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# Atmospheric Chemistry Considerations Relevant to the Ozone NAAQS

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- The frequency of ozone exceedances increases dramatically at standards below 75 ppb
  - Rather than an ozone exceedance being a relatively rare event, ozone exceedances will become common in both urban and rural areas
  - Pristine areas such as National Parks, with minimal local emissions, routinely exceed standards below 75 ppb
- Large reductions in ozone precursor emissions are required to meet lower standards
- Cumulative ozone, a surrogate for total exposure, is minimally sensitive to lower standards
  - Emission reductions can lead to either increases or decreases in average and cumulative ozone, and the magnitude of benefit/disbenefit is largely determined by what portion of the day or year is considered
  - 14 of 15 cities analyzed by EPA contained sites where May-September average ozone increases as emissions are reduced from 2007 levels
- Background ozone is high
  - Modeled peak background approaches or exceeds 60 ppb, and is likely underestimated
  - Average background drives a significant portion of modeled risk
  - Non-exceptional exceedances of standard due to background ozone will become increasingly likely. Exceptional events policy is not sufficient to deal with this issue.
  - EPA's definition of background ozone assumes complete elimination of domestic anthropogenic sources



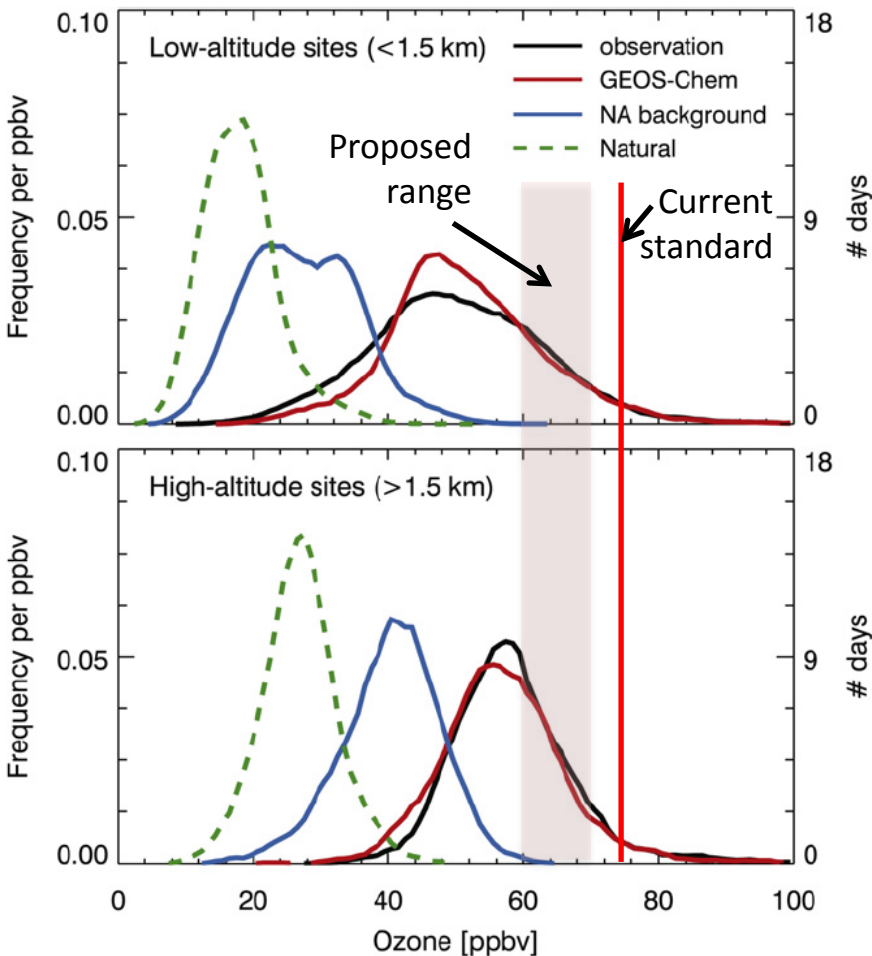
# Basic Ozone Chemistry

- Ozone is created in the atmosphere by reactions between nitrogen oxides (NO<sub>x</sub>) and volatile organic carbons (VOCs).
  - NO<sub>x</sub> and VOCs are known as ozone precursors and are the emissions that can be controlled to achieve lower ozone standards.
  - Ozone itself is not emitted to the atmosphere
- NO<sub>x</sub> is primarily emitted by combustion processes such as power plants and engines, and has natural sources including lightning and soils.
- VOCs are emitted from both human activities and from plants.
- Ozone chemistry is highly non-linear, meaning that each unit of NO<sub>x</sub> and VOC emissions do not translate into a unit change in ozone.
- When there is excess NO<sub>x</sub> in the atmosphere, it will destroy ozone
  - This leads to a very complex response of ozone to changes in precursor emissions



