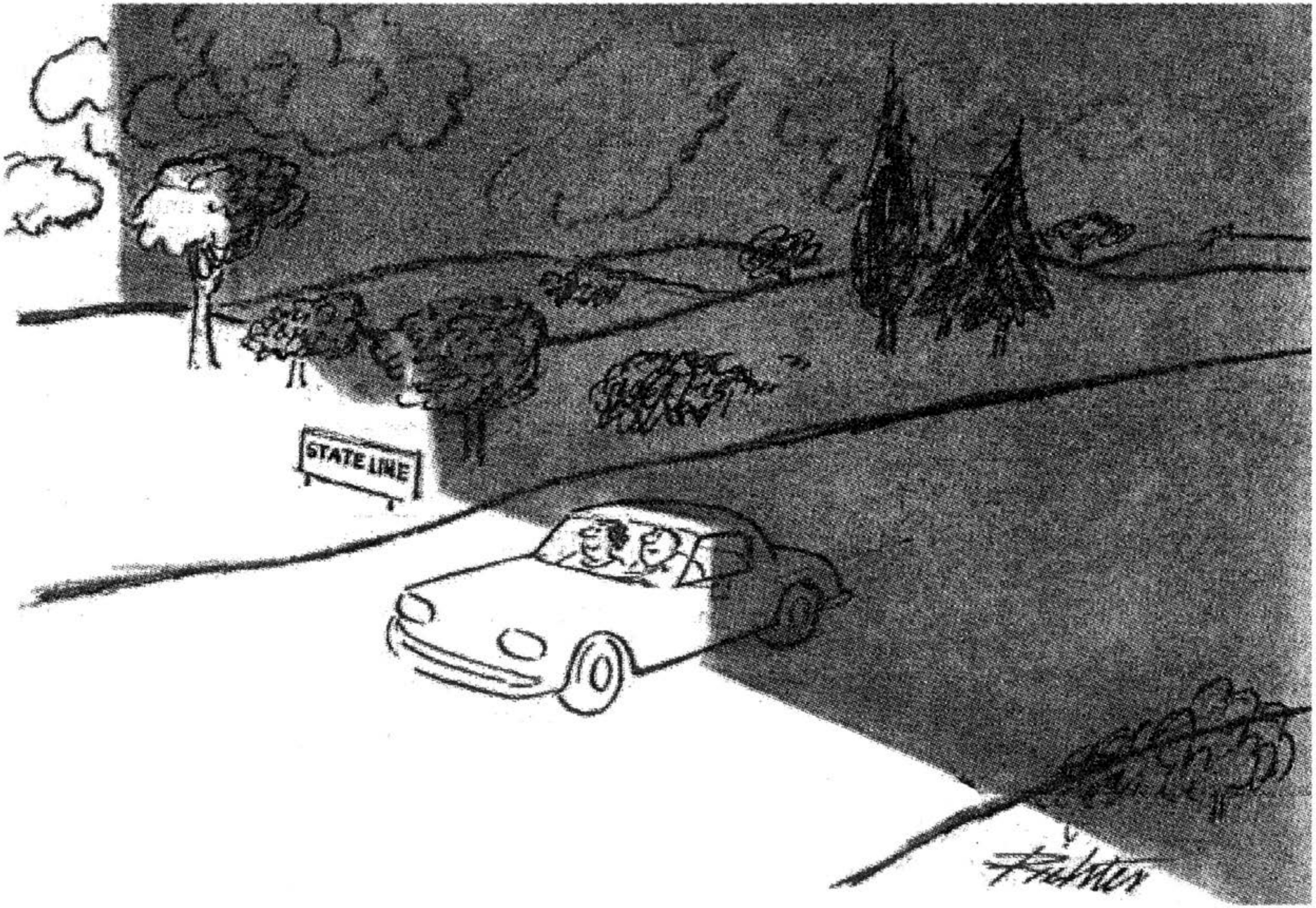
Ozone 301

Maricopa County Air Quality Department

September 4, 2014

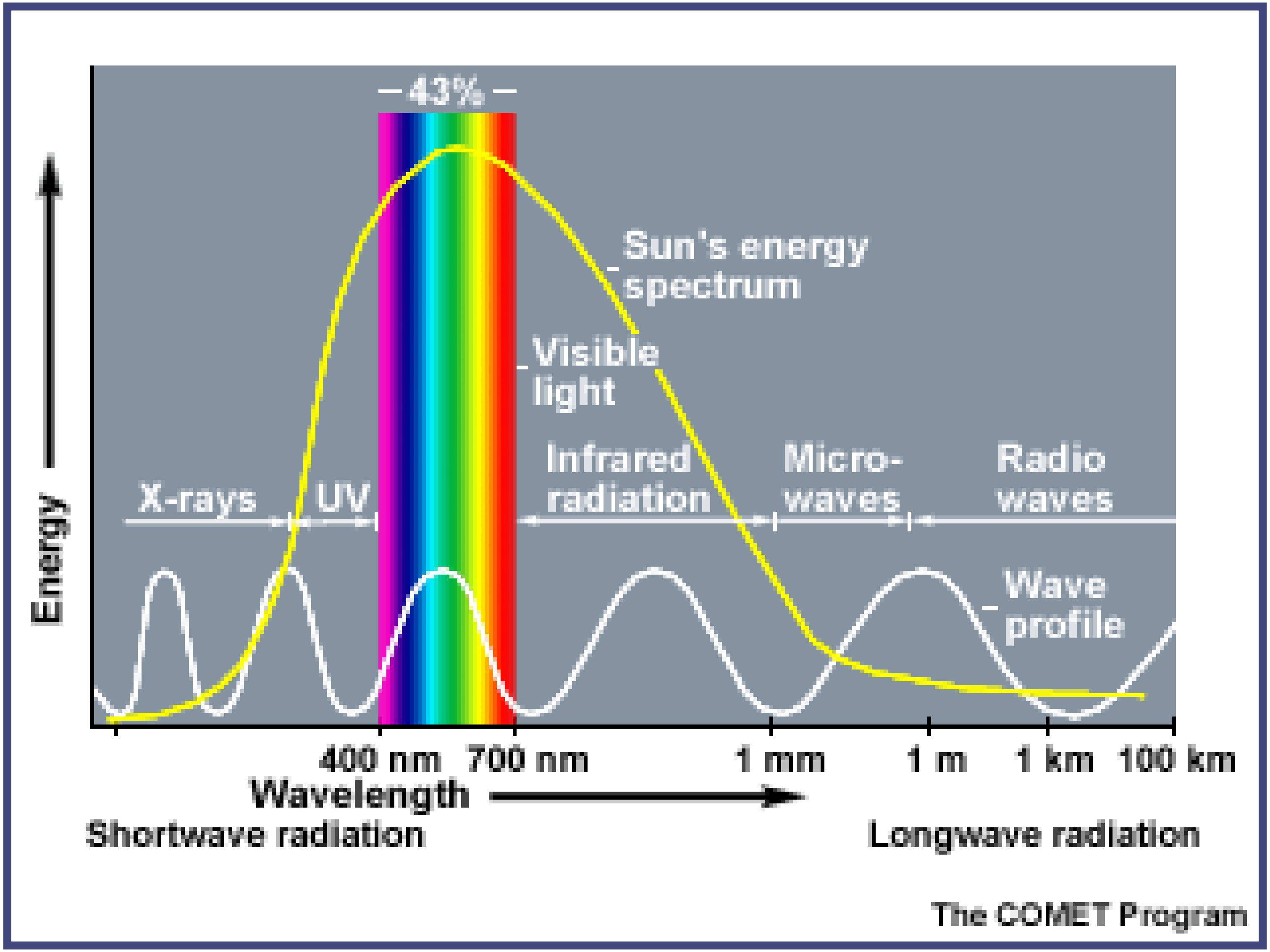
Tom Moore
WRAP Air Quality Program Manager
WESTAR Council

