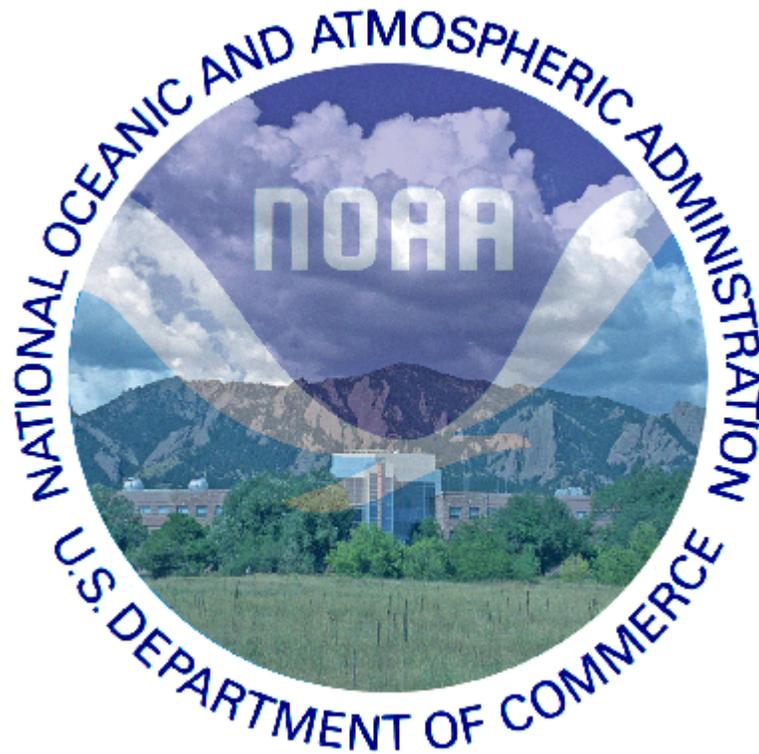


# Global Monitoring Division

## Theme 3 – Air Quality



Contents:

- 4 Presentations

# Air Quality and Regional Studies

Russ Schnell

- The Global Monitoring Division primarily produces **long term measurements** of the background atmosphere.
- **But, understanding shorter term data are required to understand the longer term measurements and trends.**
- **Following are snippets on regional gas and aerosol transport, tropospheric ozone, forest fire smoke, and Arctic methane.**



## Drivers of Air Quality Studies

- **How is intercontinental transport influencing air quality over the United States?**
- **How does the production and extraction of fossil fuels affect air quality and background concentrations?**
- **How does the cleansing capacity of the atmosphere vary over time and is it sensitive to anthropogenic emissions?**

***Following talks and posters will address the above and related topics.***



# Beijing Air Pollution Before and After Cold Front Passage, February 27, 2013

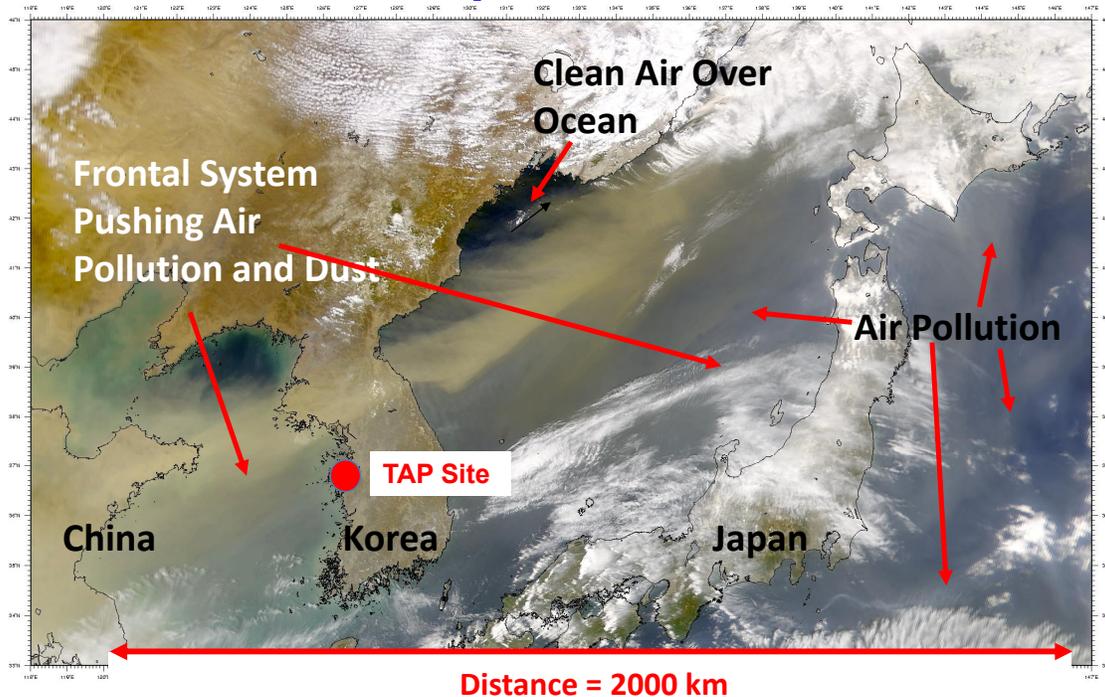


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## Dust and Air Pollution Flowing Out of Asia, April 2001

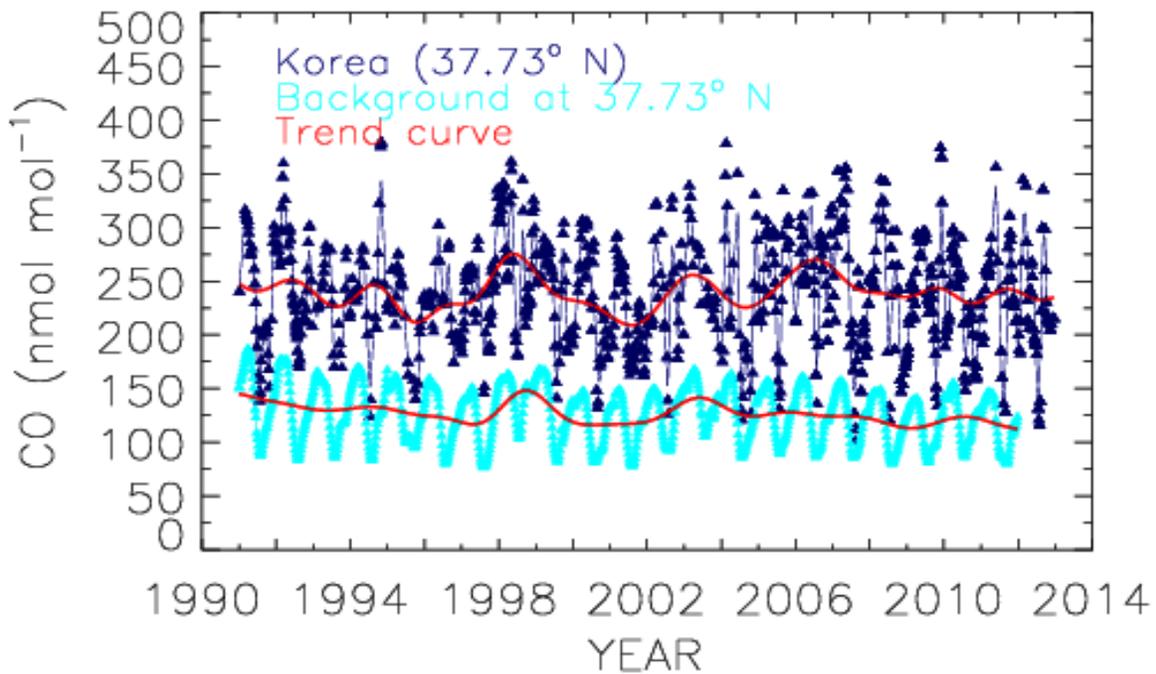


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# CO From China May Have Increased in the Past Decade



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## Mauna Loa Aerosol Samples: Passage of a Pollution/Dust Event, April 1997

Air Pollution  
Pushed by the  
Front

24 hour  
samples

Air Pollution  
and Dust Mix

In the  
Dust

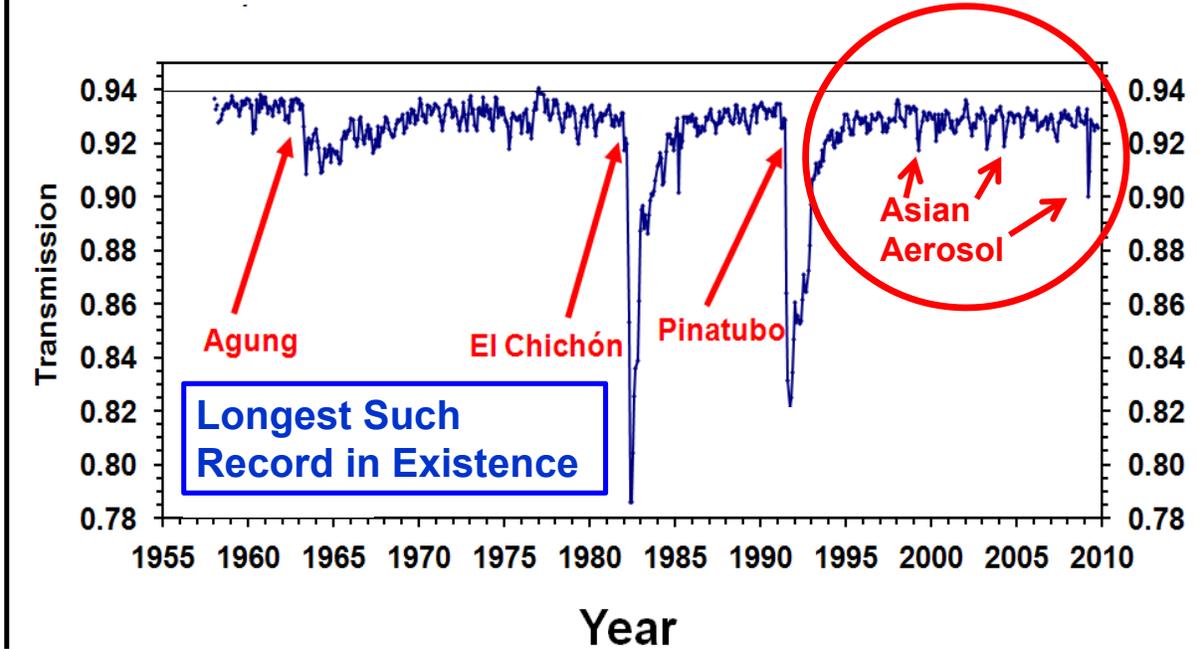


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# Annual Cycle of Dust and Air Pollution from Asia at Mauna Loa Observatory

## Mauna Loa Clear Sky Solar Transmission

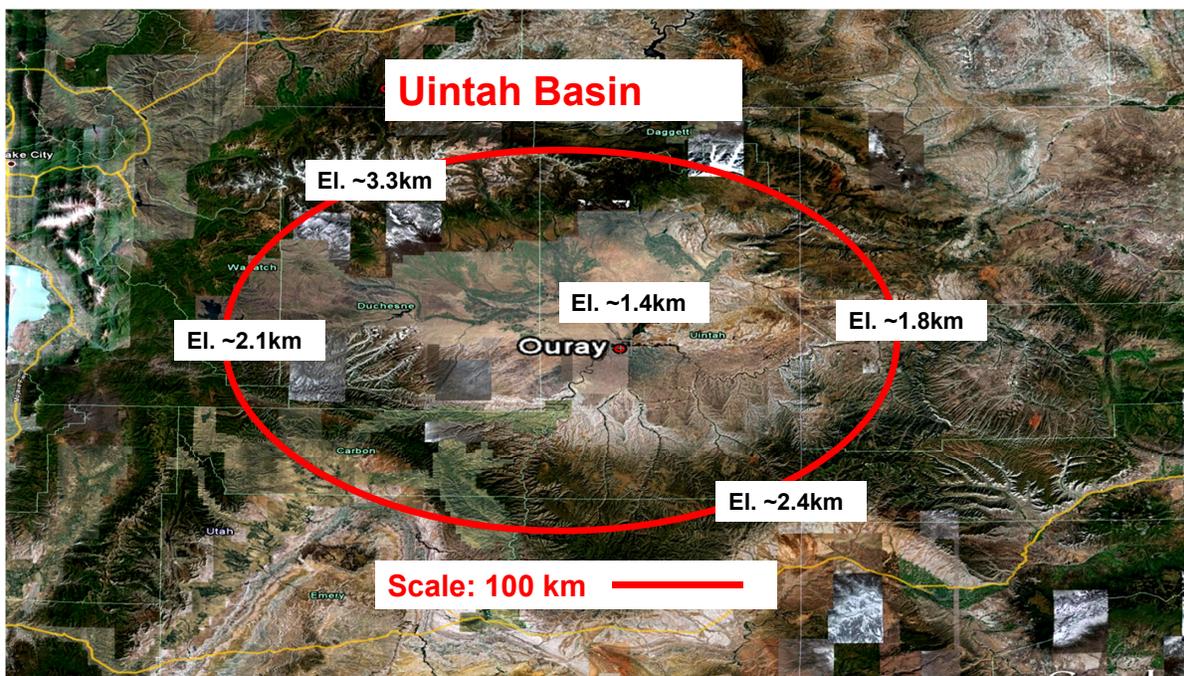


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# Elevated Wintertime Ozone (>165 ppb) and CH<sub>4</sub>, Uintah Basin, Utah