# Standards lower than 75 ppbv result in a dramatic increase in the frequency of exceedance events

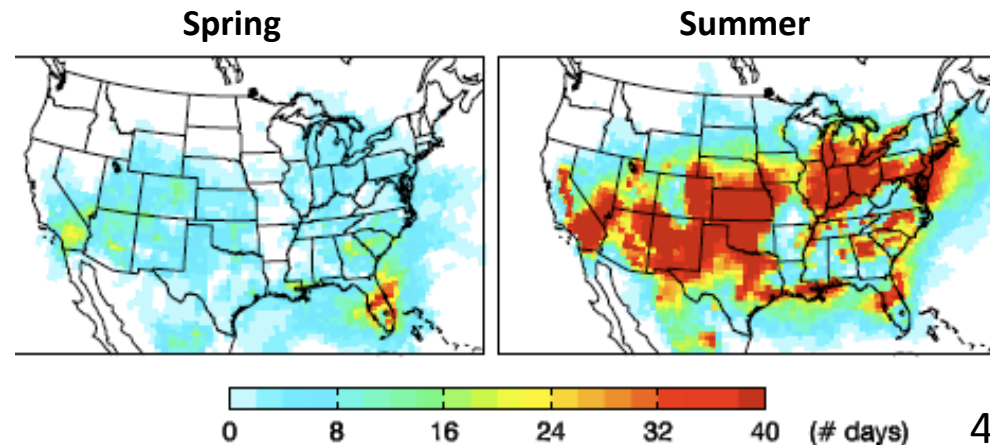
## Frequency distribution of MDA8 ozone in rural U.S. (CASTNET monitors)



(Zhang et al, 2011 and data referenced in that paper)

- Standards below 75 ppbv are no longer aimed at peak ozone, but fall into the main body of the frequency distribution
- Both urban and rural areas will experience a dramatic increase in the number of exceedance events at lower standards
- The current form of the standard allows ~4 exceedance events annually

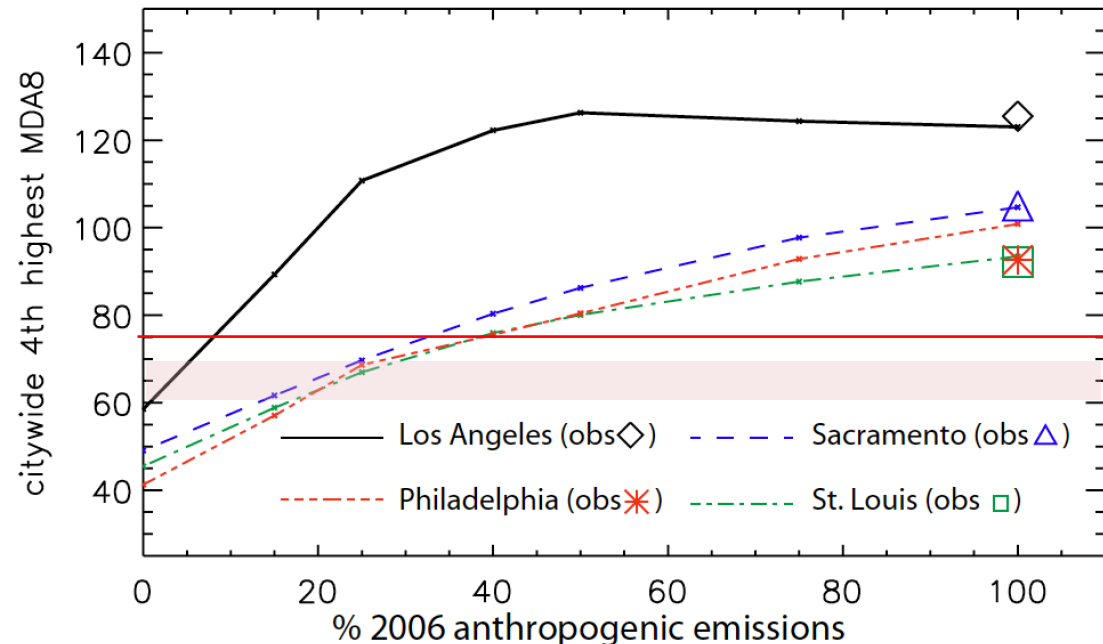
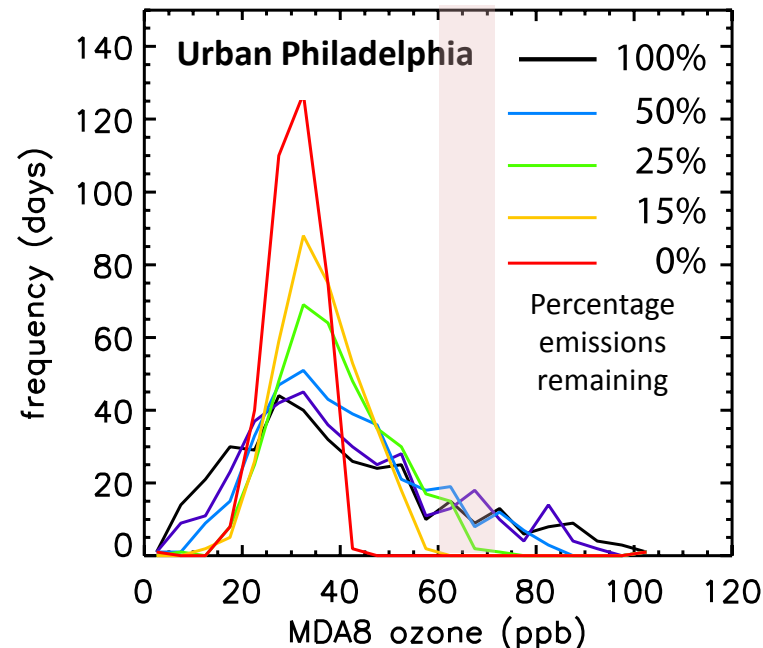
## Number of days with MDA8 ozone exceeding 60 ppbv