Western Regional Air Partnership

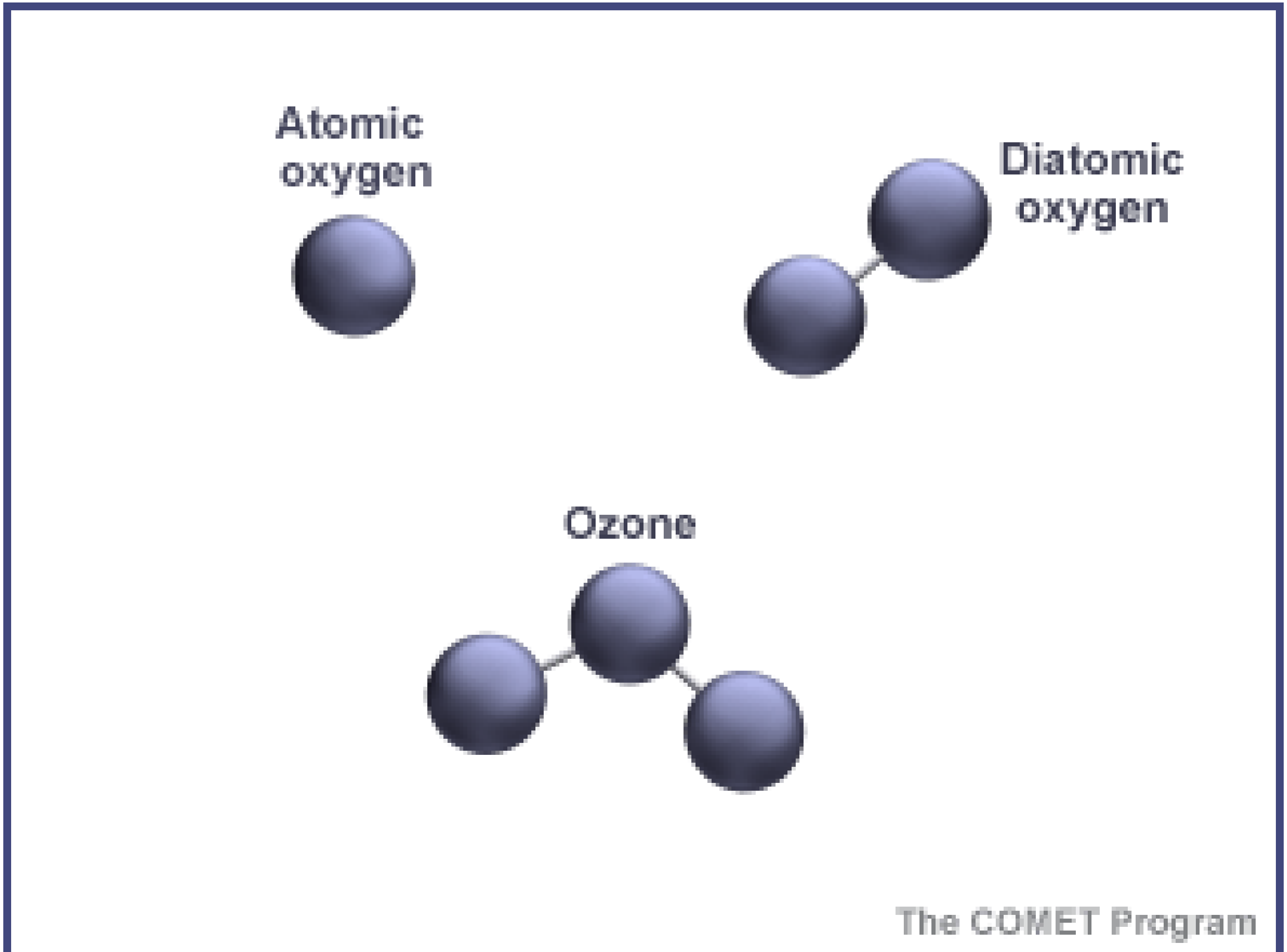


"They have very strict anti-pollution laws in this state."