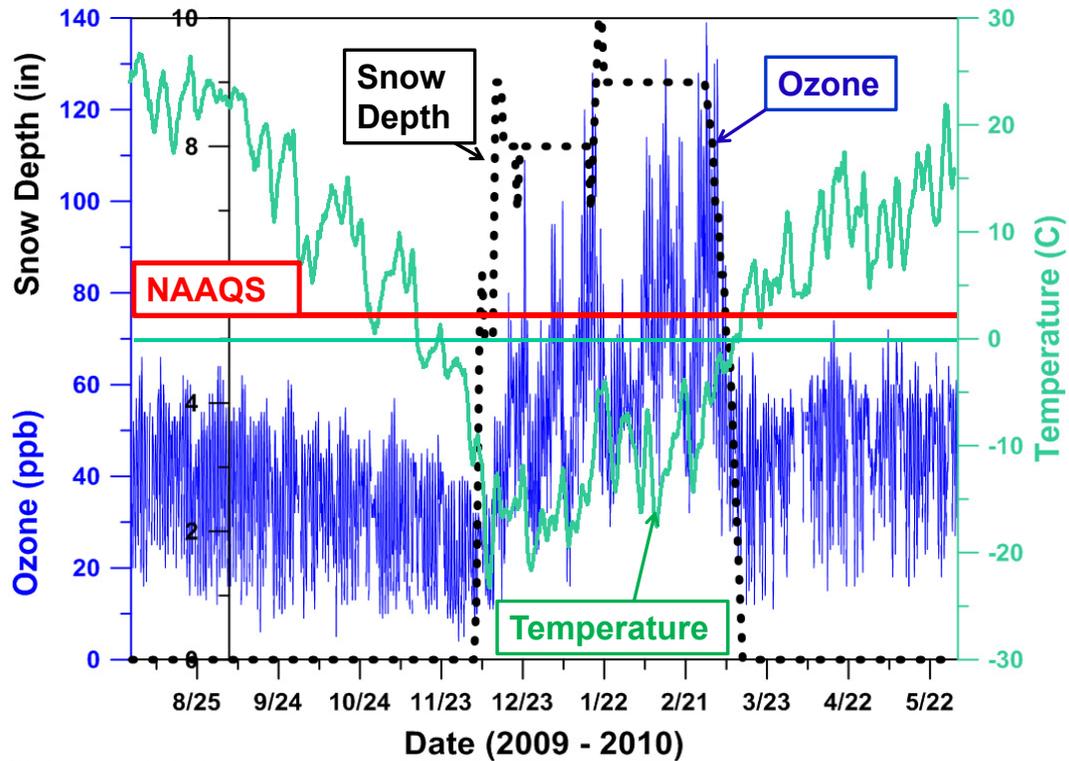


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# Wintertime Ozone Formation Ouray, Utah



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Schnell and Oltmans et al. (2009), Rapid photochemical production of ozone at high concentrations in a rural site during winter, *Nature Geoscience*, DOI:10.1038/NGEO415.

**First paper** introducing this \$ multi-billion regulatory issue and spawning large scale studies.

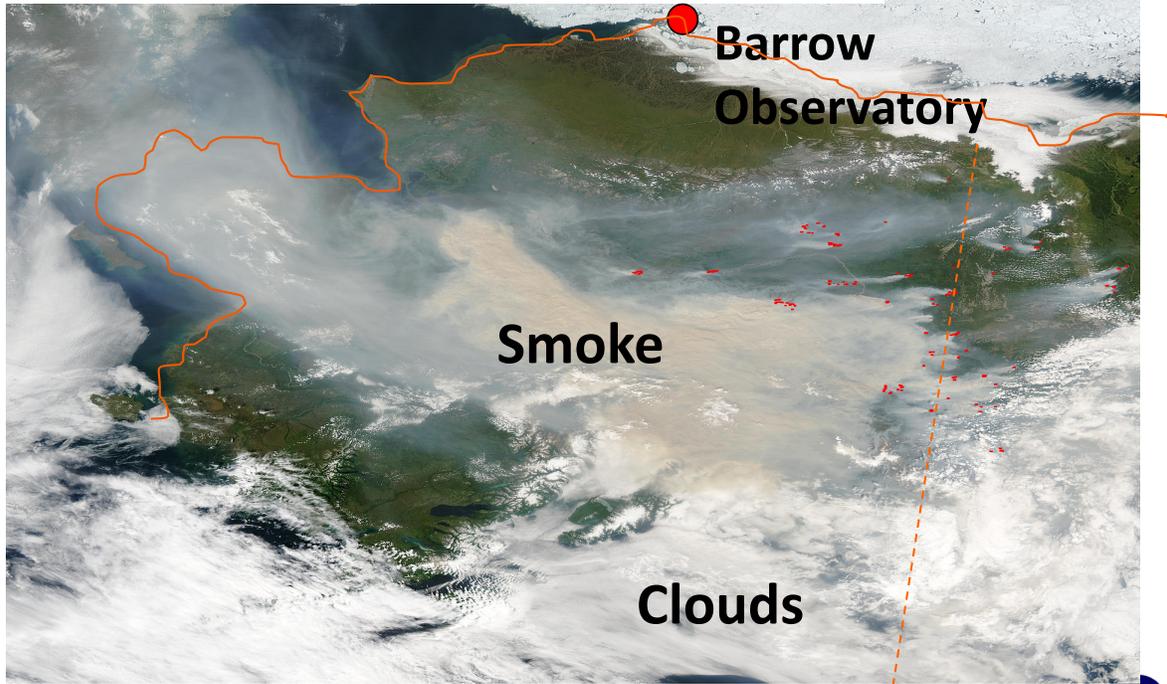
Petron and Frost et al. (2012), Hydrocarbon emissions characterization in the Colorado Front Range- a pilot study, *Jour. Geophys. Res.*, doi:10.1029/2011JD016360.

**First paper** showing that gas fields leak ~4% of methane. Recent research in Utah shows ~ 9% leakage, possibly negating the climate benefits of switching from coal to CH<sub>4</sub>.

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# Alaska/Canada Forest Fires, 30 June 2004

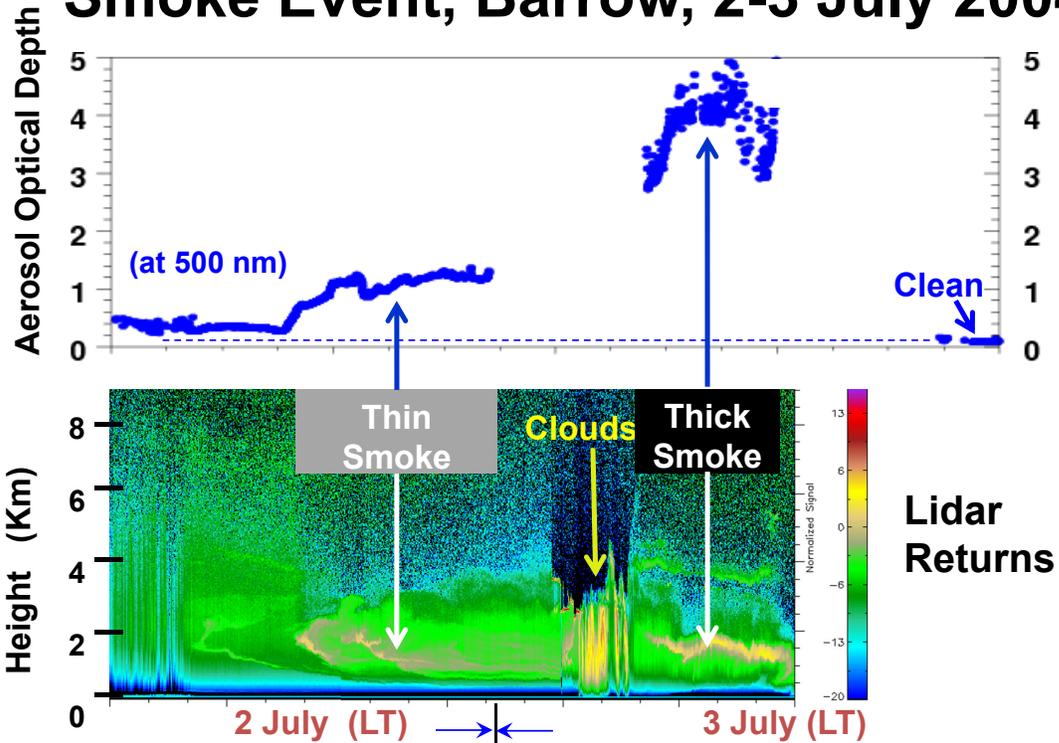


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## Smoke Event, Barrow, 2-3 July 2004



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# Cherskiy, Russia GMD Tundra CH<sub>4</sub> Measurements

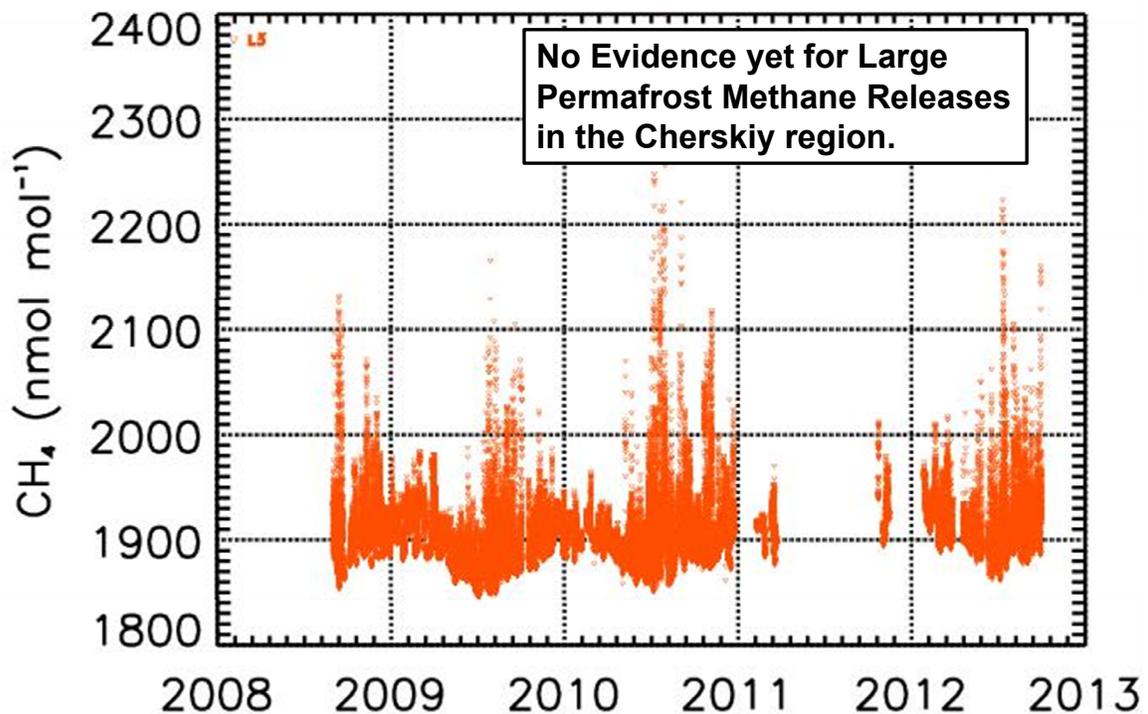


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## CH<sub>4</sub> Measurements, Cherskiy, Russia



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# **Bottom Line**

**Regional atmospheric measurements  
(months to decades)  
are crucial for understanding  
Long term measurement trends  
(decades to centuries).**

**Following Presentations:**

**Samuel Oltmans - Tropospheric Ozone**

**John Augustine - Aerosol Optical Depth**

**Gabrielle Petron - VOCs from Gas and Oil Fields**

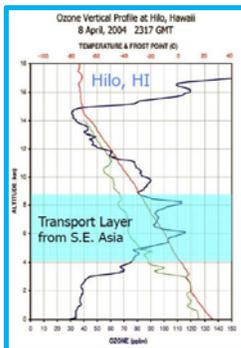


# Air Quality: Tropospheric Ozone

## Long Term Changes and Regional Influences

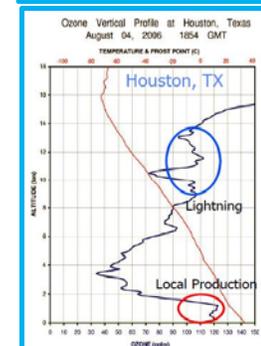
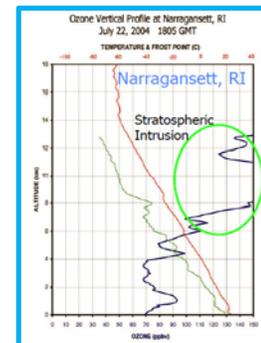
Sam Oltmans

## Tropospheric Ozone: What are the issues?



Tropospheric ozone profiles illustrating sources at different altitudes.