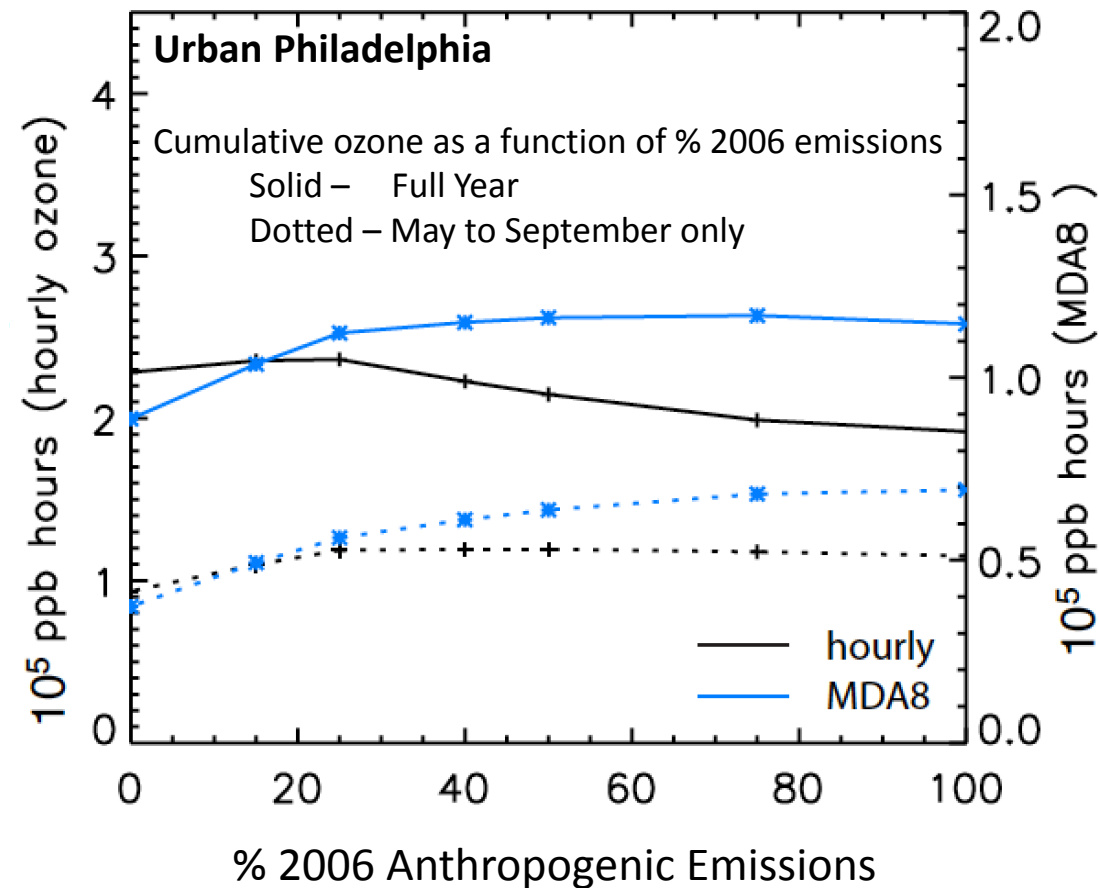
# Distribution shifts slowly with emission reductions

- Very deep NO<sub>x</sub> and VOC emission reductions are required to meet lower standards
  - ~85% of 2006 emissions must be eliminated to reach a standard of 60 ppb in Philadelphia, Sacramento and St. Louis. 97% reductions are required in Los Angeles.