Electromagnetic Spectrum

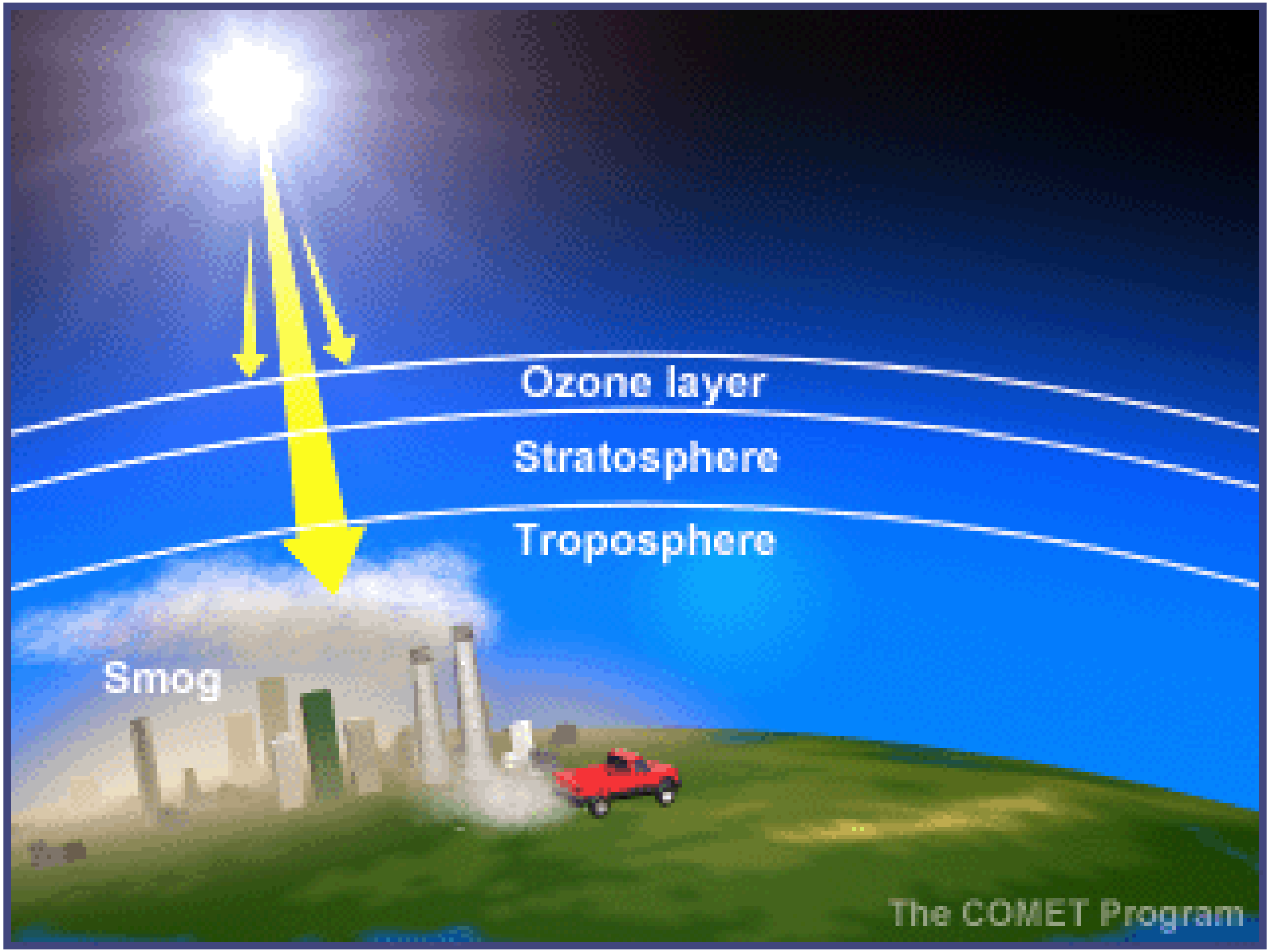


Ozone is made of three oxygen atoms



Ozone formation

- Ozone is constantly being formed
- Ultraviolet light splits the molecules apart
- A highly reactive free oxygen atom then collides with another oxygen molecule
- Because ozone is unstable, ultraviolet light quickly breaks it up, and the process begins again.



Ozone has the same chemical structure whether it is found in the stratosphere or the troposphere.

Ozone in the Stratosphere

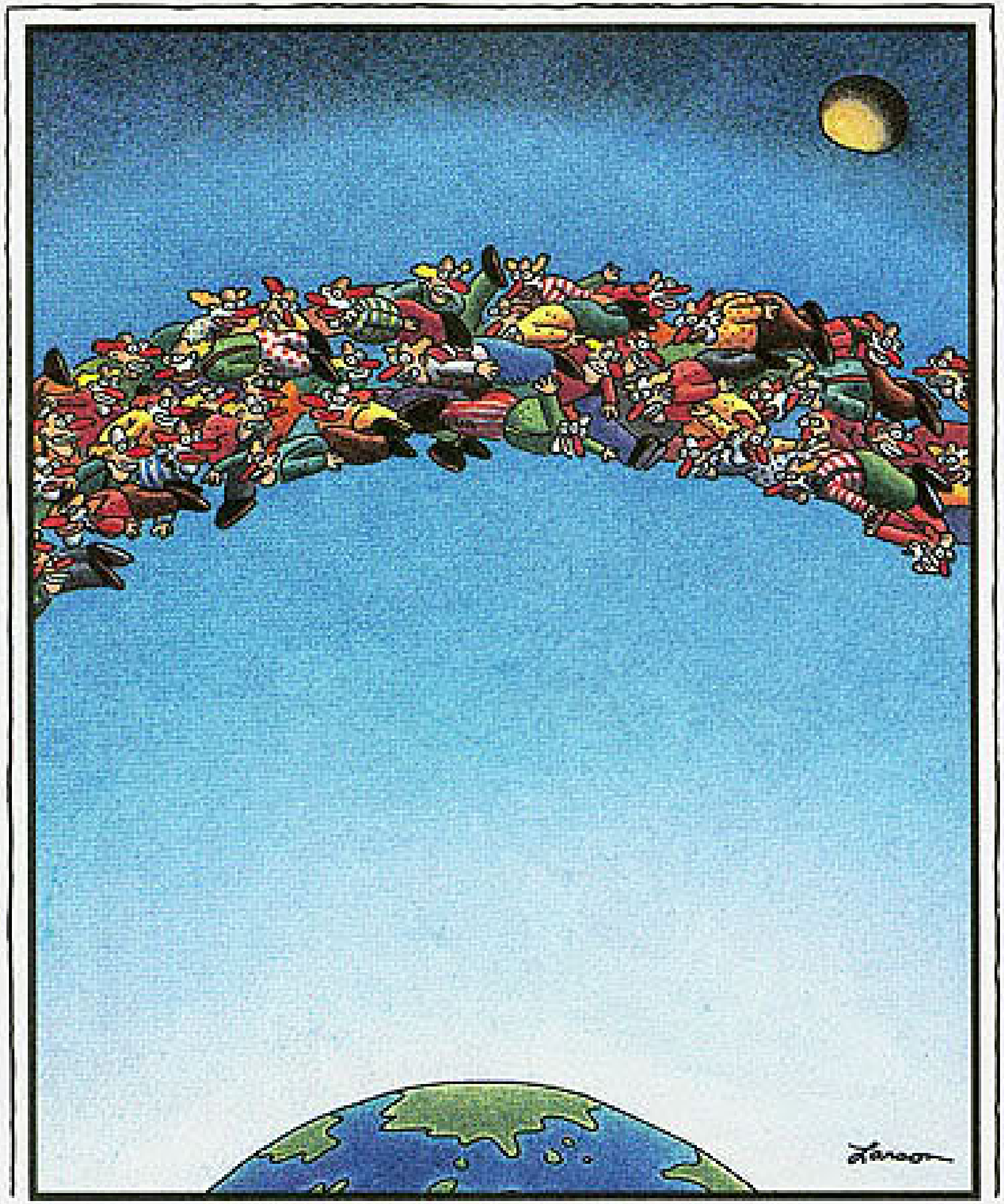
- 90% of the ozone in Earth's atmosphere lies in the stratosphere between 16 and 48 kilometers (10 and 30 miles) above the earth's surface.