- **Impacts**
  - climate forcing
  - air quality
  - oxidizing (cleansing) capacity
- **Variability in space and time**
  - requires a comprehensive measurement strategy
  - GMD operates 18 surface and 11 ozonesonde sites
- **Multiple sources**
  - Natural sources – stratosphere, lightning, biogenic emissions
  - Pollution sources – local and regional production, long-range transport
  - makes isolating human impacts complex
- **Sources vary with altitude**
  - Changes are also altitude dependent
- **Regionally representative longer-term obs are limited**



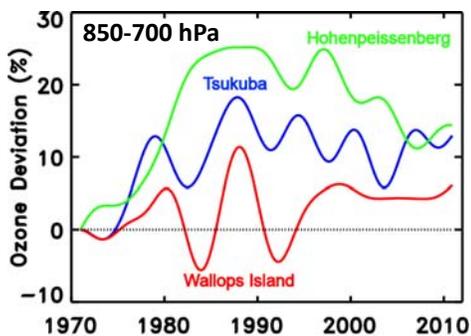
# How does the NOAA/ESRL Global Monitoring Division address these issues?

- Long-term ozone profile (30+ years) and surface ozone (40+ years) measurements.
- Process studies – for example:
  - Wintertime ozone formation
  - Arctic boundary layer ozone depletion
  - U.S. background ozone.
- Validation of satellite profiles from ozonesondes.
- Longer-term observations involve broad collaboration with U.S. and international partners (e.g. NDACC, SHADOZ, WMO).

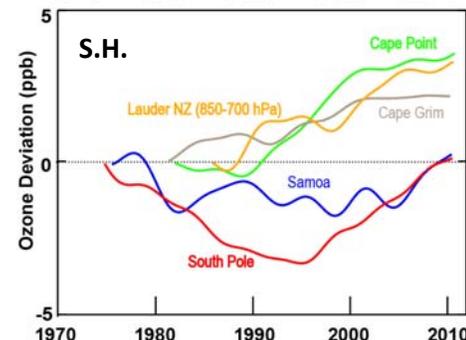
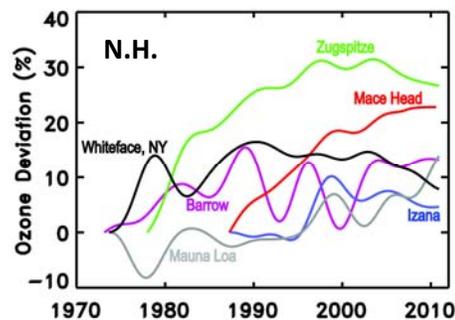


## Long Term Tropospheric Ozone Changes

- Changes have strong interannual and regional variability.
- At mid latitudes of the N.H. ozone increased into the 1990s.
- Flat or decreasing in the most recent decade - result of emission controls in North America and Europe (Oltmans et al., 2013).
- S.H. changes are largely unexplained.



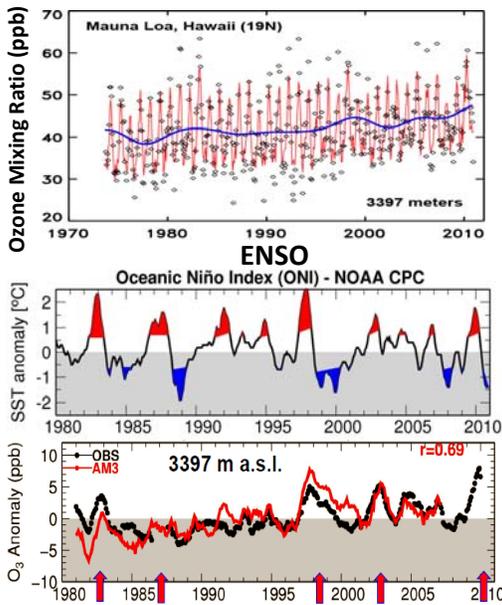
Three long term ozonesonde records in mid latitudes of the N.H. from three continents



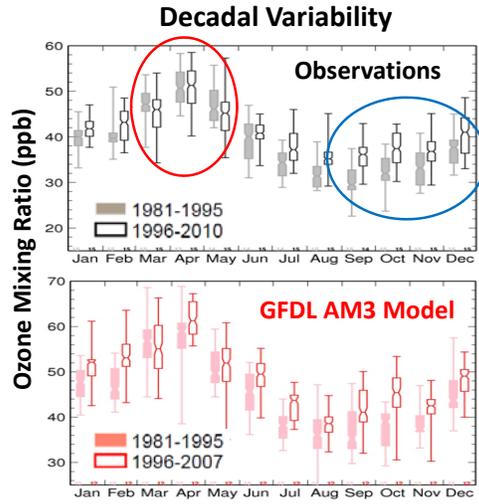
Long term changes in surface ozone at selected locations in the N.H. and S.H.

# Long Term Tropospheric Ozone Changes

- Mauna Loa is representative of free tropospheric ozone in the mid Pacific.
- Influenced by long range transport but also by strong transport variability from ENSO and decadal variations (Lin et al., 2013).

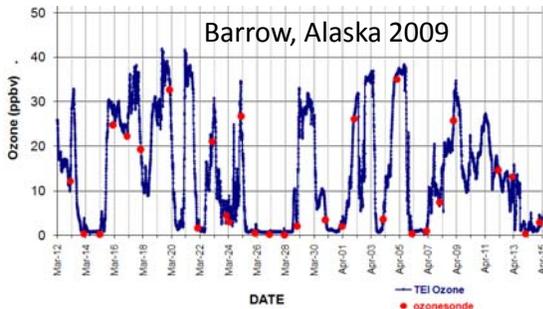


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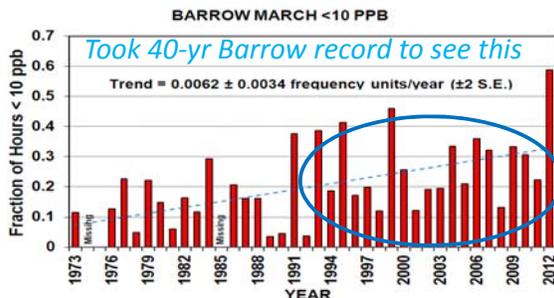
- Positive trends in the fall and winter, which is the seasonal minimum in O<sub>3</sub>
- Amplified variability with no significant trends in spring in the recent 15 years

## Spring Arctic Ground Level Ozone Depletion: Connection to Sea Ice Changes – Climate Change

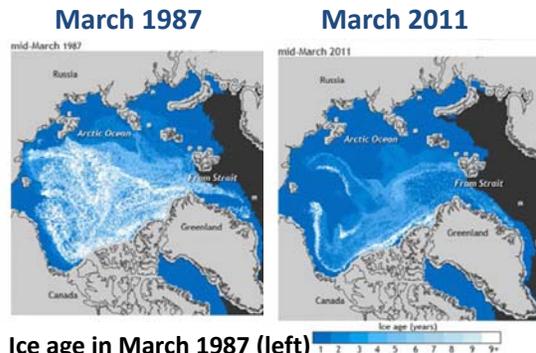


Hourly O<sub>3</sub> (ppbv) at Barrow in March and April 2009.

- Spring ground level ozone is strongly depleted in the Arctic.
- Caused by ice activated halogen reactions.
- Accompanying mercury activation events.
- Big increase in depletion events in March because of change in sea ice character – first year sea ice activates more halogens.



Fraction of hours with surface O<sub>3</sub> < 10 ppb at Barrow in March each year for 1973-2012 (Oltmans et al., 2012).



Ice age in March 1987 (left) and 2011 (right) - white is oldest ice (>9 yr)

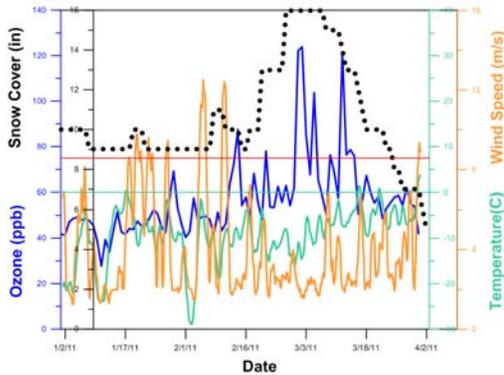
## Wintertime Ozone Production Associated with Oil and Gas Exploration and Extraction

- Dramatic wintertime ozone episodes first reported in the Upper Green River Basin of Wyoming by *Schnell et al., 2009*.
- Subsequently seen in the Uintah Basin of Utah.
- Snow cover, restricting topography, and intensive oil and gas exploration and extraction are critical.

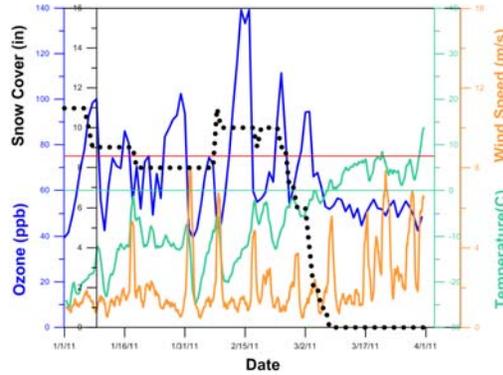


Snow covered oil field in Wyoming. Haze within the shallow inversion layer.

Wyoming - 2011



Utah - 2011



Daily 8-hr max O<sub>3</sub> (ppb), 8-hr O<sub>3</sub> standard (75 ppb), wind speed, temp., and snow cover during winter in WY and UT.

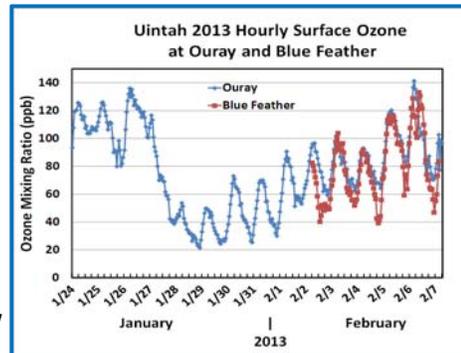
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## Wintertime Ozone Production Associated with Oil and Gas Exploration and Extraction – Utah 2013

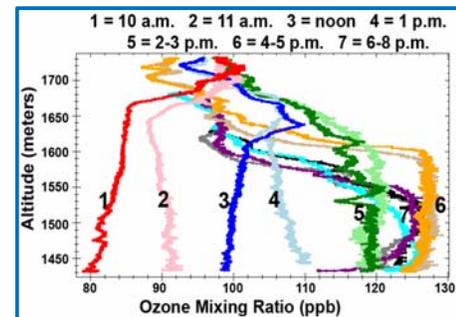


Profiles from tethered balloon ozonesondes show the development and vertical structure from rapid photochemical ozone production.

Drilling and processing are sources of ozone precursors (nitrogen oxides)



Surface ozone (ppb) in Uintah Basin for January 24 – February 7, 2013



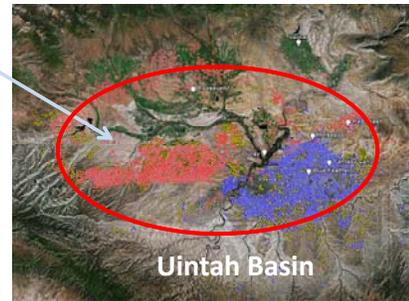
Ozone (ppb) profiles in Uintah Basin throughout the day (10 a.m. – 8 p.m.) on Feb. 5, 2013

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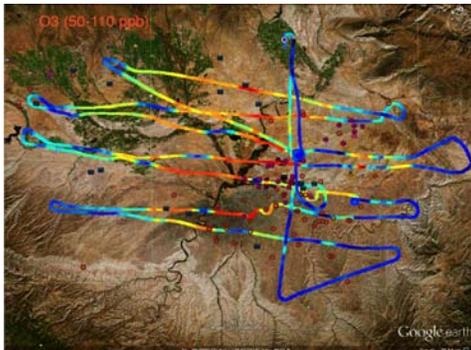
## Wintertime Ozone Production Associated with Oil and Gas Exploration and Extraction – Uintah Basin, Utah 2013

- Aircraft flights in February 2013 give the first large scale picture of ozone formation under the conditions of winter ozone production.
- Highest ozone found in areas of high methane (highly correlated with volatile organic compounds) and high carbon monoxide (from drilling and compressors).