# Cumulative ozone exposure changes slowly in response to emission reductions

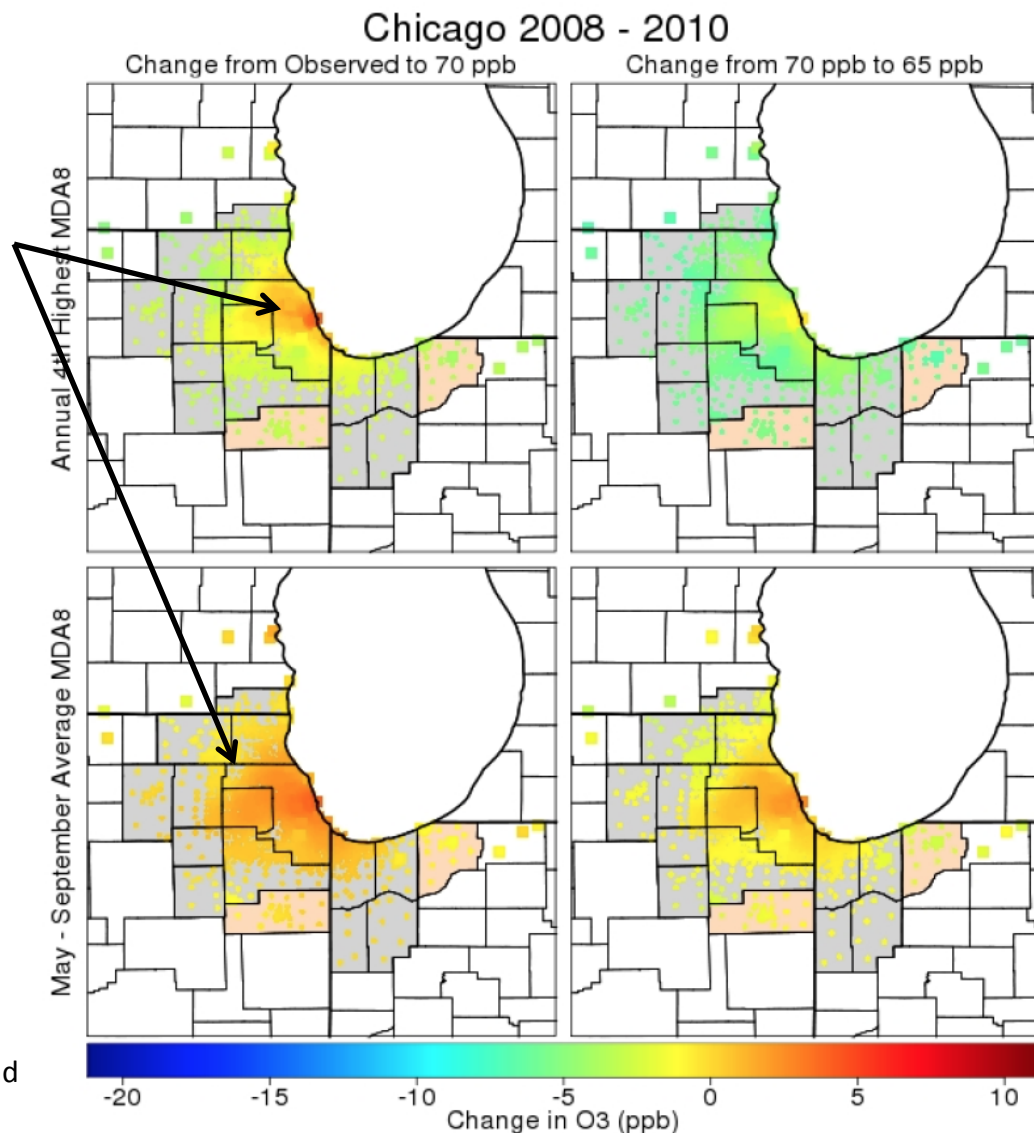


- Cumulative ozone is a surrogate for ozone exposure
  - equivalent to a linear concentration response function with a threshold at zero (as assumed by epidemiology studies used by EPA)
- Minimal changes in cumulative ozone as emissions are reduced
- Magnitude and sign of changes are sensitive to period of year and portion of year considered
  - Increases in total exposure if full year, hourly data are considered
  - EPA uses May-Sept MDA8 in REA



# Urban core ozone disbenefits under lower proposed NAAQS

- According to EPA modeling, 14 of 15 modeled cities contain areas with increases in May-Sept ambient ozone as precursor emissions are reduced from present levels
- These areas are currently NO<sub>x</sub> saturated
- Driven by strong non-linear chemistry of ozone