- Ozone forms a kind of layer in the stratosphere, absorbing ultraviolet light

- Ozone absorbs 95 to 99.9% of the sun's ultraviolet radiation
  - Absorbs the most energetic ultraviolet light, known as UV-C and UV-B, which causes biological damage

- “Shield" as a description of ozone in the stratosphere is a bit misleading

- “Shield" changes constantly - atmospheric chemical processes maintain a dynamic equilibrium



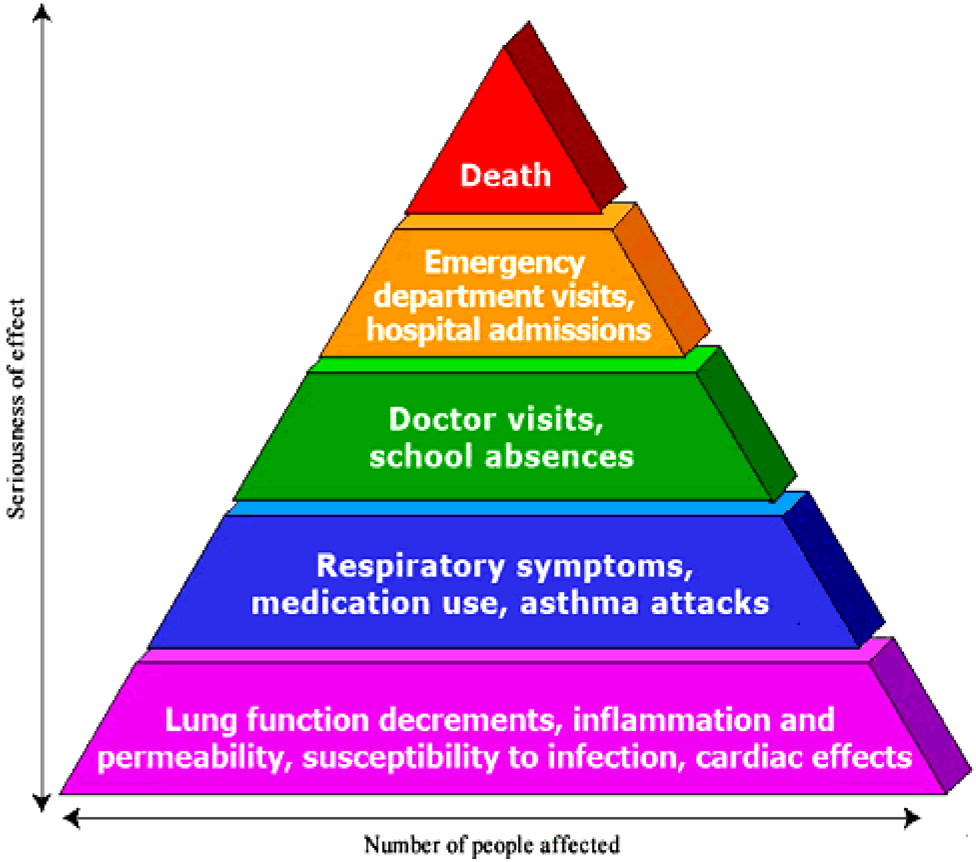
The bozone layer: shielding the rest of the solar system from the Earth's harmful effects.

Ozone in the Troposphere

- Other 10% of the ozone in the earth's atmosphere is found in the troposphere, which is the portion of the atmosphere from the earth's surface to about 12 km or 7 miles up
- In the troposphere, ozone is not wanted
- Tropospheric ozone is even more scarce than the stratosphere with concentrations of about 0.02 to 0.3 ppm (20 to 300 ppb)
- Ozone in the troposphere is one of the greenhouse gases
- In the troposphere, accelerated ozone levels deal us a double whammy - as a key ingredient in smog and as a powerful greenhouse gas.

Ozone

- Ozone is an air pollutant of concern, regulated under the Clean Air Act
- High ozone at ground level is unhealthy, especially affecting those with asthma and other upper respiratory illnesses
- At-risk groups include children, the elderly, and those who work or exercise outdoors



Ozone Health Effects

- Health effects from ozone depend on availability of precursors primarily generated during the combustion of fossil fuels
- Ozone is known to have the following health effects at concentrations common in urban air:
  - Respiratory system irritation
  - Reduced lung function
  - Aggravation of asthma - when ozone levels are high, more people with asthma have attacks
    - Elevated ozone makes people more sensitive to allergens, which in turn trigger asthma attacks
  - Increased susceptibility to respiratory infections
  - Inflammation and damage to the lining of the lungs
  - Example: A statistical study of 95 large urban communities in the United States found significant association between ozone levels and premature death.

How Does Ozone Affect the Environment?

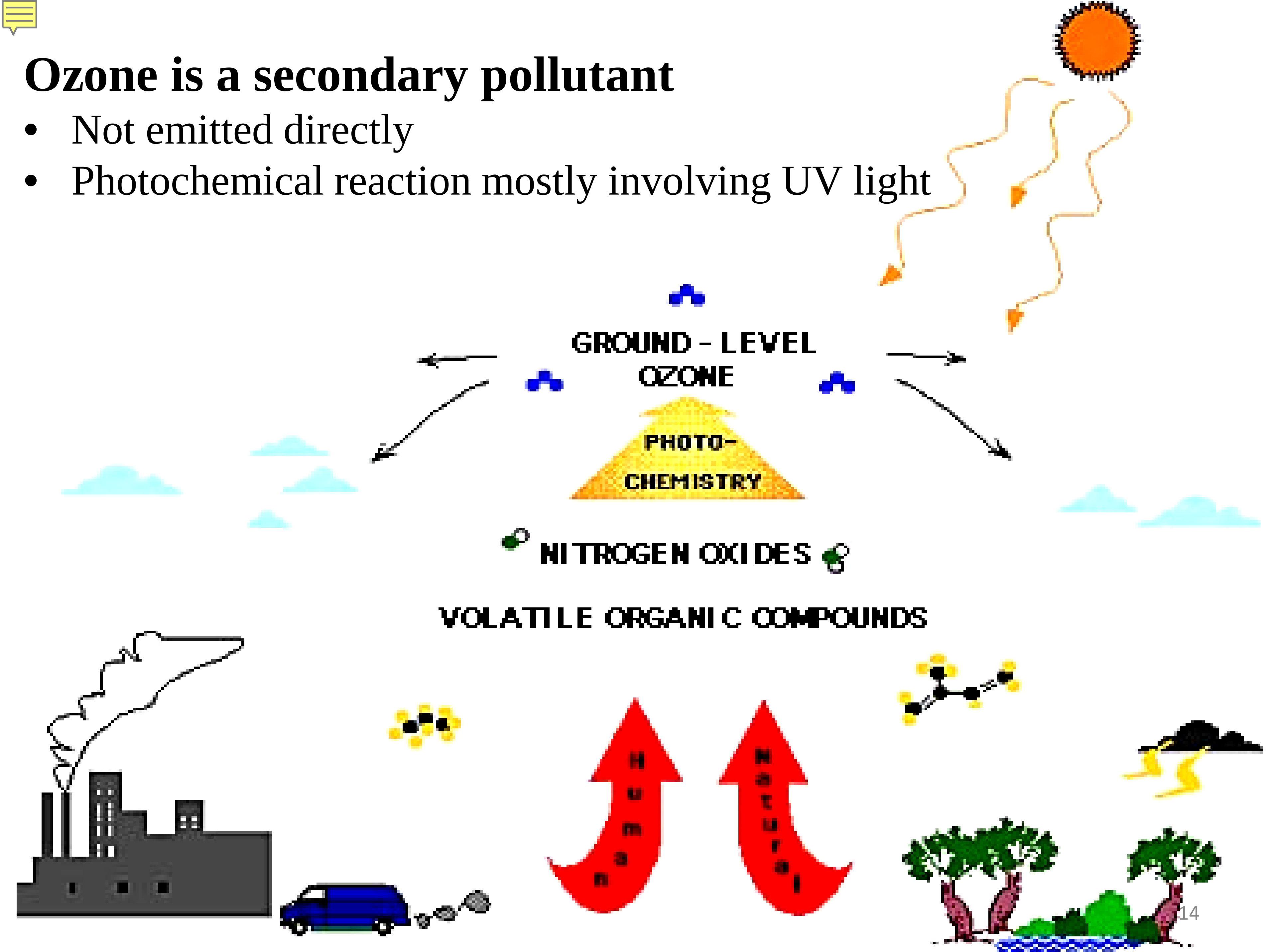
- Ground-level ozone damages vegetation and ecosystems

