxides	Reacts with VOCs to create ozone.
F H_2S	Hydrogen sulfide	Toxic gas found in some gas fields. Causes illness and death at certain concentrations.

Fugitive emissions: pipelines, valves, pneumatic devices etc. leak methane, VOCs, H_2S and CO_2 throughout the entire process.

https://insideclimatenews.org/infographics?topic=All&project=&keywords=&page=16

Concern #3: Air Quality

- Fracking is a major contributor to anthropogenic VOCs



https://ehp.niehs.nih.gov/120-a272/

Concern #3: Air Quality

- Fracking is a major contributor to anthropogenic VOCs

VOC Emissions by Sector, 2008

Sector	Emissions (in tons)
Vegetation and Soil	31,743,795.67
Solvent Utilization	3,299,117.52
On-Road Vehicles	3,055,361.80
Wildfires	2,847,133.50
Off-Road Vehicles	2,492,752.86
Prescribed Fires	1,696,594.50
Oil and Gas Production	1,688,454.83
Gas Stations	643,277.44
Residential Fuel Combustion	367,023.10
Storage and Transport	237,737.78
Miscellaneous Nonindustrial Sources	226,996.24
Miscellaneous Industrial Sources	216,635.89
Waste Disposal	179,769.43
Pulp and Paper Processing	129,903.19
Chemical Manufacturing	99,470.59
Bulk Gasoline Terminals	92,808.65
Agriculture/Livestock Waste	92,448.42
Industrial Fuel Combustion	80,142.47
Petroleum Refineries	68,004.53
Agricultural Field Burning	53,269.51
Locomotives	44,198.42
Electric Utility Fuel Combustion	43,246.70
Ferrous and Nonferrous Metals Processing	35,721.12
Aircraft	35,445.09
Commercial Marine Vessels	20,645.64
Commercial/Institutional Fuel Combustion	13,454.01
Commercial Cooking	13,366.75
Cement Manufacturing	9,189.33
Mining	1,886.09
Construction Dust	16.63

Source: U.S. Environmental Protection Agency[8]

https://ehp.niehs.nih.gov/120-a272/

Tropospheric Ozone Production

$$
\begin{aligned}
CO + OH &\rightarrow CO_2 + H \\
H + O_2 + M &\rightarrow HO_2 + M \\
HO_2 + NO &\rightarrow OH + NO_2 \\
NO_2 + h\nu &\rightarrow NO + O \\
O + O_2 + M &\rightarrow O_3 + M \\
\text{Net:}\quad CO + 2\,O_2 &\rightarrow CO_2 + O_3
\end{aligned}
$$

$$
\begin{aligned}
RH + OH &\rightarrow R + H_2O \\
R + O_2 + M &\rightarrow RO_2 + M \\
RO_2 + NO &\rightarrow RO + NO_2 \\
RO + O_2 &\rightarrow HO_2 + R'CHO \\
HO_2 + NO &\rightarrow OH + NO_2 \\
2 \times \quad NO_2 + h\nu &\rightarrow NO + O \\
2 \times \quad O + O_2 + M &\rightarrow O_3 + M \\
\text{Net:}\quad RH + 4O_2 &\rightarrow R'CHO + H_2O + 2\,O_3
\end{aligned}
$$

VOC: Volatile Organic Compounds

Produced by trees and fossil fuel vapor

Strong source of HO_x (OH & HO_2) & O_3 (depending on NO_x levels)

Examples of RH and R'CHO : CH_4 (methane) $\rightarrow$ CH_2O (formaldehyde)
: C_2H_6 (ethane) $\rightarrow$ CH_3CHO (acetaledhyde)
: C_3H_8 (propane) $\rightarrow$ CH_3COCH_3 (acetone)

Ozone Production "limited" by $k[HO_2][NO] + \Sigma\, k_i\, [RO_2]_i\, [NO]$

Concern #3: Air Quality (Case Study: Wyoming)

http://deq.state.wy.us/out/downloads/UGRBTaskForce02212012WDEQAQD.pdf

Concern #3: Air Quality (Case Study: Wyoming)