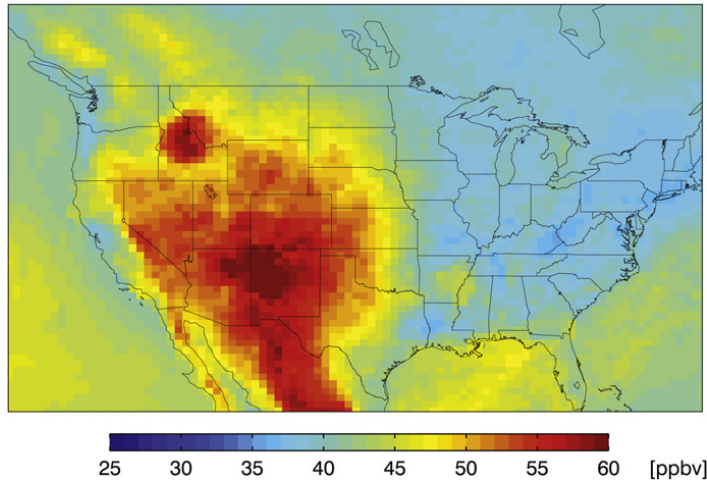




# Background Ozone is High

Peak Background

(4<sup>th</sup> highest 8-hour daily average)



Modeled peak background approaches or exceeds 60 ppb, and likely underestimates peak background impacts (EPA ISA)

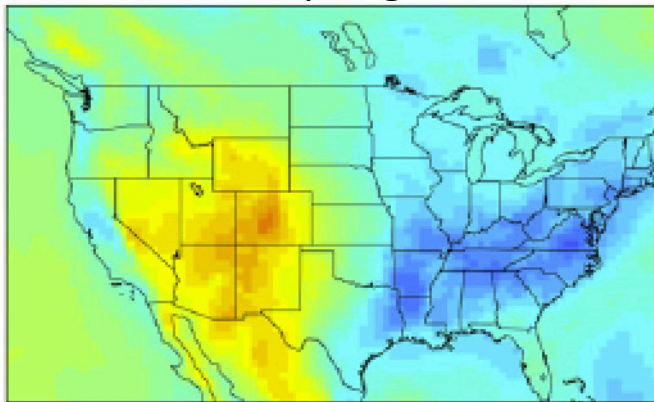
Modeled background comprises a significant fraction of total cumulative ozone exposure

Background ozone is comprised of multiple sources of ozone including:

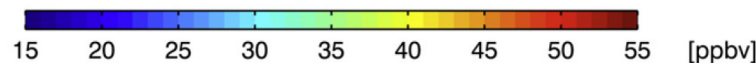
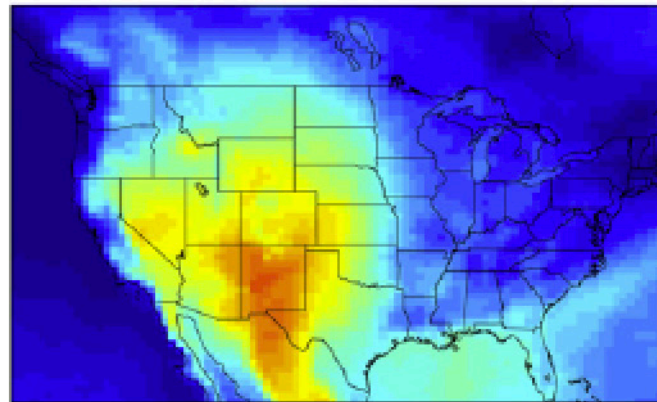
- International anthropogenic precursor emissions
- Natural precursor emissions including Wildfires, Lightning, Soils and Vegetation
- Stratospheric ozone
- Assumes complete elimination of domestic anthropogenic precursor emissions