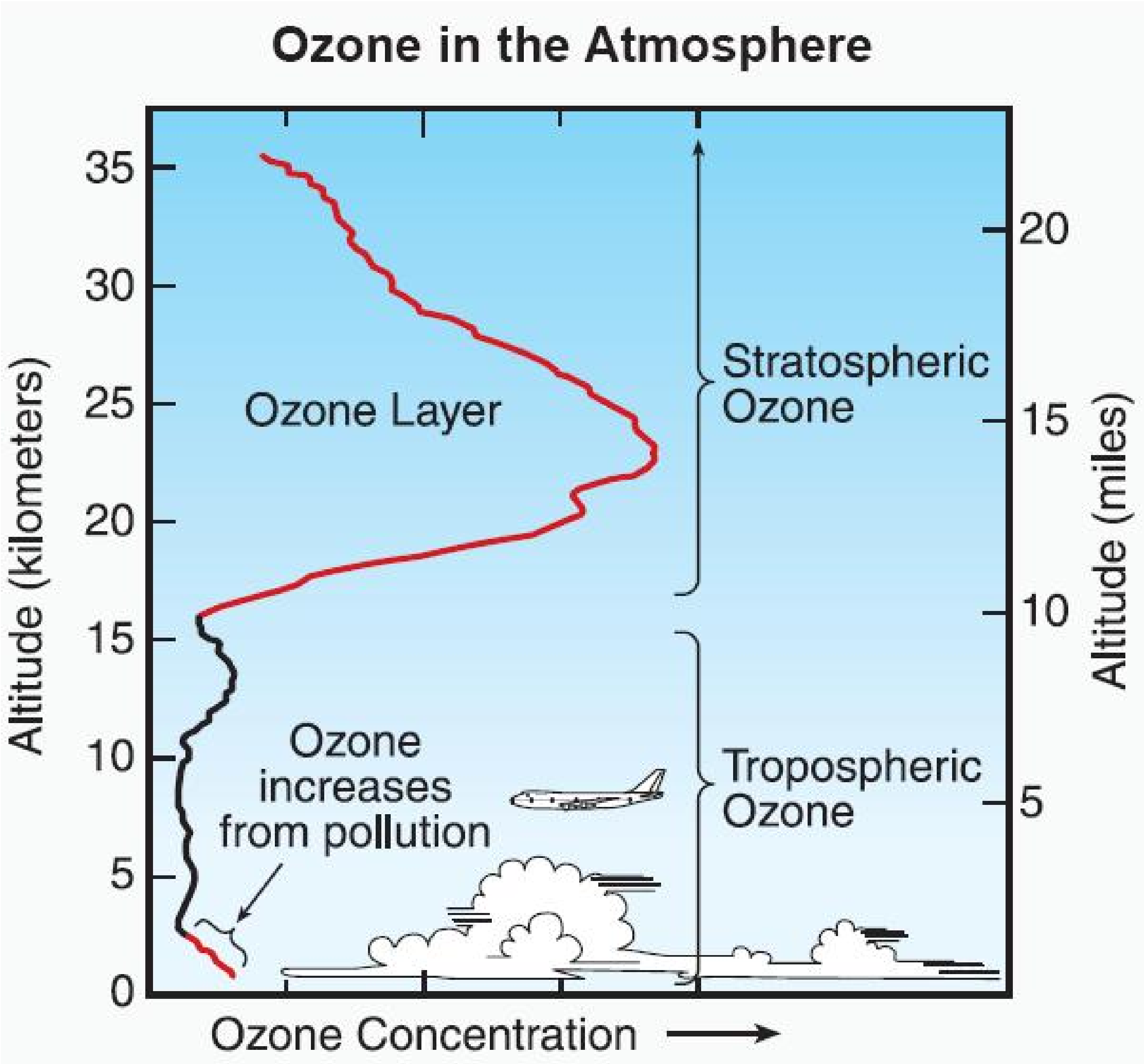
- Crop damage in the United States alone is estimated at $500 million