Oil (red) & gas (blue) wells in the Uintah Basin

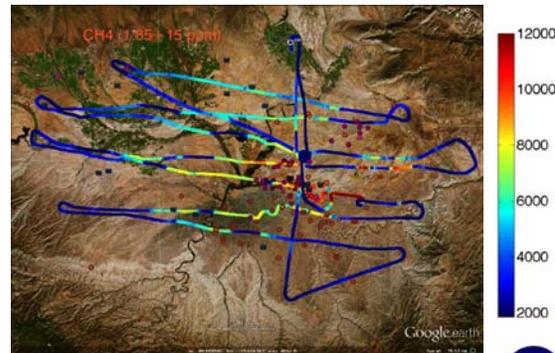


**Ozone (ppb) over the Uintah Basin – February 2, 2013**



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**Methane (ppb) over the Uintah Basin – February 2, 2013**



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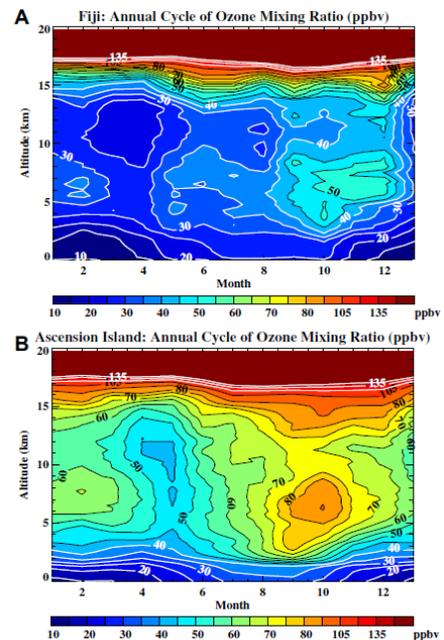


## Tropical Ozone Profiles

- The SHADOZ ozonesonde network has been the linchpin of tropical tropospheric ozone measurements for understanding processes, satellite validation, and model improvement.
- These sites are also the backbone for regional studies such as SEAC4RS.
- Long term collaboration between NOAA GMD and NASA (Funding from Upper Atmosphere Program, Aura Validation, TOMS Science Team)



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**Contrast in tropospheric ozone seasonal variation in the S.H. Pacific and Atlantic (Thompson et al., 2003, 2007, 2012).**

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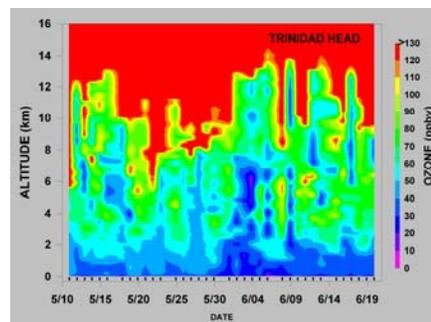
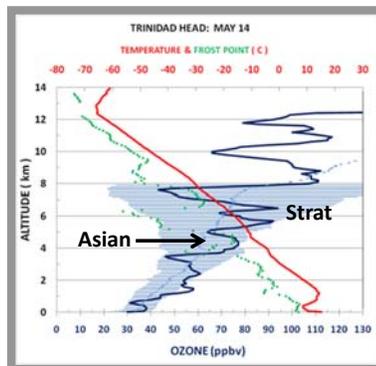
## Intensive Ozonesonde Network Studies (IONS)

- Multiple campaigns using ozonesonde (IONS)  
Upcoming - SEACIONS (SEAR4RS)
- CALNEX (IONS2010) – Did daily sondes at 6 sites
  - Identified multiple sources (Cooper et al., 2011)
  - GFDL AM3 model performed well (Lin et al., 2012)
- Collaboration between GMD and NASA (Funding from Tropospheric Chemistry, Upper Atmosphere, Aura Validation)

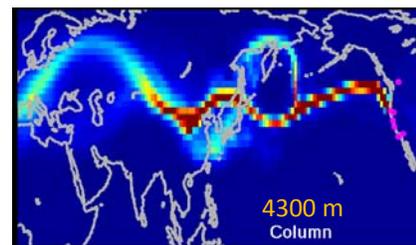


**Ozonesonde network during CALNEX**

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**Cross section of daily ozone profiles at Trinidad Head, CA in May and June 2010 during CALNEX**



**O<sub>3</sub> profile at Trinidad Head, CA and retroplume showing transport from Asia.** Page AR2-11



## Tropospheric Ozone: Summary

- GMD tropospheric ozone observations have been crucial in both long-term (trends) and regional studies.
- Some Results:
  - Tropospheric ozone is now flat or decreasing over much of the mid latitude N.H. (East Asia the exception) likely due to precursor emission reductions in North America and Europe.
  - Changes in other regions probably not linked to emissions (interannual changes such as ENSO and decadal circulation variations may play a role).
  - Warming Arctic (switch from multi-year to first year ice) has significantly altered ozone (and likely mercury) behavior.
  - Significant impacts from oil and gas exploration activity on regional ozone.
- Regional studies complement long term observations.



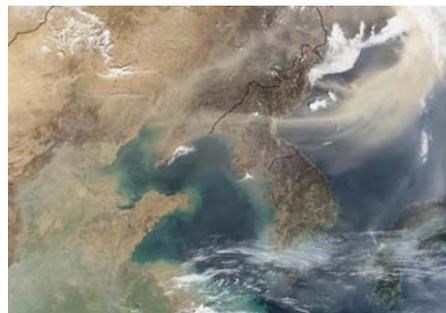
# Aerosol Optical Depth Measurements and Related Research

John A. Augustine  
GMD Radiation Group



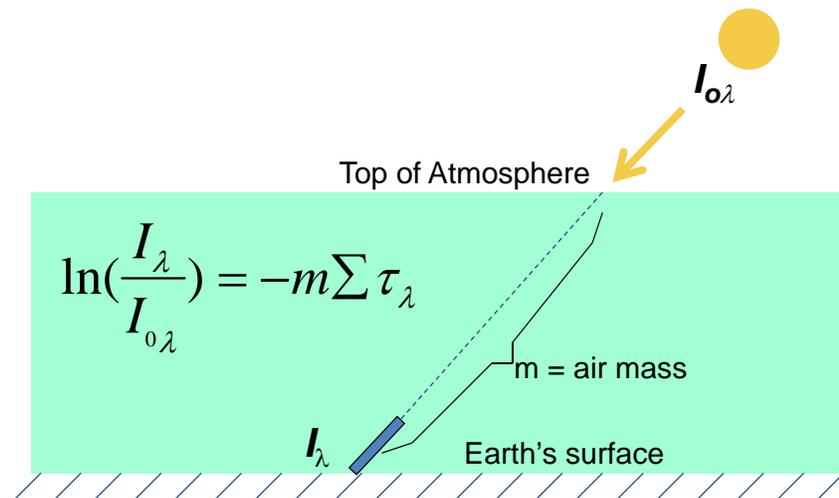
## Why measure Aerosol Optical Depth?

- Aerosols cool the surface; AOD helps to quantify that effect
- Monitor long-term trends in aerosol loading, air quality
- How well do weather and climate models handle aerosols?
- How do aerosols affect the solar energy resource?
- Satellite validation:
  - ✓ Satellite-derived AOD over land (MODIS, MISR)
  - ✓ How do aerosols impact satellite-derived surface irradiance?



# What is Aerosol optical depth?

A measure of the extinction of radiation from the sun's beam by aerosols

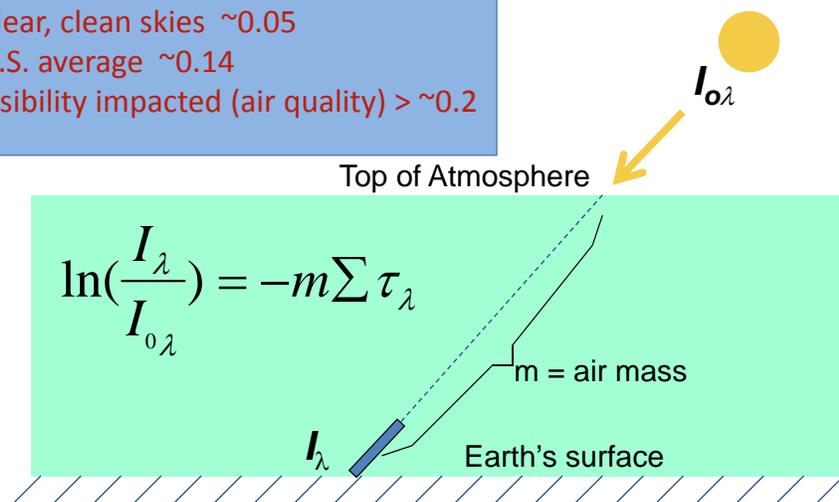


$$\tau_{\lambda\text{aerosol}} = \sum \tau_\lambda - \tau_{\lambda\text{molecular}} - \tau_{\lambda\text{ozone}}$$

# What is Aerosol optical depth?

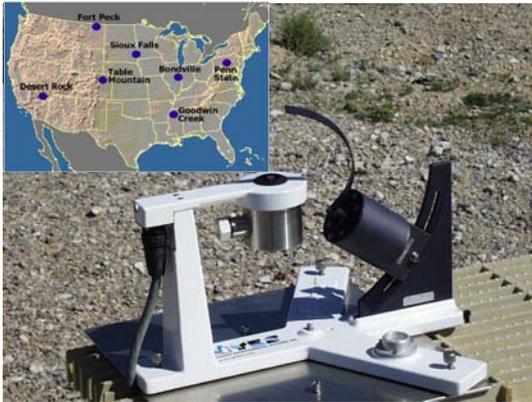
A measure of the extinction of radiation from the sun's aerosols

Typical AOD<sub>500nm</sub> values:  
Clear, clean skies ~0.05  
U.S. average ~0.14  
visibility impacted (air quality) > ~0.2



$$\tau_{\lambda\text{aerosol}} = \sum \tau_\lambda - \tau_{\lambda\text{molecular}} - \tau_{\lambda\text{ozone}}$$

# Sunphotometers used to measure Aerosol Optical Depth

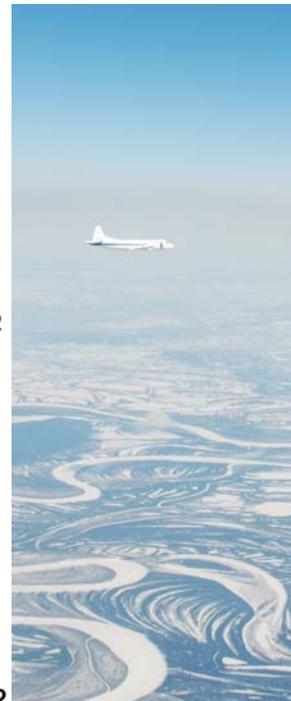
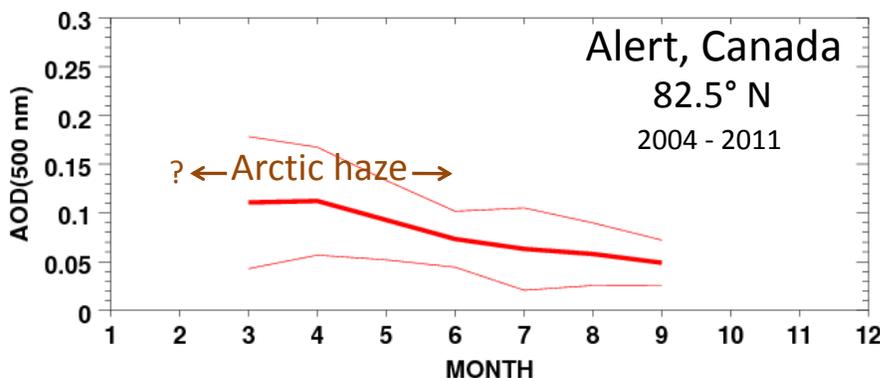
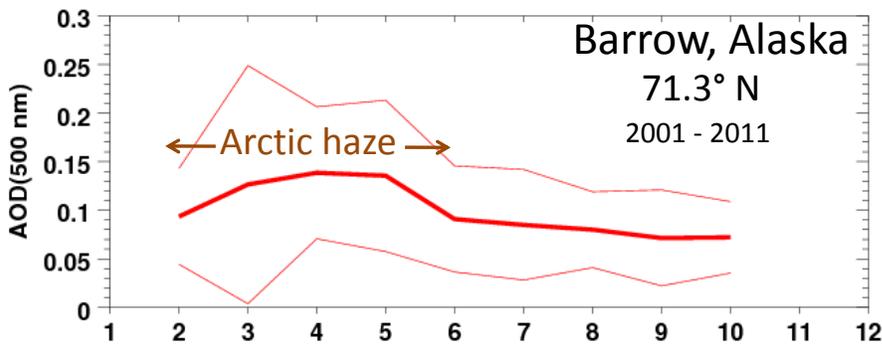


MultiFilter Rotating Shadowband Radiometer used at U.S. sites (SURFRAD Network)