Average Background

Spring



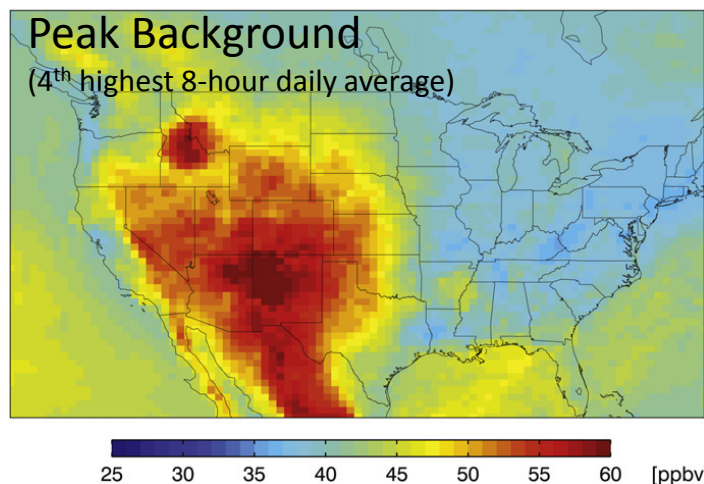
Summer







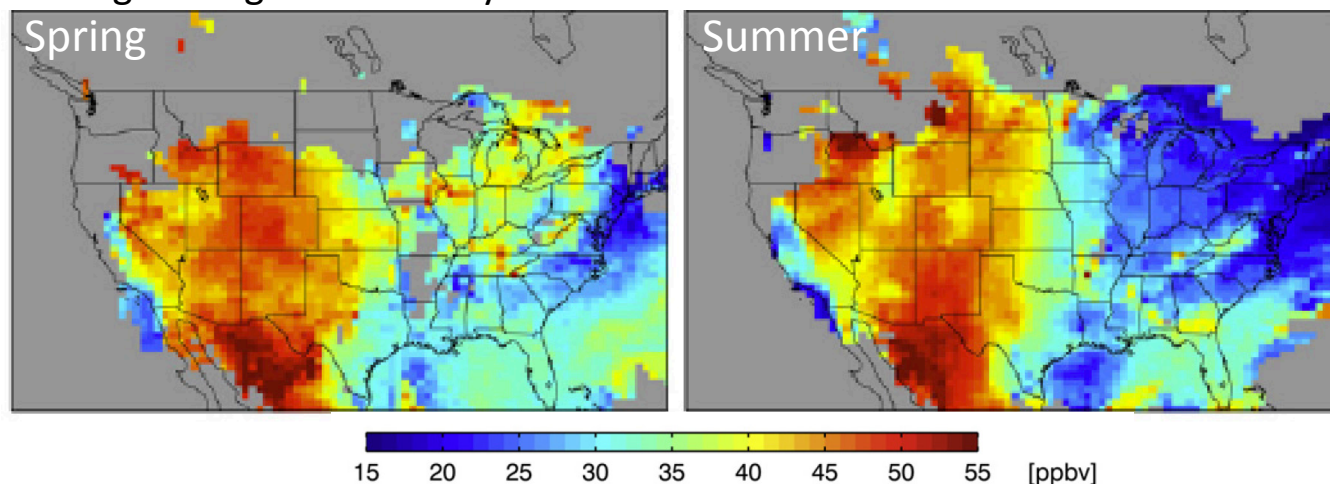
# Background Ozone Leaves a Small Margin for Domestic Precursor Emissions



For days with 4<sup>th</sup> highest MDA8 ozone greater than 60 ppb, background ozone can constitute a very large fraction of total ozone.

This leaves a very small margin for ozone production from domestic emissions across wide areas of the US.

Average Background for days with MDA8 > 60

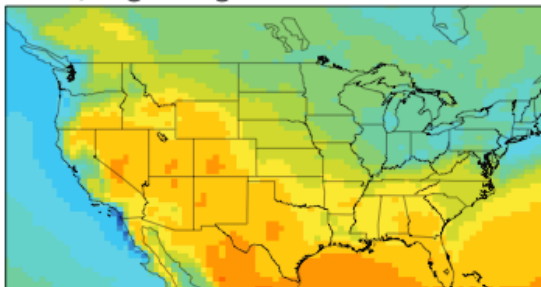




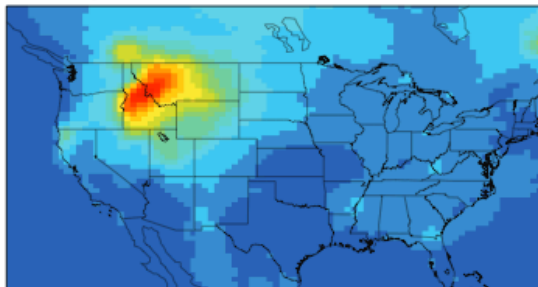
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# Background Ozone cannot be addressed by the Exceptional Events Policy

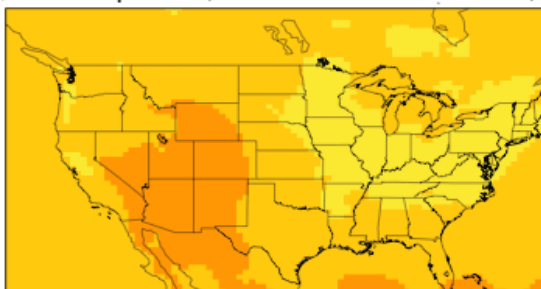
a) Lightning enhancements



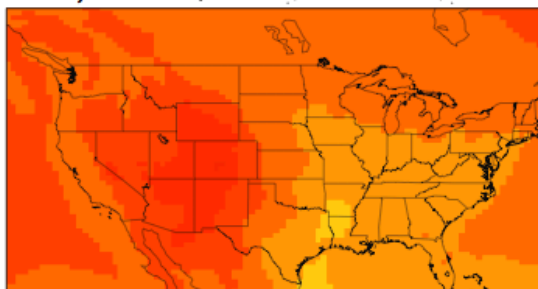
b) Wildfire enhancements



c) Stratosphere (GEOS-Chem definition)



d) Stratosphere (e90 tracer)