- Also damages foliage of trees and other plants

Ozone is a secondary pollutant

- Not emitted directly
- Photochemical reaction mostly involving UV light

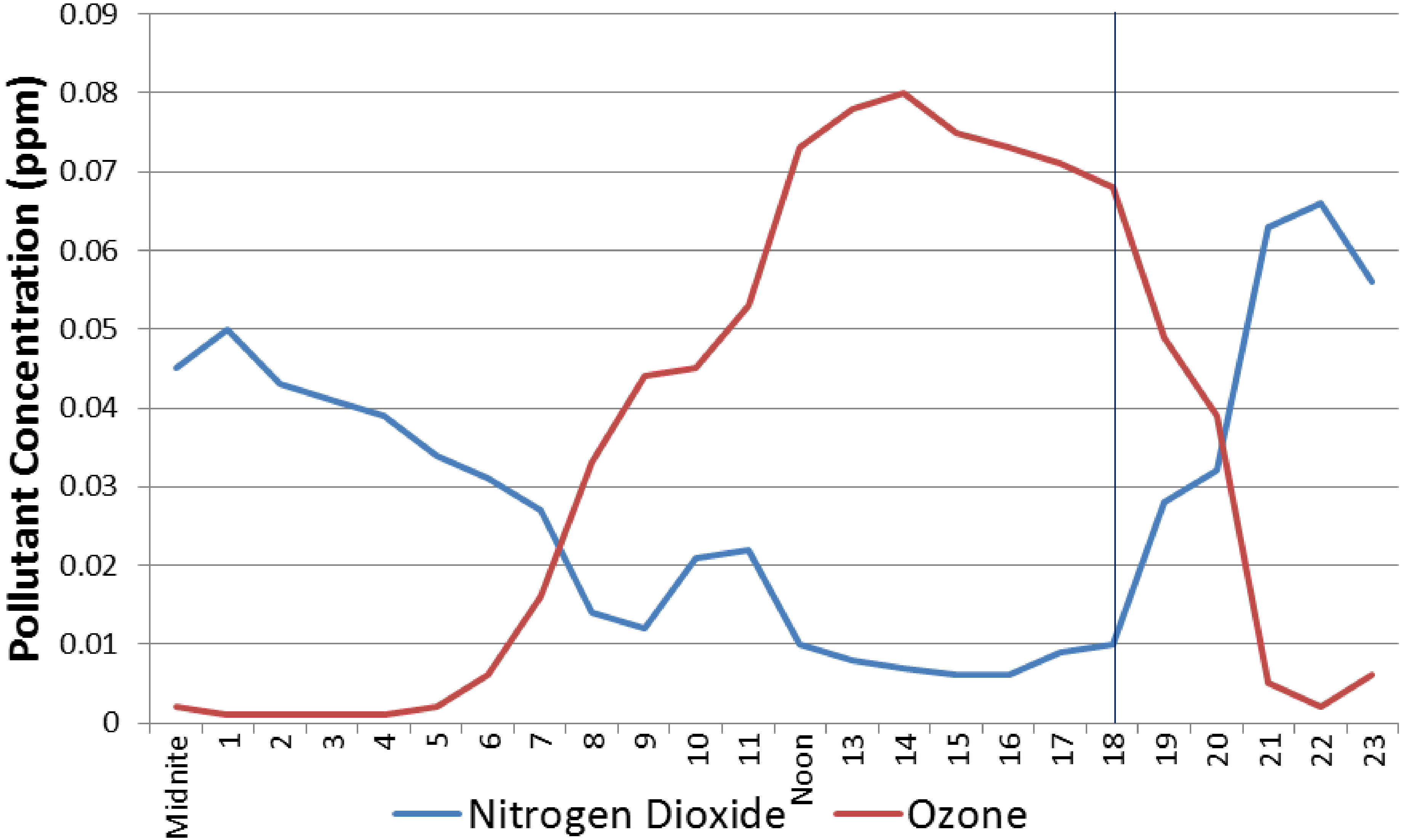



Ozone in the Atmosphere
Altitude (kilometers)
35
30
25
20
15
10
5
0
Ozone Layer
Ozone increases from pollution
Stratospheric Ozone
Tropospheric Ozone
20
15
10
5
Altitude (miles)
Ozone Concentration

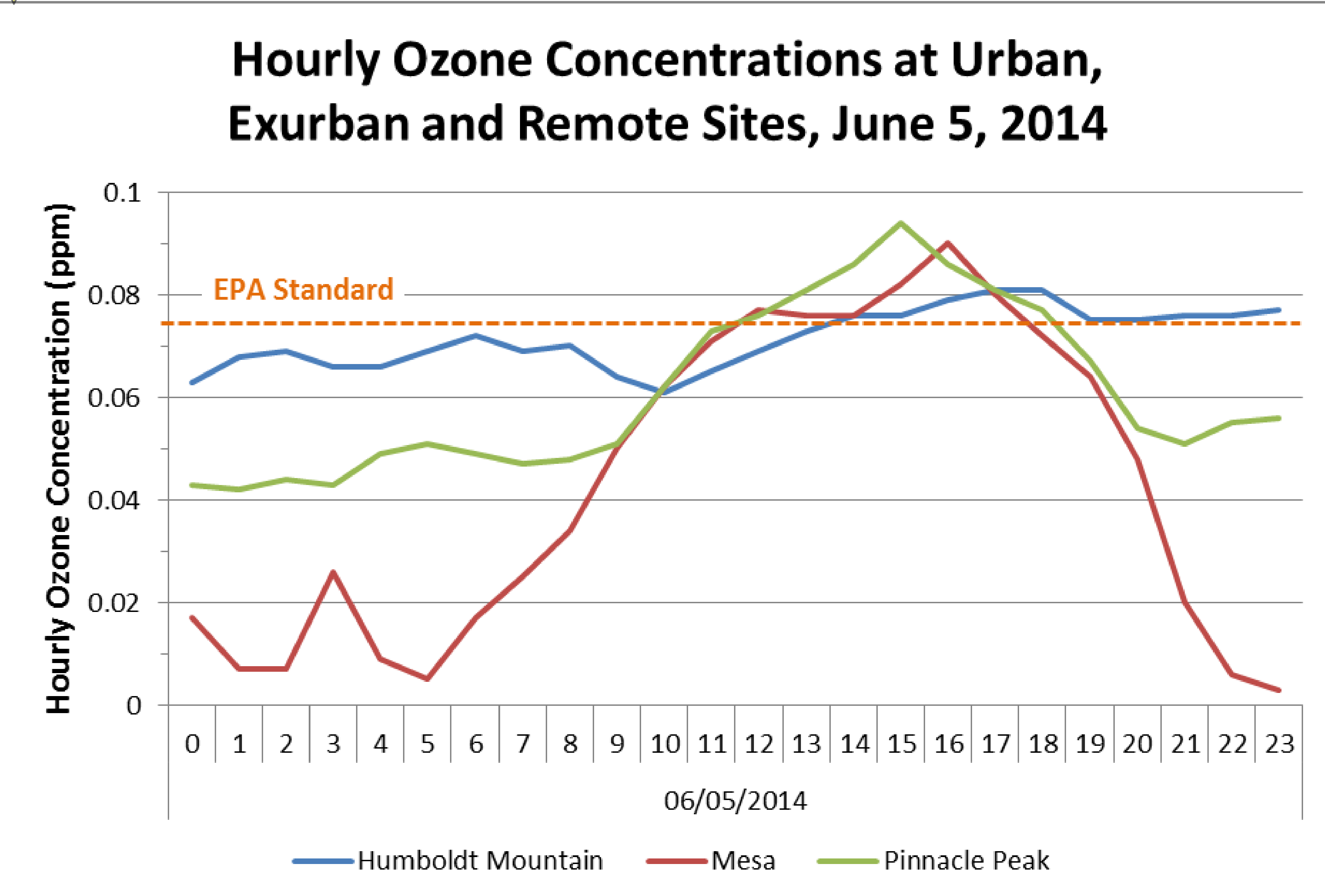
Complex Photochemistry near the ground

- Not a simple path to forming ozone
- NOx in the atmosphere
  - Older, aged NOx emissions drive ozone formation
  - Fresh NOx attacks existing ozone
  - Reduces ozone downwind of high traffic areas and smokestacks
  - Increases ozone as NOx plume ages and mixes away from source
- NOx and ozone peak at different times of day