2011 Preliminary Data

(as of 3/20/2011)

10 Advisory Days

- February 28
- March 1, 2, 4, 5, 10, 13, 14, 15, 18

13 Elevated 8-Hour Ozone Days

- February 14, 15, 21
- March 1, 2, 3, 5, 6, 9, 10, 12, 14, 15

2011 Preliminary Raw Data (as of 3/20/2011)
Monitored Ozone Top Four 8-Hour Daily Maximum (ppb)

Wyoming Range	Pinedale	Daniel 2011 (2008)	Boulder 2011 (2008)	Juel Spring
84	90	85 (76)	124 (122)	95
81	84	80 (76)	121 (104)	86
80	81	77 (74)	116 (102)	85
73	77	76 (74)	104 (101)	77

NOTE: Three (3) year average of 4th high 8-Hour Daily Maximum is compared to NAAQS.

http://deq.state.wy.us/out/downloads/March22PublicMtg_2011Ozone_WDEQ.pdf

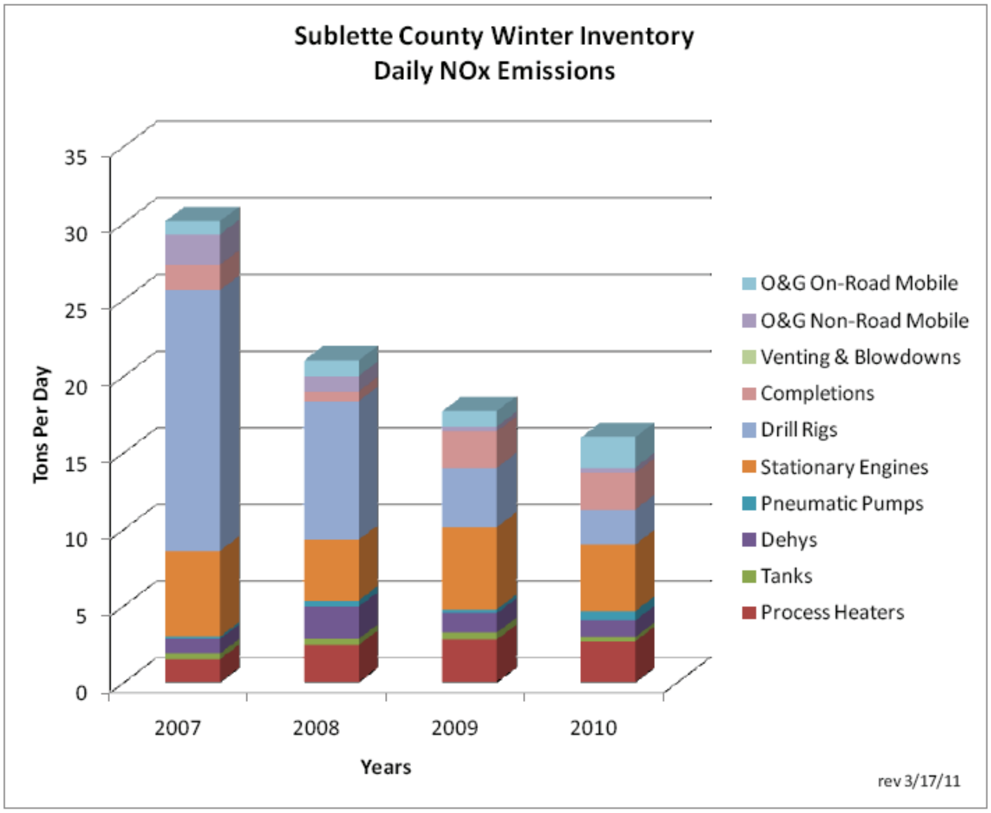
Concern #3: Air Quality (Case Study: Wyoming)

Sublette County Ozone & Weather History (2005 – 2011)