**As written, the Exceptional Events Rule will not cover exceedances of the NAAQS due to the contribution of background ozone.**

**Consequently, in many areas, there is no way to meet the NAAQS if it is set near or at the background level.**

Although many sources of background ozone can lead to an exceptional event that can be excluded from attainment, a mix of these sources leading to generally high background cannot be excluded

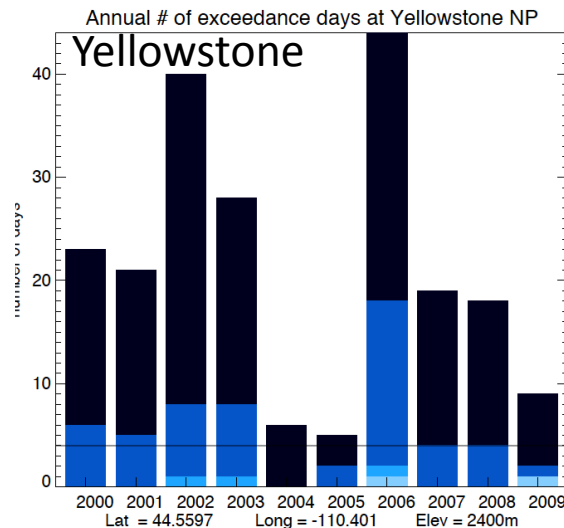
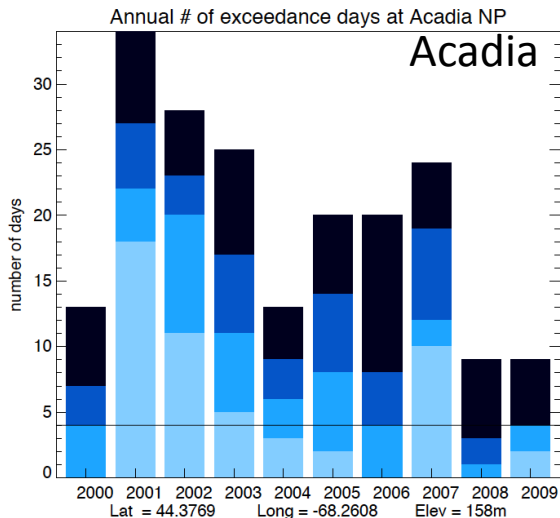
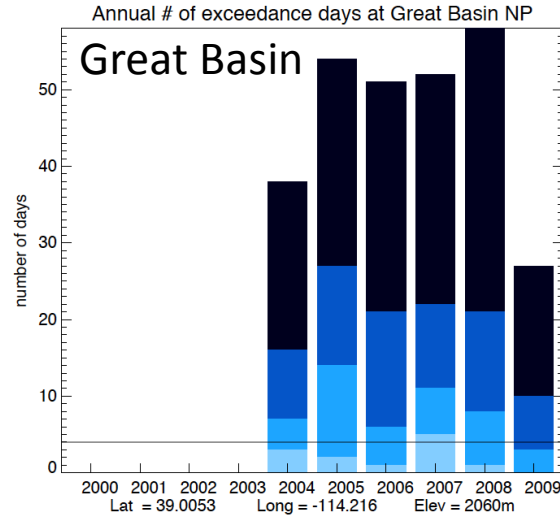
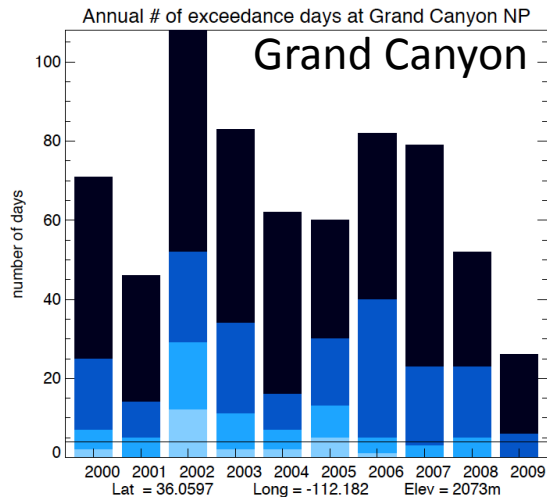
State-of-the-science observation and modeling techniques cannot easily identify sources of background ozone without high uncertainty.

‘An exceptional event is a natural event (excluding stagnations, inversions, high temperatures, or precipitation) or an anthropogenic event that is unlikely to recur in the same location. Both exceptional events and North American background can involve emissions from natural events like forest wildfires or stratospheric ozone intrusions. However, exceedances due to natural emissions that occur every day and contribute to policy relevant background, such as biogenic emissions, do not meet the definition of an exceptional event and are thus not eligible for exclusion under the EER. Routine anthropogenic emissions outside of the U.S. contribute to policy relevant background, but are not exceptional events.’