Typical Hourly Profile for Ozone and NO_2 Concentrations at an Urban Site



Data for the Central Phoenix monitoring site, June 5, 2014

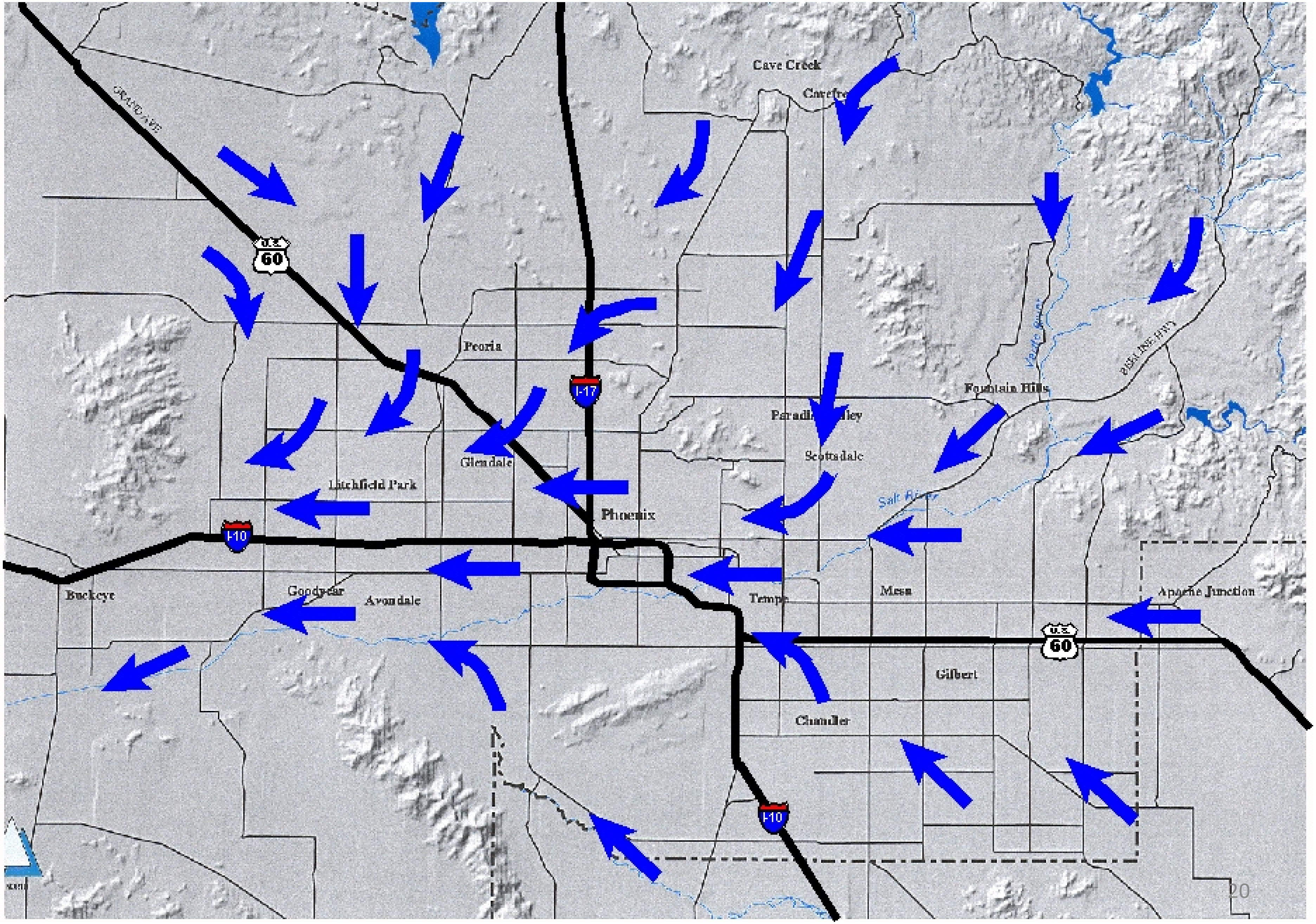


Hourly Ozone Concentrations at Urban, Exurban and Remote Sites, June 5, 2014
Hourly Ozone Concentration (ppm)
0.1
0.08
0.06
0.04
0.02
0
EPA Standard
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
06/05/2014
Humboldt Mountain
Mesa
Pinnacle Peak

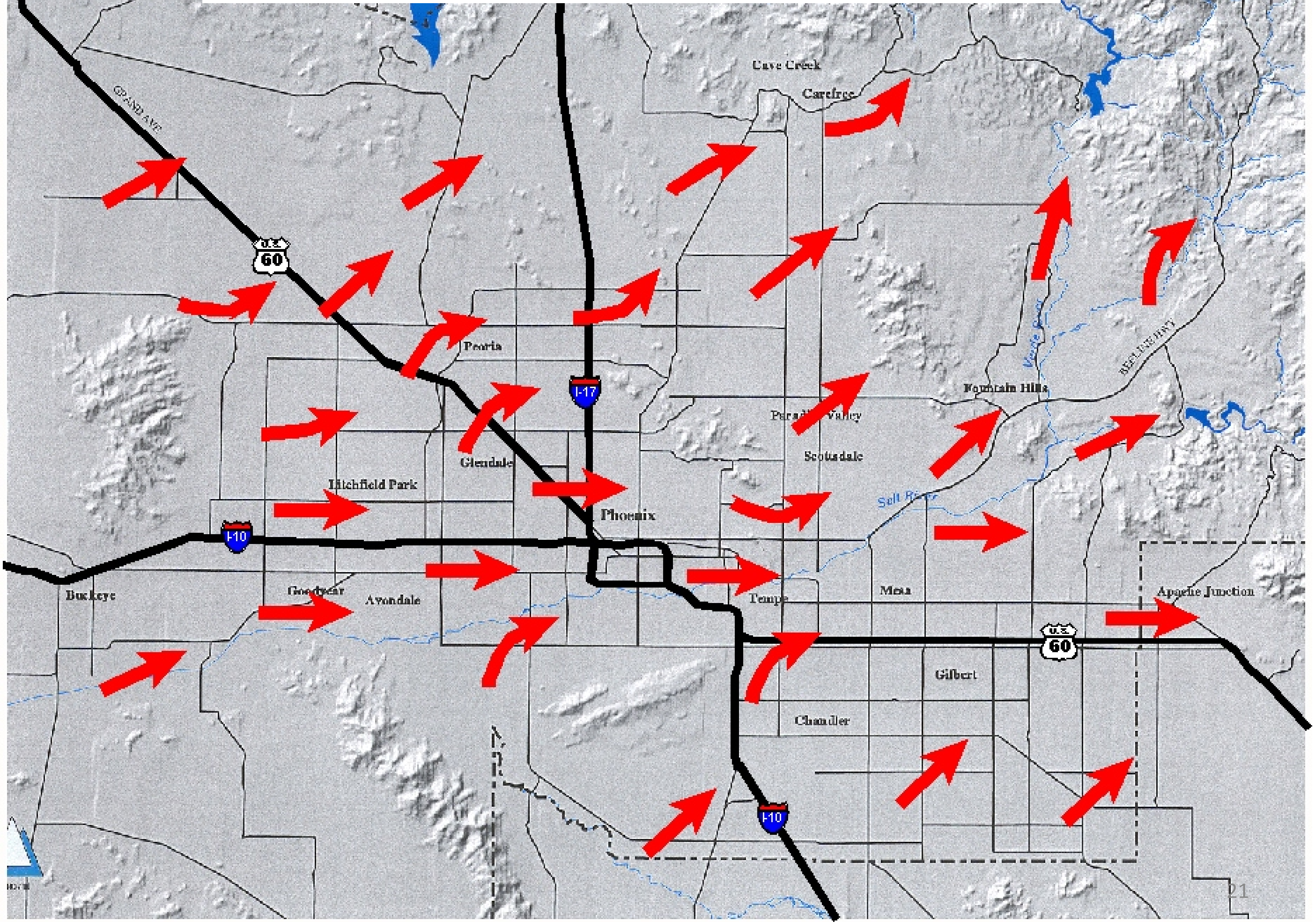
Weather and geography are the most important influences