- Mid-January – March 2005
  - 8 Elevated 8-Hour O_3 Days > 75 ppb
- Mid-January – March 2006
  - 2 Elevated 8-Hour O_3 Days > 75 ppb
- Mid-January – March 2007
  - 0 Elevated 8-Hour O_3 Days > 75 ppb
  - Meteorological conditions not conducive to formation of elevated ozone levels.
- Mid-January – March 2008
  - 14 Elevated 8-Hour O_3 Days > 75 ppb
  - Higher magnitude than previous years
  - Met. conditions conducive to formation of elevated ozone levels.
- Mid-January – March 2009
  - 0 Elevated 8-Hour O_3 Days > 75 ppb
  - Limited met. conditions conducive to formation of elevated ozone levels.
- Mid-January – March 2010
  - 0 Elevated 8-Hour O_3 Days > 75 ppb
  - Met. conditions not conducive to formation of elevated ozone levels.
- Mid-January – March 2011
  - 13 Elevated 8-Hour O_3 Days > 75 ppb
  - Higher magnitude than previous years
  - Met. conditions conducive to formation of elevated ozone levels.

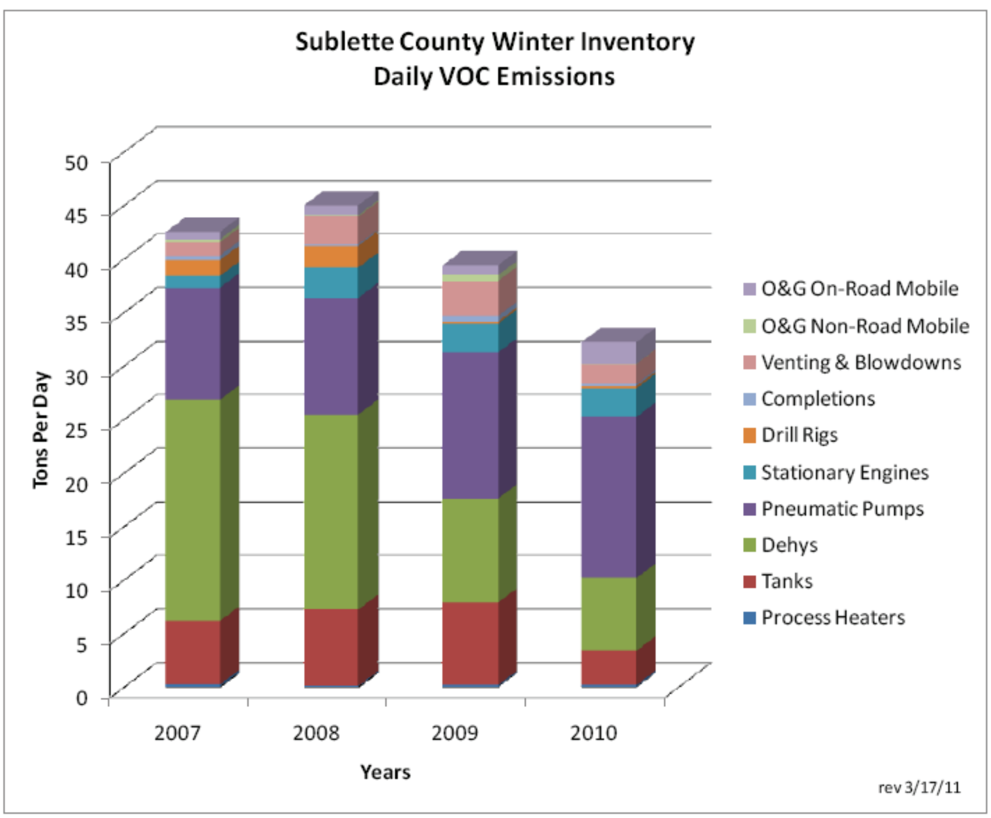
http://deq.state.wy.us/out/downloads/March22PublicMtg_2011Ozone_WDEQ.pdf

Concern #3: Air Quality (Case Study: Wyoming)



http://www.shalegas.energy.gov/resources/071311_corra.pdf

Concern #3: Air Quality (Case Study: Wyoming)



http://www.shalegas.energy.gov/resources/071311_corra.pdf

Concern #3: Air Quality (Case Study: Wyoming)

MENU Star Tribune News Obituaries Sports E-edition Buy & Sell 40°

Dramatic ozone spikes puzzle regulators, locals in Wyoming gas field

Heather Richards 307-266-0592, Heather.Richards@trib.com

Joel Bousman wasn't sure if ozone would be a problem Friday, despite a warning from the state. The snow covered the sage brush and the wind was less than 10 miles per hour — both bad signs. On the other hand, it had been overcast most of the day at the Sublette County commissioner's ranch near Boulder — a small community about 12 miles southeast of Pinedale, within view of the Wind River Mountains.