EPA Interim Exceptional Events Rule, FAQ Q#16’ (May 2013)



# Ozone in National Parks will regularly exceed lower standards



**National parks will exceed NAAQS below 75 ppb on a regular basis**

Percentage of CASTNET Monitored National Parks, Monuments and Wildlife Refuges that will exceed ozone NAAQS

Standard	2006 to 2008	2007 to 2009
60 ppb	85%	85%
65 ppb	78%	70%
68 ppb	67%	63%
70 ppb	67%	52%
75 ppb	41%	22%

Notice the Y-axis scale is # of exceedance days. The current form of the standard allows for ~4 exceedance days per year (horizontal black lines).



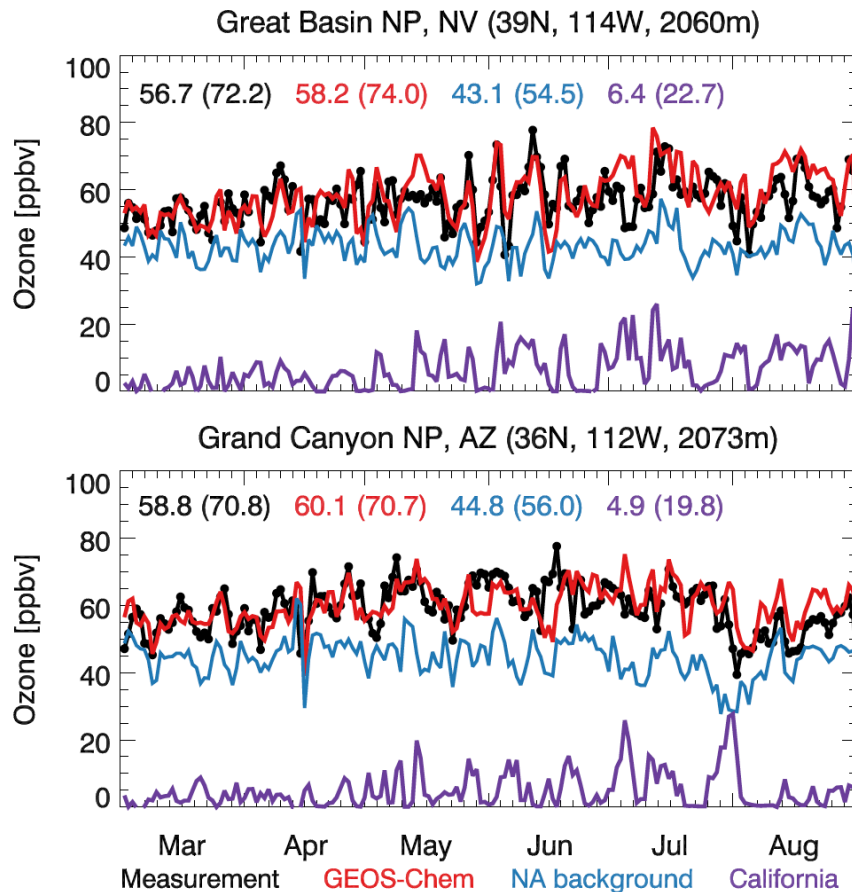
# Local vs. Regional vs. Background Sources

**By lowering the ozone standard you greatly expand the non-attainment area into rural counties with relatively low emissions.**

**Rural counties will be unable to offset emissions from new development because they have few existing sources.**

**These rural areas will be dependent on upwind urban areas reducing emissions in order to reach attainment.**

Example: Great Basin NP and Grand Canyon NP  
The sum of ozone due to Background plus impact from California leaves nearly zero room for state or local policies to influence local ozone because it is not a product of local emissions.



**Black** lines are measurements

**Red** lines are model

**Blue** line is modeled North American Background

**Purple** line is modeled California impact



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- Environmental Protection Agency. Environmental Protection Agency. Health Risk and Exposure Assessment for Ozone. **2014a**, Report No. EPA-452/P-14-004a. Office of Air Quality Planning and Standards. Research Triangle Park, NC
- Zhang, L., D. J. Jacob, X. Yue, N.V. Downey, D.A. Wood, and D. Blewitt, **2014**. Atmospheric Chemistry and Physics. Sources contributing to background surface ozone in the US intermountain West. doi:10.5194/acpd-13-25871-2013
- Zhang, L., D.J. Jacob, N.V. Downey, D.A. Wood, D. Blewitt, C.C. Carouge, A. van Donkelaar, D.B. Jones, L.T. Murray, and Y. Wang, **2011**. Atmospheric Environment. Improved estimate of the policy-relevant background ozone in the United States using the GEOS-Chem global model with 1/2 x 2/3 degree horizontal resolution over North America. Issue 45, 6769-6776, doi:10.1016/j.atmosenv.2011.07.054