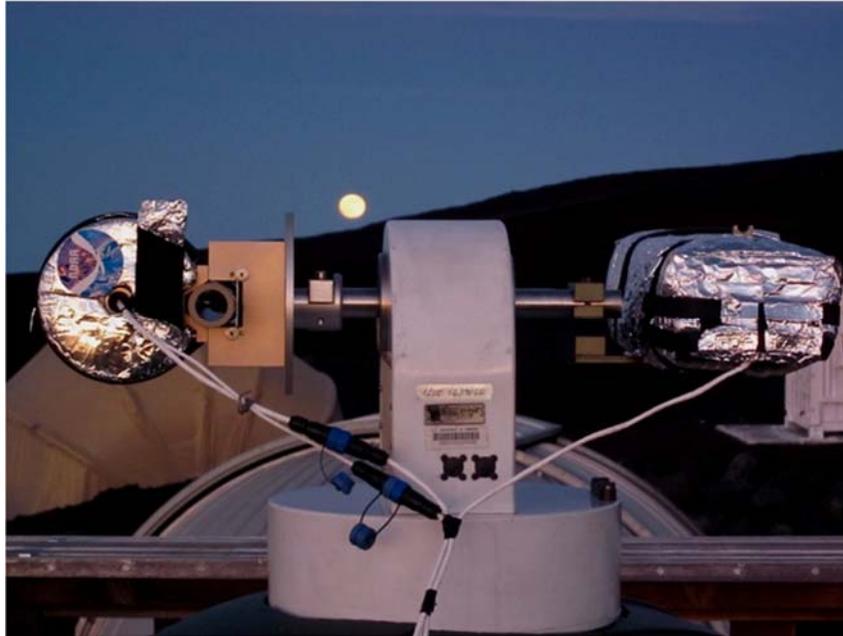


Middleton SP02 Sunphotometer used at global sites

## AOD Climatologies



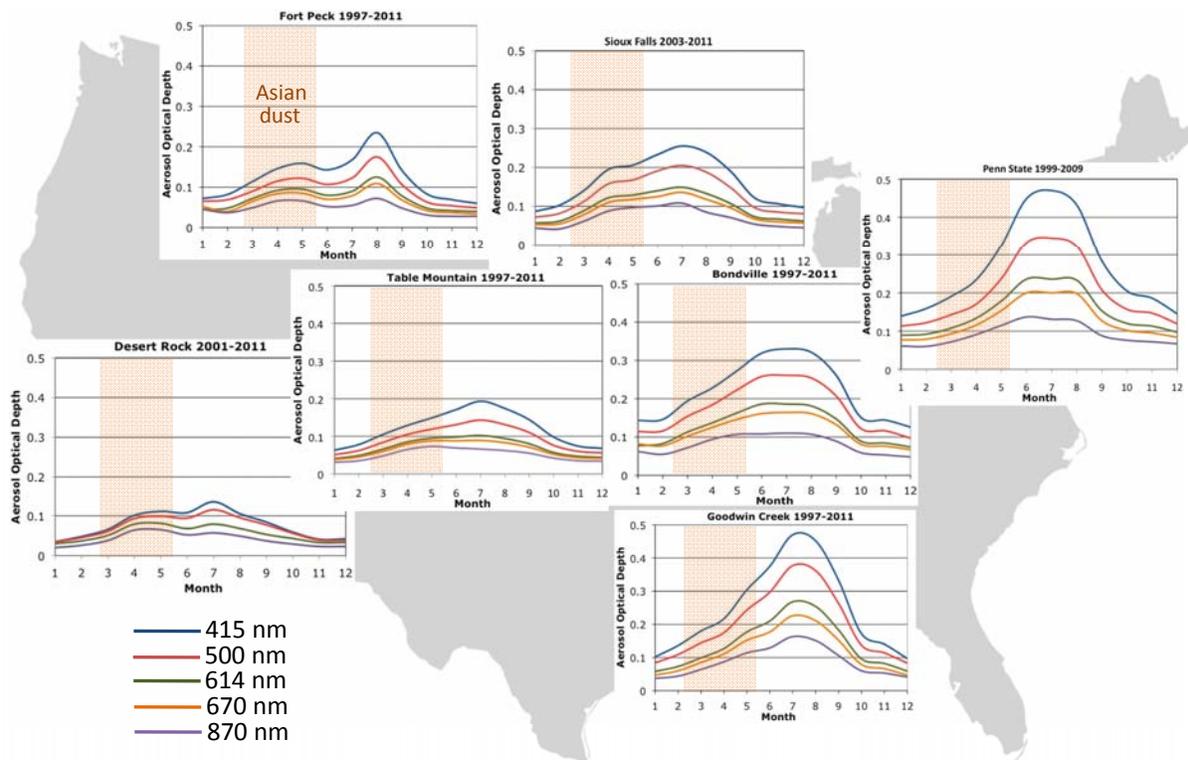
# Testing the Lunar-photometer at Mauna Loa for use in the Arctic



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## U.S. AOD Climatology

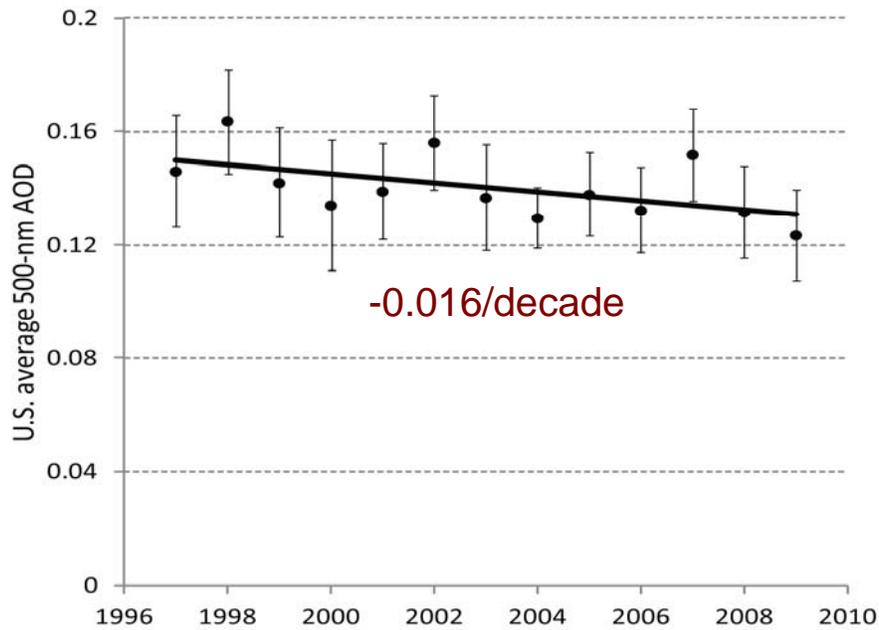


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Augustine et al., 2008, *J. Geophys. Res.*, 113, D11204, doi:10.1029/2007JD009504.

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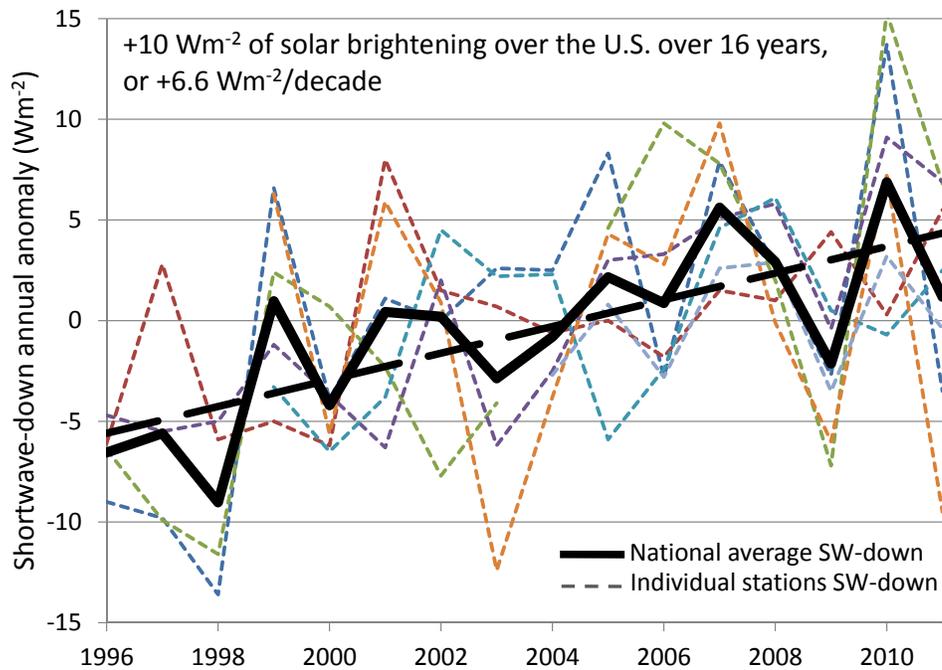
# Network-wide decrease in U.S. AOD from 1997 to 2009



Augustine, J. A. and E. G. Dutton, 2013, *J. Geophys. Res.*, 118, 10.1029/2012JD018551.

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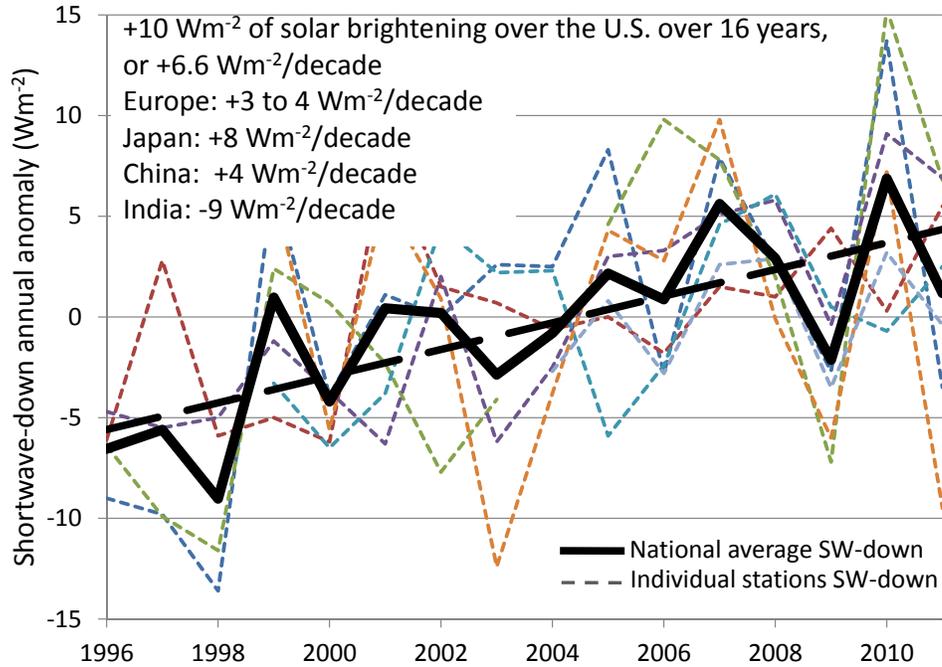
# How did the measured decrease in U.S. AOD affect surface radiation?



Augustine, J. A. and E. G. Dutton, 2013, *J. Geophys. Res.*, 118, 10.1029/2012JD018551

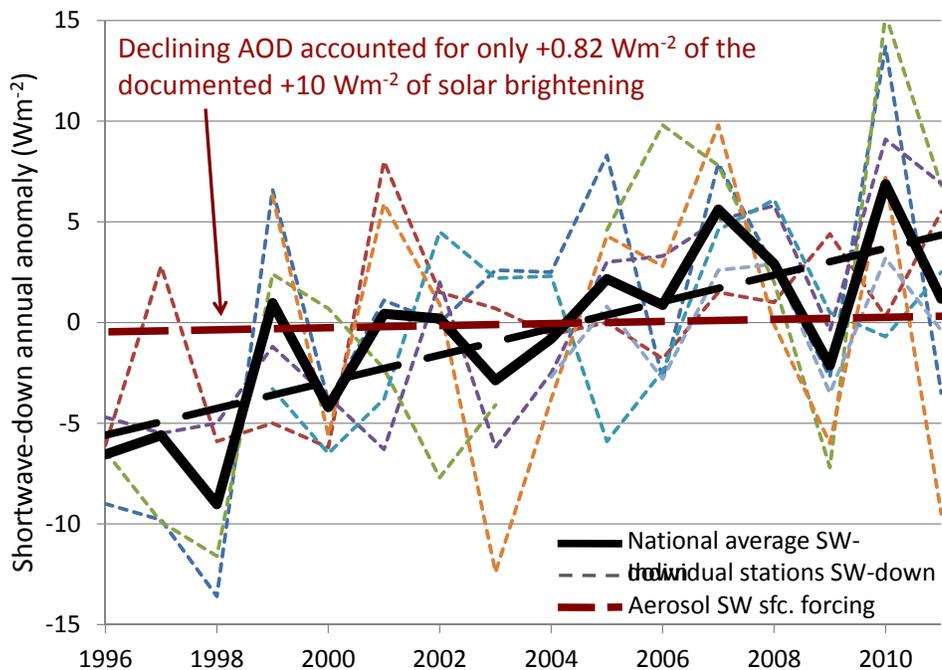
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## How did the measured decrease in U.S. AOD affect surface radiation?



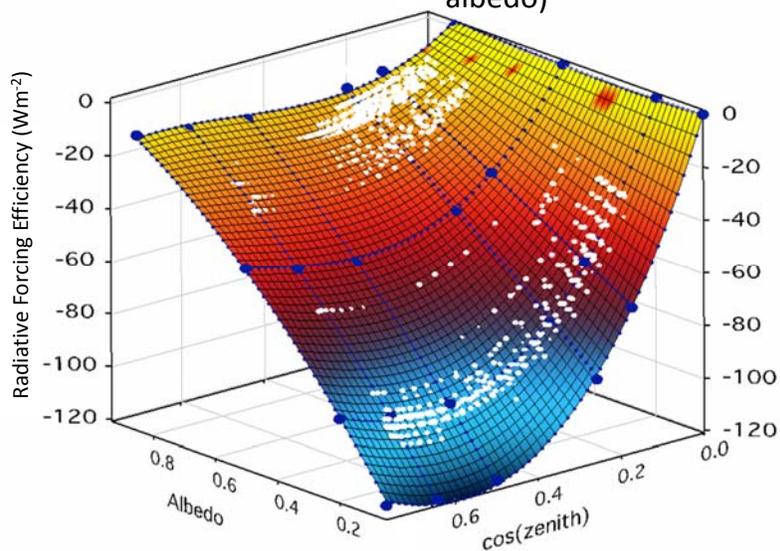
Augustine, J. A. and E. G. Dutton, 2013, *J. Geophys. Res.*, 118, 10.1029/2012JD018551