You need the right mix of factors to create ground-level ozone: sunlight, snow cover, little to no wind and, of course, emissions from the oil and gas industry — which arrived in force more than a decade ago in the Jonah and Pinedale gas field.

And this year the factors have been right more often than usual.

Friday was the 12th ozone action day of the season — a warning system from the Wyoming Department of Environmental Quality that forces industry to pull back when conditions for ozone are expected. It's a record number for recent years, and another action day was forecast for Saturday.

But there's something more troubling in the case of the Boulder area: ground-level ozone is regularly forming despite precautions. Breathing it in can cause a variety of health problems, from chest pain to reduced lung function.

For reasons still unclear to state regulators, in one corner of the Upper Green, the rules and regulations that reversed an air quality crisis more than a decade ago haven't been enough. "We don't have all the answers, yet," said Keith Guille, spokesman for the state Department of Environmental Quality. "It's definitely not being ignored. We understand that the public is concerned, as we are."

https://trib.com/business/energy/dramatic-ozone-spikes-puzzle-regulators-locals-in-wyoming-gas-field/article_82837053-a70d-5591-b4a4-e83c24e8565b.html

Concern #3: Air Quality (Colorado)

NEWS > ENVIRONMENT

Colorado lets oil and gas companies pollute for 90 days without federally required permits that limit emissions

State health officials say they'll review whether exemption for fossil fuels industry violates Clean Air Act

By **BRUCE FINLEY** | bfinley@denverpost.com | The Denver Post April 7, 2019 at 6:00 am

Michael Ciaglo, Special to the Denver Post

Stephanie Nilsen, left, and her partner Janis Butterfield walk down the road next to their small ranch — and in front of Extraction Oil and Gas' Trott pad — on Thursday, March 28, 2019, in Berthoud. Butterfield and Nilsen live about 1,000 feet south of the oil and gas site, which they say emitted harmful pollution last year. The site is one of nearly 200 in Colorado that was allowed to pollute without a federally required permit limiting emissions for its first 90 days.

Colorado public health officials have let oil and gas companies begin drilling and fracking for fossil fuels at nearly 200 industrial sites across the state without first obtaining federally required permits that limit how much toxic pollution they can spew into the air.

Air pollution control officials at the Colorado Department of Public Health and Environment allow the industry to emit hundreds of tons of volatile organic chemicals, cancer-causing benzene and other pollutants using an exemption tucked into the state's voluminous rules for the industry — rules that former Gov. John Hickenlooper, state leaders and industry officials long have hailed as the toughest in the nation.

They rely on this 27-year-old state exemption to give oil and gas companies 90 days to pollute, then assess what they need from Colorado regulators before applying for the air permits that set limits on emissions from industrial sites.

"It is a loophole that allows pollution at some of the times when the pollution is the most extreme," said U.S. Rep. Diana DeGette, D-Denver, who chairs a congressional panel that oversees the Environmental Protection Agency.

https://www.denverpost.com/2019/04/07/colorado-oil-gas-air-pollution

Concern #4: Climate

Combustion of 1 gram of CH_4 results of 50.1 kJ of energy
Combustion of 1 gram of C results in 32.8 kJ of energy

Alas, coal is not pure carbon in the real world. Rather, notational formula for coal is $C_{135}H_{96}O_9NS$ (page 162 of Chemistry in Context): i.e., coal has a carbon content of 85% by mass.

Therefore, we'd state:

natural gas is actually 1.33 × 50.1 / (32.8/0.85) = 1.73; i.e., 73% more efficient than coal.