## How did the measured decrease in U.S. AOD affect surface radiation?



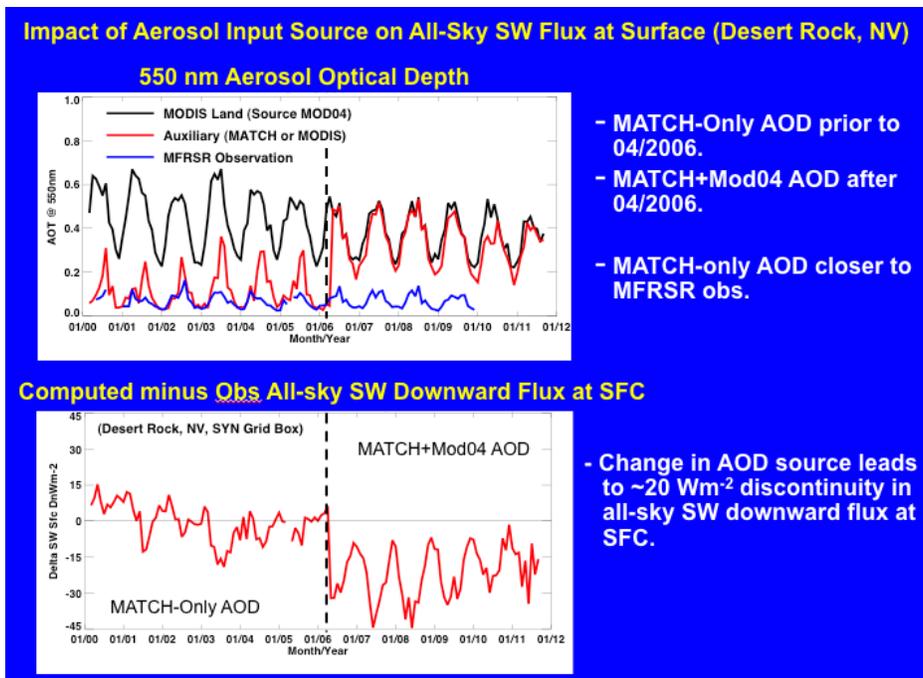
# Radiative Forcing Efficiency (RFE) of Boreal wildfire smoke

$$\text{RFE} = \Delta\text{NetRad}/\text{unit AOD}_{500\text{nm}} \quad f(\text{solar zenith angle, sfc. albedo})$$



Useful for validating model performance for boreal wildfire smoke conditions

## GMD's AOD used by NASA for MODIS AOD validation



Courtesy of David Rutan, NASA Langley

# Summary

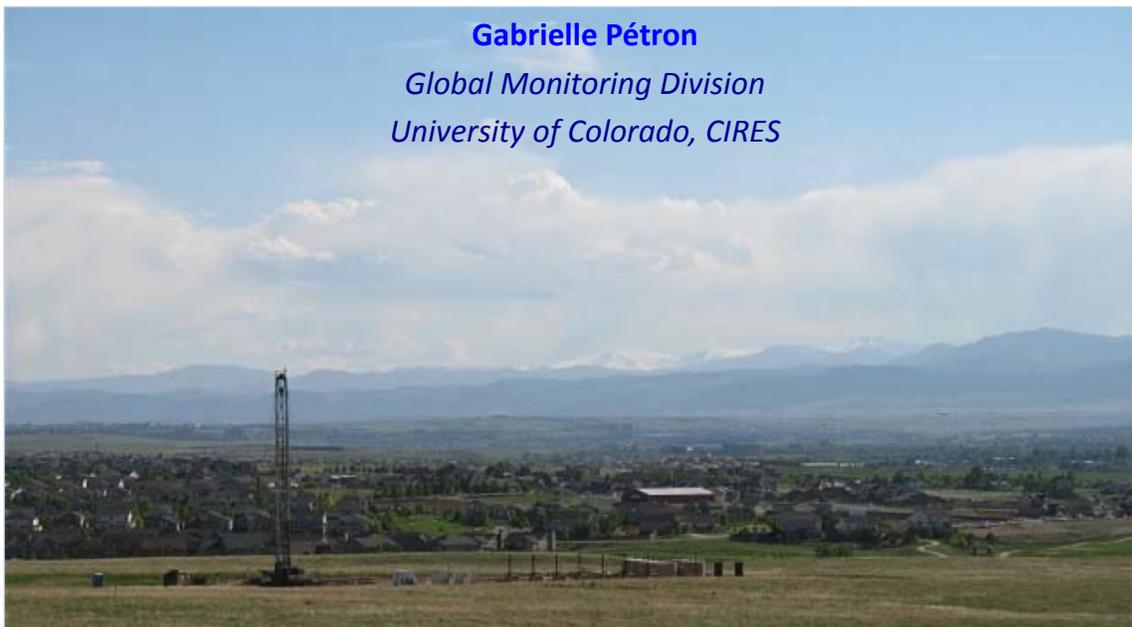
- ✓ Aerosol optical depth is a quantitative measure/proxy for air quality
- ✓ AOD climatologies developed for all stations
- ✓ Collocated AOD and surface radiation budget data are rare, but useful for research
- ✓ Small decreasing AOD trend from 1997 to 2009 had little impact on solar brightening over the U.S.
- ✓ Parameterized the radiative forcing of boreal wildfire smoke
- ✓ GMD's coupled radiation and AOD data indispensable to NASA and NOAA satellite validation

END

# Methane and Volatile Organic Compounds Emissions from Oil and Gas Operations

Gabrielle Pétron

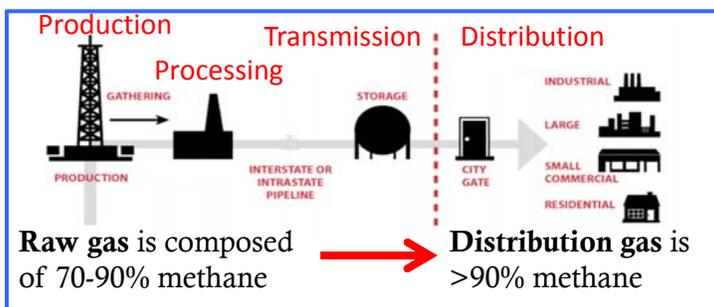
Global Monitoring Division  
University of Colorado, CIRES



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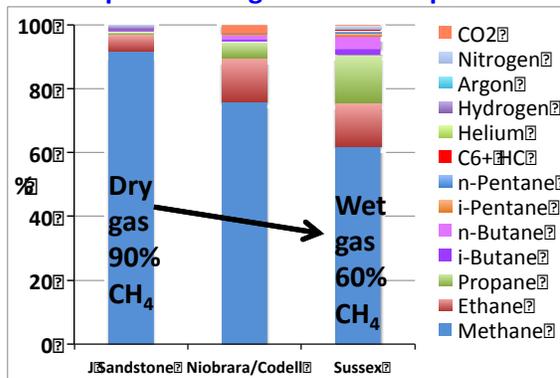


## Natural Gas and Oil Systems



Fugitive emissions or leaks of natural gas along the production and supply chain result in direct emissions of CH<sub>4</sub> and VOCs (ozone precursors).

### Examples of raw gas molar composition



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# Atmospheric Impacts from Oil and Natural Gas Systems

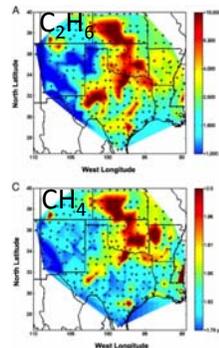
- Field measurements in the US suggest that methane and VOC emissions are likely under-estimated:

- Oil and gas production

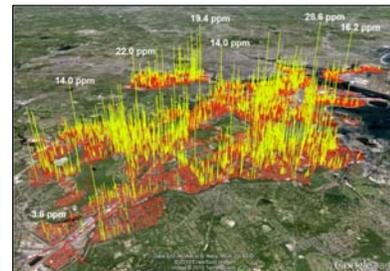
- in TX, OK, KS: Katzenstein et al. 2003
- in CO and UT: Pétron et al., 2012, Karion et al., submitted

- Natural gas distribution in cities

- In Boston: Phillips et al., 2012
- In Washington DC: Jackson et al., on-going



Surface enhancements of alkanes and alkyl nitrates in Texas & Oklahoma, Katzenstein et al., 2003

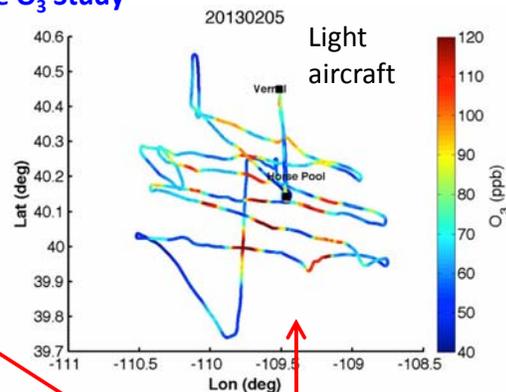
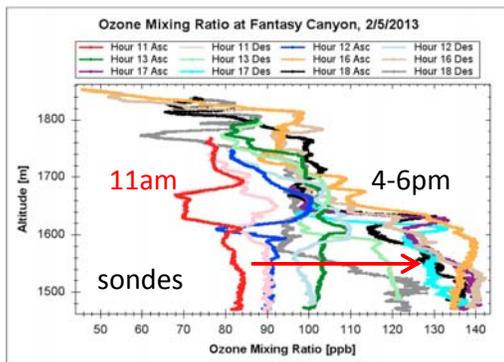


Methane leaks in Boston, Phillips et al., 2012



# Atmospheric Impacts from Oil and Natural Gas Systems

## Uintah Basin, February 5, 2013 - Wintertime O<sub>3</sub> Study

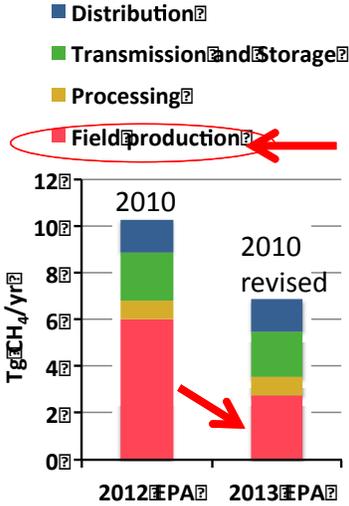


- Emissions from oil and gas operations can contribute to surface O<sub>3</sub> pollution
  - Wintertime: Utah & Wyoming, Schnell et al., 2009, S. Oltmans and R. Schnell talks.
  - Summertime: Colorado



# How well do we know emissions from oil and gas systems? CH<sub>4</sub> example

NG systems emissions in two versions of the US inventory

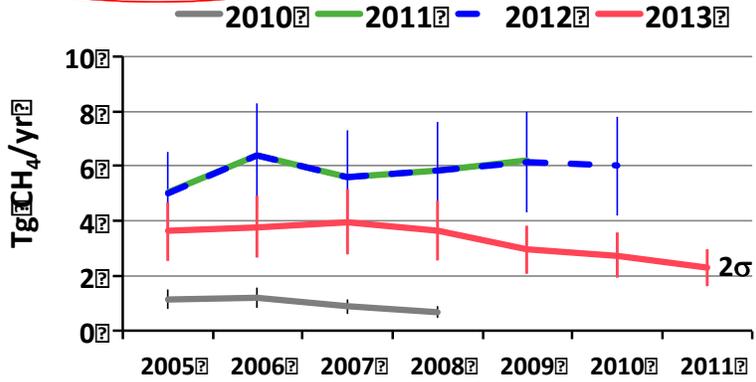


US 2010 Total CH<sub>4</sub> source: 28-32 Tg  
 Petroleum systems: 1.5 Tg  
 Coal Mining: 3 Tg

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 Laboratory Review, April 3-5, 2013

In 2011 and 2013, the US EPA revised its methodology to calculate CH<sub>4</sub> emissions from natural gas systems. The production (upstream) sector saw the largest changes.

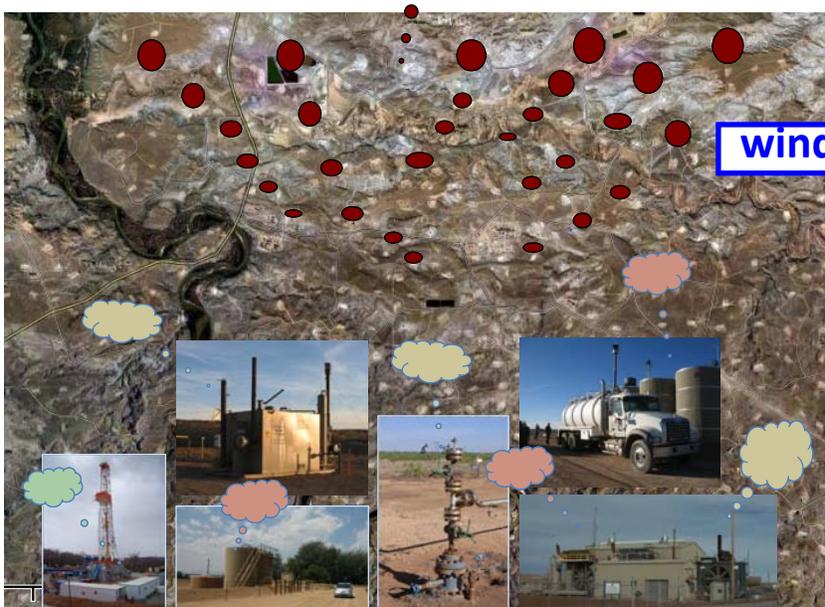
NG field production emissions in four versions of the inventory



Can atmospheric measurements be used to assess emissions from oil and gas basins?

# Can we detect methane emissions in the atmosphere?

## Methane and VOC cloud



*In-situ measurements and discrete air samples are collected by instrumented van, tower or aircraft upwind and downwind of point or area sources.*

# North American GHG and VOC measurements



Tower, aircraft and van flask sampling system

CCGG MAGICC

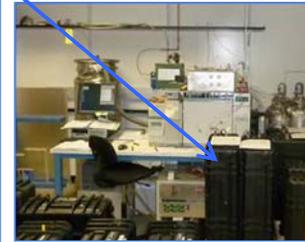
$CO_2$   $CH_4$   $N_2O$   $SF_6$   $CO$   $H_2$



Mobile Laboratory

**GMD's List of VOCs measured in flasks**

propane  
n-butane  
i and n-pentane  
benzene,  
acetylene  
2007-present  
More species in a few months  
See B. Miller's poster



HATS GC/MS

43 species

Multiple species can be used to attribute emissions of long-lived GHGs such as carbon dioxide or methane.

# Intensive campaigns in Oil and Gas Basins

Map of unconventional oil and gas reservoirs and dates of GMD campaigns



Wyoming 2008  
Utah 2012, 2013

Colorado  
2008-present

Texas  
2013

**Research Questions:**

- Emissions of methane and non-methane hydrocarbons
- Summertime ozone
- Wintertime ozone



Instrumented airplane



Instrumented van

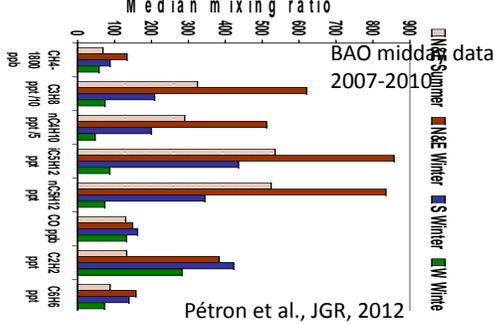
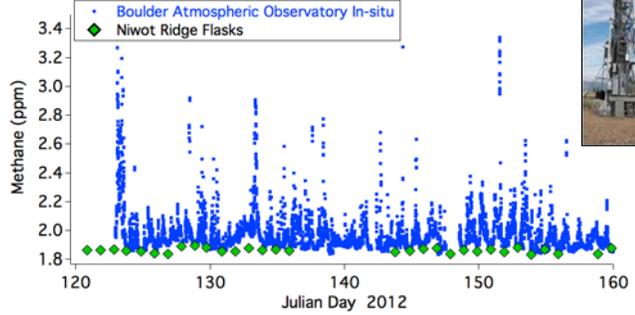
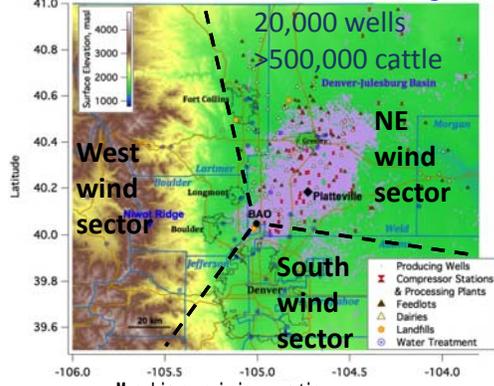


NOAA CSD  
Wind Doppler Lidar

# Denver-Julesburg Basin, Colorado



## Colorado Northern Front Range



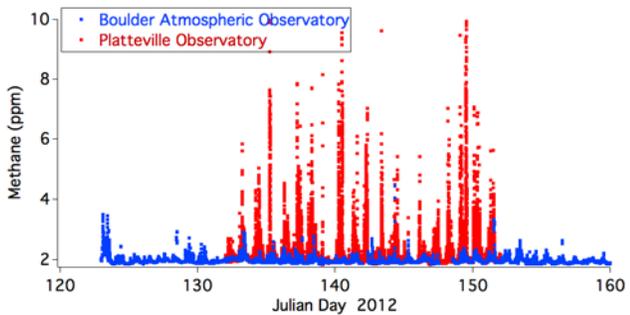
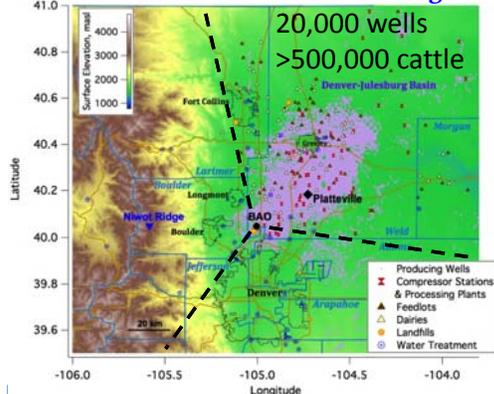
Pétron et al., JGR, 2012

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Laboratory Review, April 3-5, 2013

- In-situ measurements in the DJB show a diurnal cycle in methane with night-time levels elevated by hundreds of ppb to a few ppm above background at BAO.
- Methane at the surface is much higher at night at the Platteville site, located in the middle of the basin.

# Denver-Julesburg Basin, Colorado

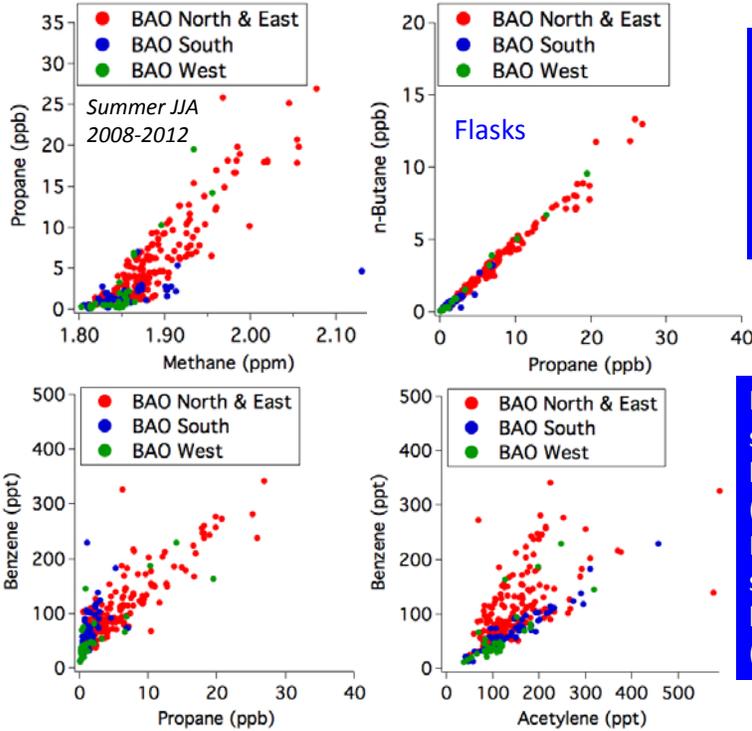
## Colorado Northern Front Range



- In-situ measurements in the DJB show a diurnal cycle in methane with night-time levels elevated by hundreds of ppb to a few ppm above background at BAO.
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# BAO Tower: Multiple species flask analysis

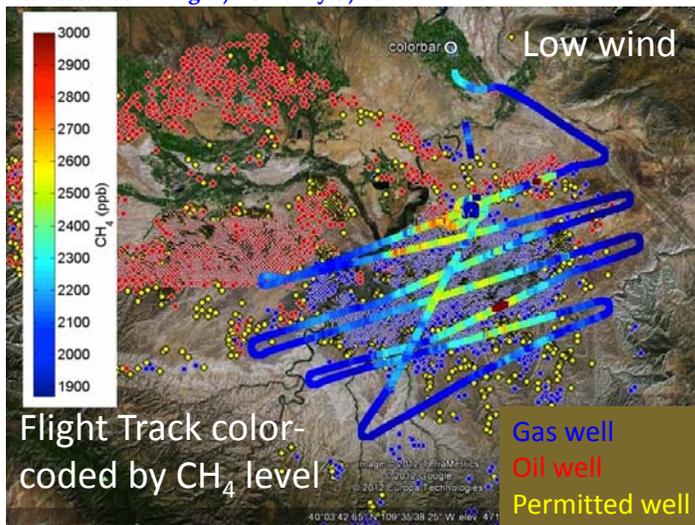


Air coming from the North-East has larger levels of hydrocarbons. The various alkanes measured correlate very well ( $R^2 > 0.9$ ) in most samples.

For South and West wind sectors, mobile sources are the largest contributors to benzene (correlation with acetylene). For the North and East wind sector, benzene is also emitted by oil and gas activities (correlation with propane)

# Uinta Basin - February 2012 13 flights with in-situ measurements and flask sampling

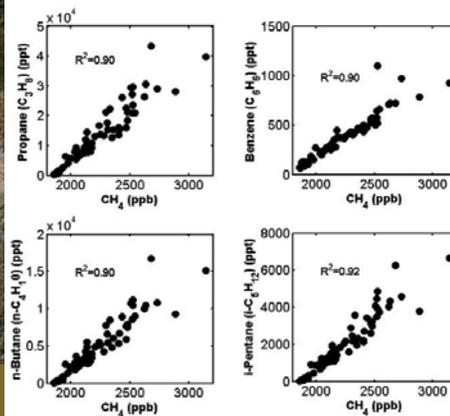
Uintah Basin Flight, February 7, 2012



**Oil and Gas production is the main activity in the Uintah Basin.**

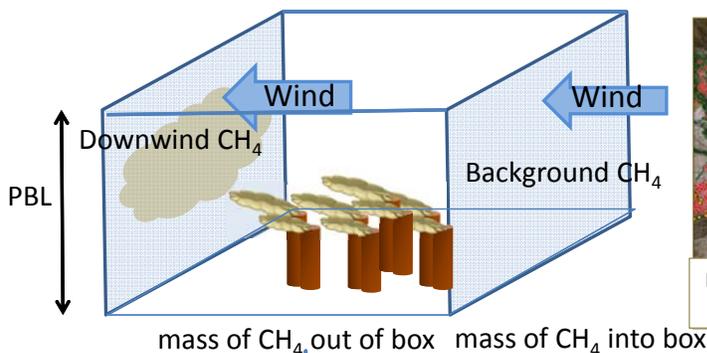
*Multi-laboratory campaign coordinated by  
EPA region 8 and State of Utah*

Uintah Basin - February 2012  
Aircraft discrete samples data

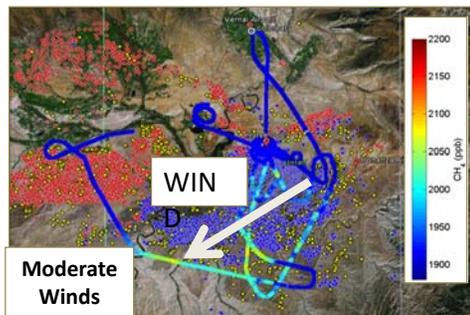


Strong correlation between methane, the light alkanes and benzene in samples collected in the Uintah Basin in 2012.

# Mass-balance methane flux estimation

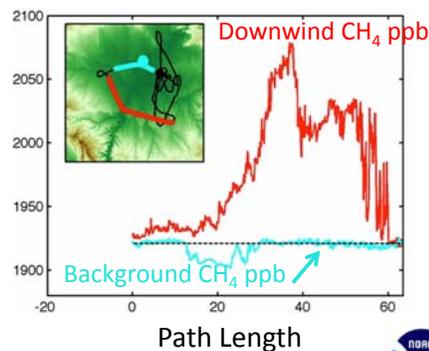


Uintah Basin Flight, February 3, 2012

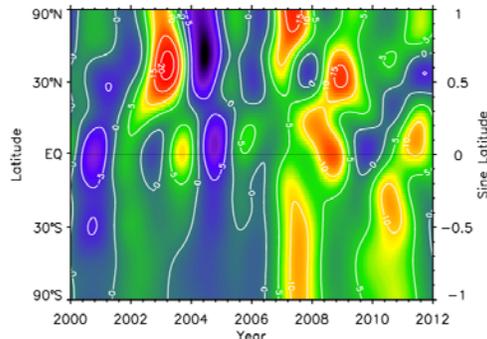
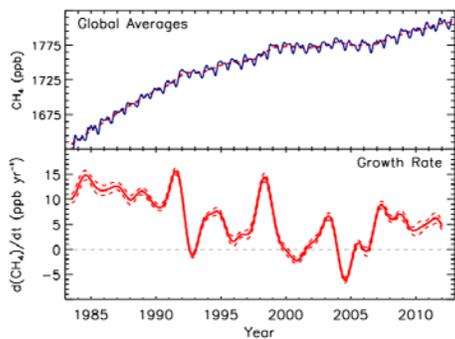


$$\dot{m}_{CH_4} = \iint_{CS} \rho_{CH_4} V_n dA_{out} - \iint_{CS} \rho_{CH_4} V_n dA_{in}$$

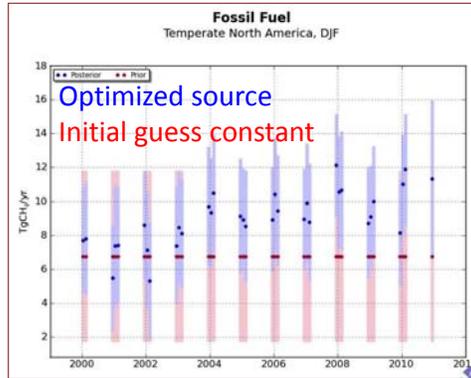
Hourly CH<sub>4</sub> leak estimated on that day is 8.8 ± 2.6% of hourly averaged gas production for February 2012 (Karion et al., submitted).  
 VOC emissions in regulatory inventory are underestimated by a factor of 2 (Pétron et al., in prep)



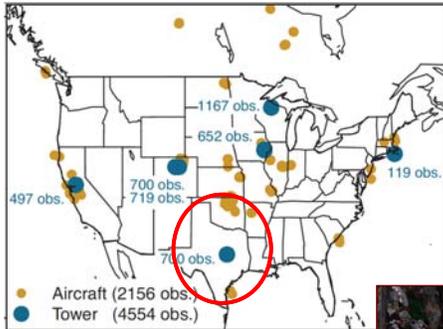
# What do long-term CH<sub>4</sub> measurements show?