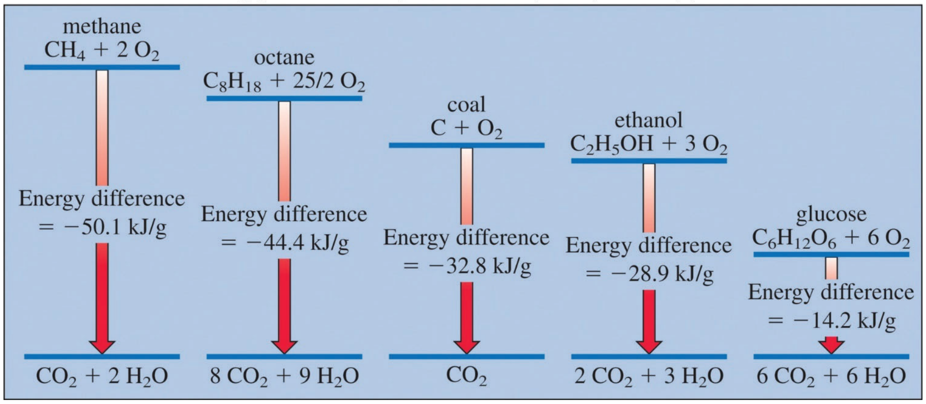


Fig 4.26. Energy differences (in kJ/g) for the combustion of methane (CH_4), n-octane (C_8H_{18}), coal (assumed to be pure carbon), ethanol (C_2H_5OH), and wood (assumed to be glucose).

Concern #4: Climate

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Break even point, for leakage of CH_4

First, would like GWP on a per molecule basis, rather than a per mass basis

GHG	IPCC (2013) per mass	IPCC (2013) per molecule
100 Year Time Horizon		
CH_4	28	
20 Year Time Horizon		
CH_4	84	

Next, must balance energy gain from combustion of CH_4 relative to coal versus climate penalty.

If CH_4 is inadvertently released, then for the per molecule GWP on 100-year time horizon, break even point is:

CO_2 + Leak Fraction × 10.2 = 1.73 × CO_2
Leak Fraction =
⇒ leakage of of CH_4 causes climate penalty to balance climate benefit

Concern #4: Climate

Combustion of 1 gram of CH_4 results of 50.1 kJ of energy
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GHG	IPCC (2013) per mass	IPCC (2013) per molecule
100 Year Time Horizon		
CH_4	28	
20 Year Time Horizon		
CH_4	84	

Next, must balance energy gain from combustion of CH_4 relative to coal versus climate penalty.

If CH_4 is inadvertently released, then for the per molecule GWP on 20-year time horizon, break even point is:

CO_2 + Leak Fraction × 30.5 = 1.73 × CO_2
Leak Fraction =
⇒ leakage of of CH_4 causes climate penalty to balance climate benefit

Concern #4: Climate

Break Even Points: **7.2%** (100-yr time horizon) and **2.4%** (20-yr time horizon)

Leakage (%)	Region	Method	Citation
4.2 – 8.4	Bakken Shale, North Dakota	Aircraft Sampling	Peischel et al. (2016)
1.0 – 2.1	Haynesville Shale, Louisiana and Texas	Aircraft Sampling	Peischel et al. (2015)
1.0 – 2.8	Fayetteville Shale, Arkansas		
0.18 – 0.41	Marcellus Shale, Pennsylvania		
9.1 ± 6.2	Eagle Ford, Texas	Satellite Sampling	Schneising et al. (2014)
10.1 ± 7.3	Bakken Shale, North Dakota		
0.42	190 production sites including Gulf Coast, Rocky Mountain, and Appalachia	In situ within facility grounds	Allen et al. (2013)
6.2 – 11.7	Unitah County, Utah	Aircraft sampling	Karion et al. (2013)
2.3 – 7.7	Julesburg Basin, Denver, Colorado	Tall tower and ground level mobile sampling	Pétron et al. (2012)

Table 4.4 Estimates of % of CH_4 leakage relative to production in the US, selected studies

Paris Climate Agreement, Beacon of Hope