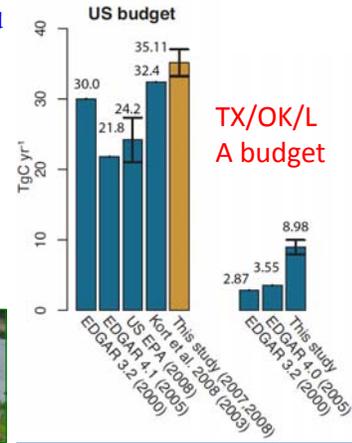
- Data from the GMD measurement network show that global methane is on the rise again (see E. Dlugokencky's talk).
- In 2002 the SGP Oklahoma site comes online CT-CH<sub>4</sub> increases fossil fuel emissions in North America after 2002 compared to the prior (EDGAR 3.2 constant at year 2000 level).
- CT-CH<sub>4</sub> suggests that the recent trend is due in part to wetlands and in part to anthropogenic emissions in temp. latitudes.



# US Inverse modeling results using GMD data



S. Miller et al., submitted  
Evidence for a large fossil  
fuel methane source over  
the south-central US



2008 US CH <sub>4</sub> source	Tg CH <sub>4</sub> /yr
US EPA 2012 inventory	32.2±10
US EPA 2013 inventory	29.5±9
Miller et al. inversion	46.8±2.5 (12 in TX/OK/LA)

S. Miller et al. regional inverse modeling study indicates that:

- Methane emissions in the US in 2007-2008 are underestimated in the official inventory.
- TX/OK/LA emissions are 2.5 to 3.1 times too low compared with EDGAR inventory

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## Concluding remarks

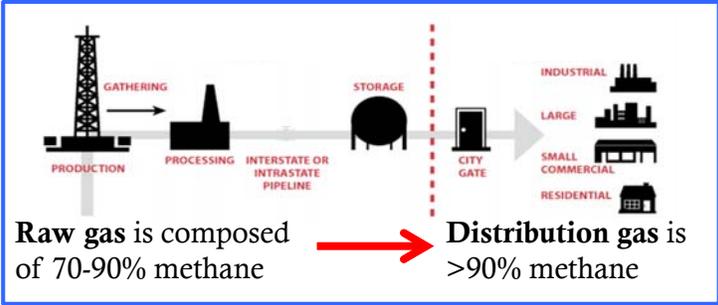
- GMD's field campaigns in Utah and Colorado show that inventories may underestimate methane and VOC emissions by a factor of 2 or more. More work is needed to evaluate emissions over other regions and for longer time periods.
- Oil and gas producing States assess the air impact of existing and future operations using VOC and NO<sub>x</sub> emission inventories. If emissions are underestimated, modeling efforts and mitigation strategies might not be effective.



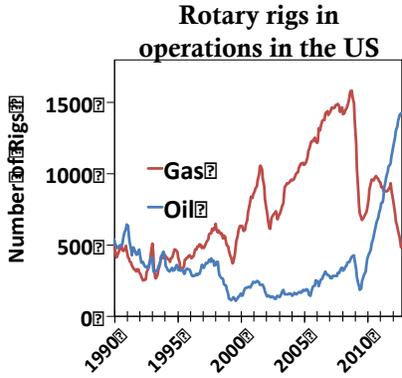
GMD long-term measurements and participation in intensive campaigns provide unique independent information on emissions from natural and anthropogenic sources, including methane and VOC emissions from oil and gas systems.



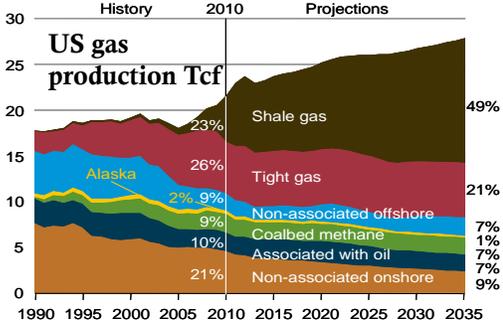
# Natural Gas and Oil Systems



Fugitive emissions or leaks of natural gas along the production and supply chain result in direct emissions of CH<sub>4</sub> and VOCs (ozone precursors).

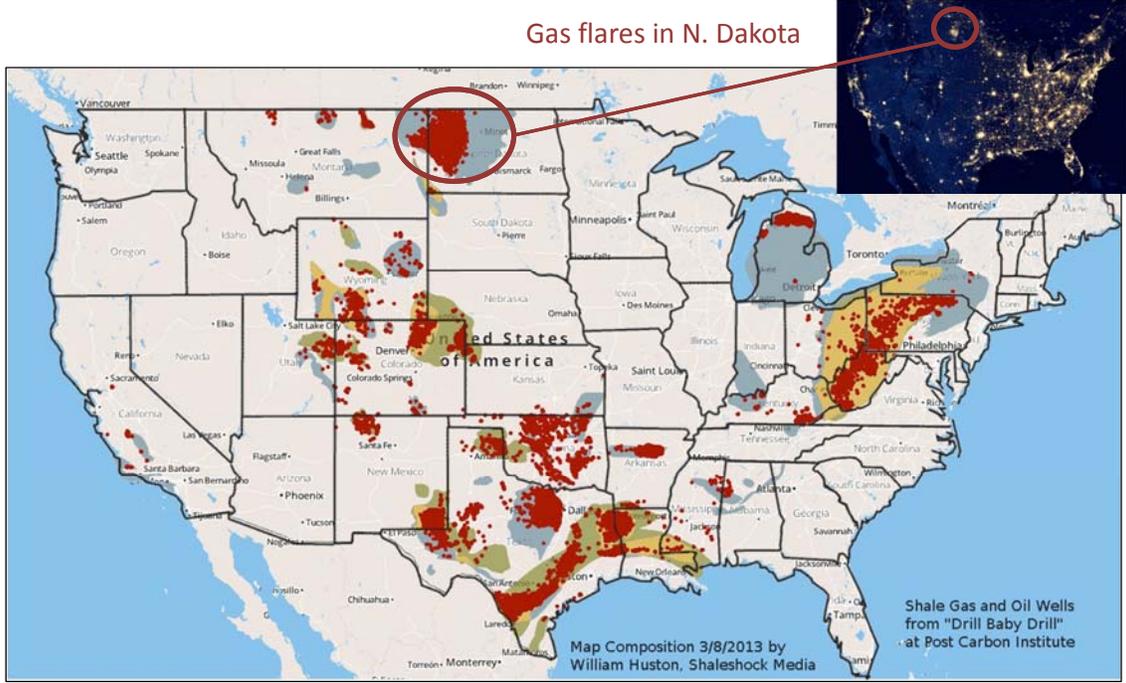


Oil and gas production from unconventional reservoirs have been made possible by new technologies.



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## Recent boom in unconventional plays



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# Global Monitoring Division

## Review Summary



### Contents:

- 1 Presentation – Dr. James Butler

# Summary

James Butler

NOAA/ESRL Global Monitoring Division  
Laboratory Review, April 3-5, 2013



## Data Products and Visualization

([www.esrl.noaa.gov/gmd/products](http://www.esrl.noaa.gov/gmd/products))



### Annual Greenhouse Gas Index

The AGGI index provides a point of comparison for tracking annual changes in levels of atmospheric greenhouse gases.



### FTP Data Finder

Search for and download datasets available on the GMD public FTP server.



### Interactive Atmospheric Data Visualization

A data exploration tool for GMD measurements.



### GLOBALVIEW

The GLOBALVIEW data products enhance the spatial and temporal distribution of atmospheric observations of CO<sub>2</sub>, CH<sub>4</sub> and other related greenhouse gases.



### Ozone and Water Vapor

View data of the South Pole Ozone hole, plus profiles of ozone from Greenland, and water vapor from Boulder.



### Solar Radiation

View plots of various types of surface solar and infrared radiation measurements from around the globe.



### Atmospheric Transport

View back trajectories from some of the global GMD observations sites using the ESRL/GMD IADV web app.



### Observation Sites

Information and maps of sites where GMD makes measurements.



### Ozone Depleting Gas Index

The ODGI is an index that relates changes in atmospheric amounts of ozone depleting gases and the recovery of the stratospheric ozone layer.



### Current Trends in CO<sub>2</sub>

View graphs and get data for the most recent CO<sub>2</sub> atmospheric data at Mauna Loa, Hawaii and for global averages.



### Solar Calculator

Generate estimates for sunrise, sunset, solar noon and the position of the sun in the sky for a desired location and date.



### Carbon Tracker

CarbonTracker is a tool to keep track of time dependent emissions and uptake of atmospheric carbon dioxide (CO<sub>2</sub>), both natural and man made.



### Trace Gases

View graphs from the CATS trace gas measurement system.



### Aerosols

Plots of measured aerosol properties.



### Calibrations of Reference Gases

NOAA ESRL GMD is the World Meteorological Organization (WMO), Global Atmosphere Watch (GAW) Central Calibration Laboratory (CCL) for CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, SF<sub>6</sub>, and CO.

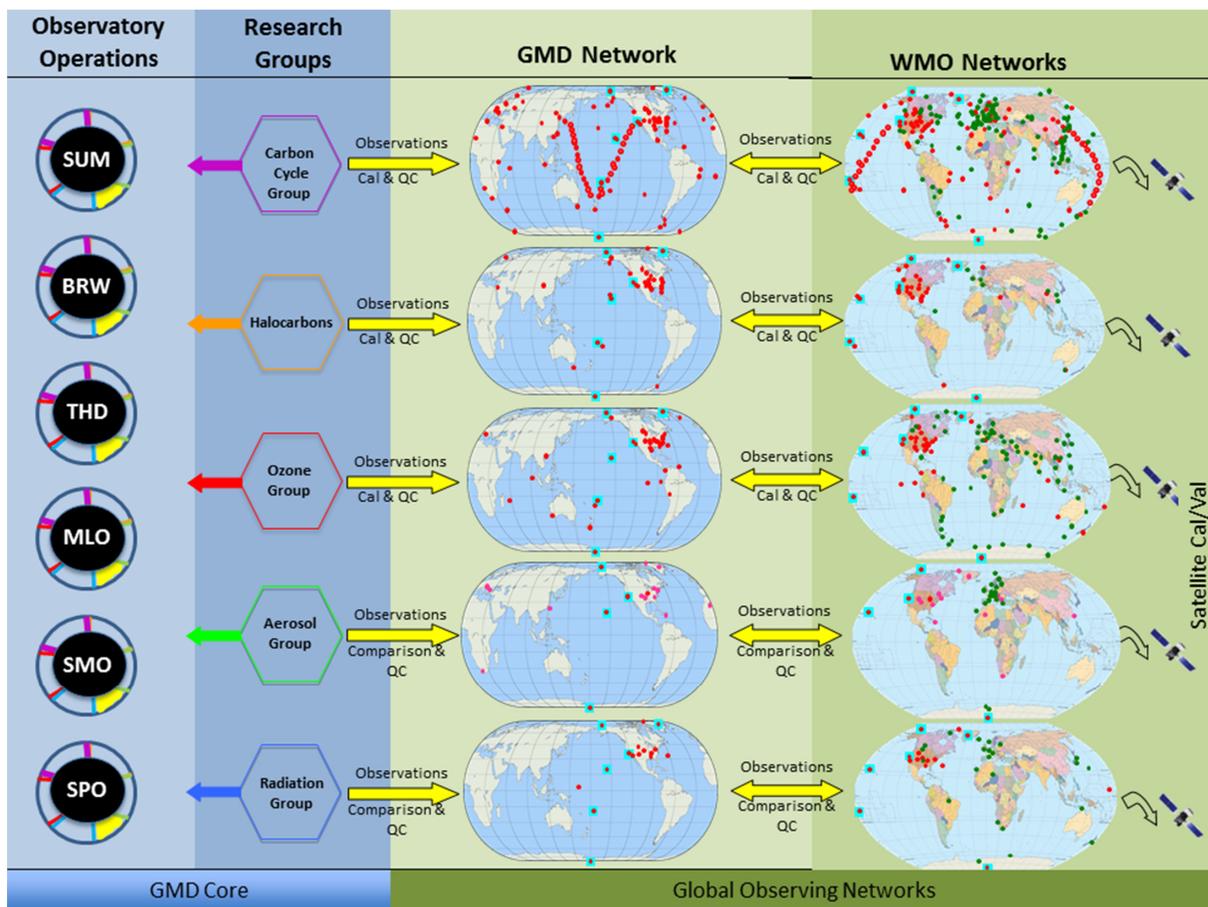


### Station Meteorology

Most recent weather information from the GMD observatories and a few other locations.

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## Priorities

### By Capability

1. Nurture and Sustain Long Term Observing Networks
  - Calibration and quality control
  - High quality, experienced, scientific and technical staff
  - Observing site operations

### By Theme

1. Climate Forcing
2. Ozone Depletion
3. (Background Air Quality)

### By Emerging Issue (?)

1. Climate Change
2. Long-Range Transport
3. Renewable Energy

# Questions?



## NOAA Global Monitoring Division

- *... providing the best possible information on atmospheric constituents that drive climate change, stratospheric ozone depletion, and baseline air quality.*

## GMD Mission

- *To acquire, evaluate, and make available accurate, long-term records of atmospheric gases, aerosol particles, and solar radiation in a manner that allows the causes of change to be understood.*