- Atmospheric stability
  - Phoenix area has lowest average wind speeds of major metro areas in U.S.
  - Temperature inversions occur in summer too
- Topography
  - Broad alluvial basin, surrounded by small mountain ranges
  - Surface heating and cooling direct air movement

General Late Night/Early Morning Wind Patterns



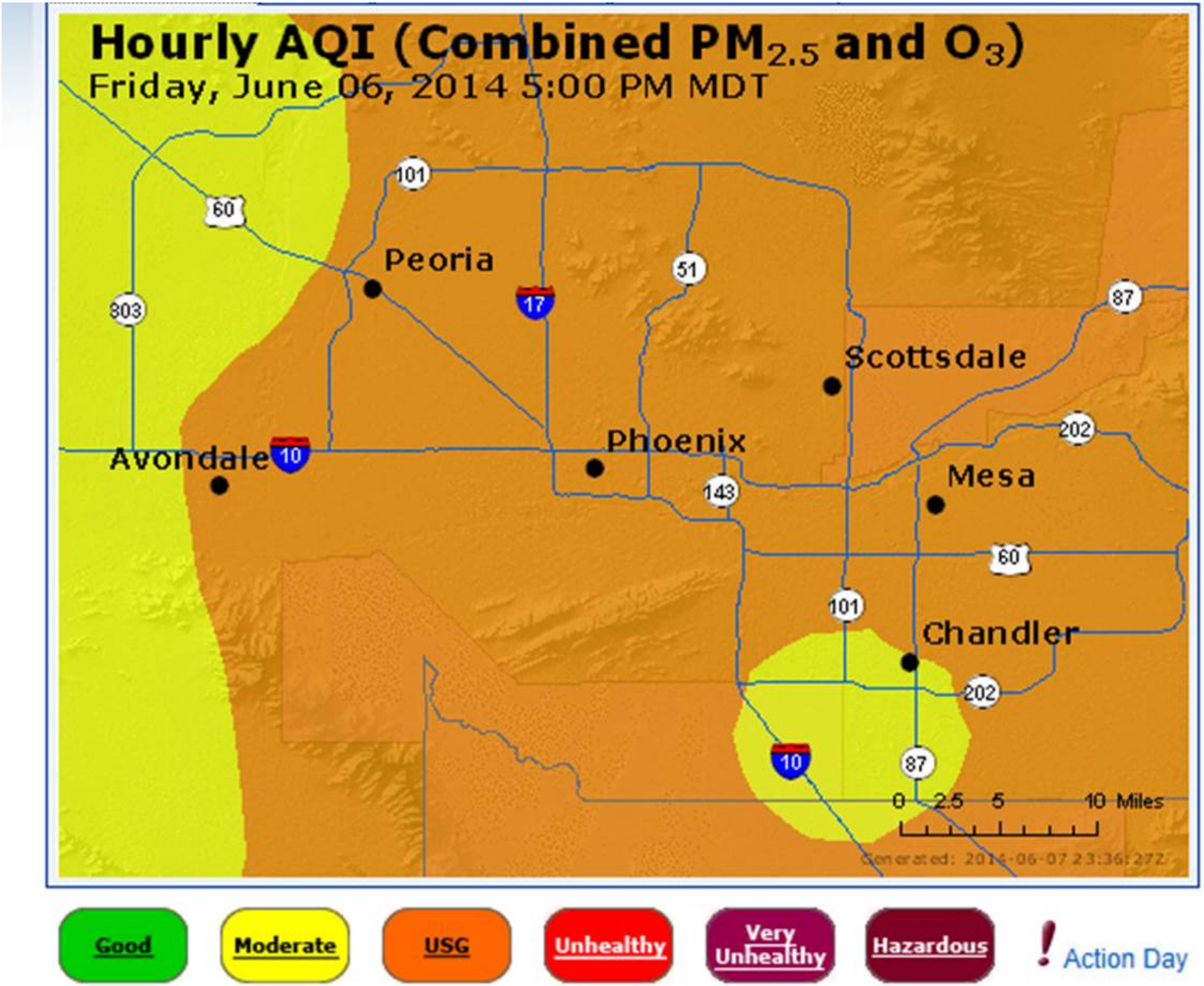
General Afternoon Wind Patterns



Regional Ozone impacts

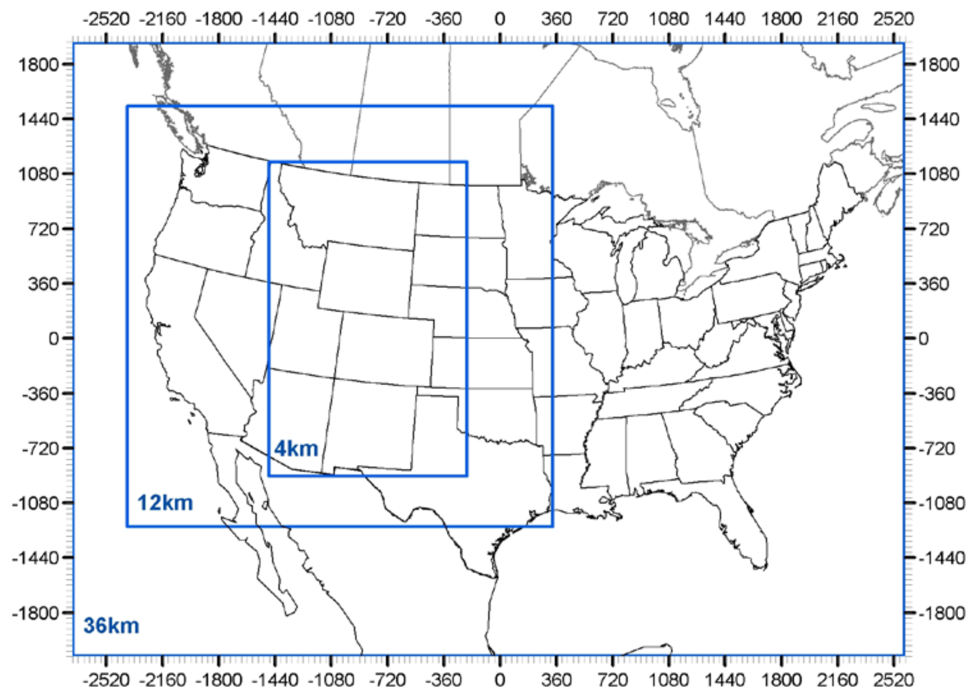
- USEPA has developed an Air Quality index to help explain air pollution levels to the general public
- 8-hour average ozone concentrations
  - 76 to 95 ppb is described as "Unhealthy for Sensitive Groups“
  - 96 to 115 ppb is "unhealthy“
  - 116 to 404 ppb is "very unhealthy“
- USEPA has designated over 300 counties of the United States, clustered around the most heavily populated areas (especially in California and the Northeast), as failing to comply with current National Ambient Air Quality Standards.

June 6, 2014 Phoenix metro area Ozone and PM pollution from MCAQD & ADEQ monitors



West-wide JumpStart Air Quality Modeling Study
(completed Sept. 2013)

- Regional photochemical modeling - air pollution transport and source apportionment study

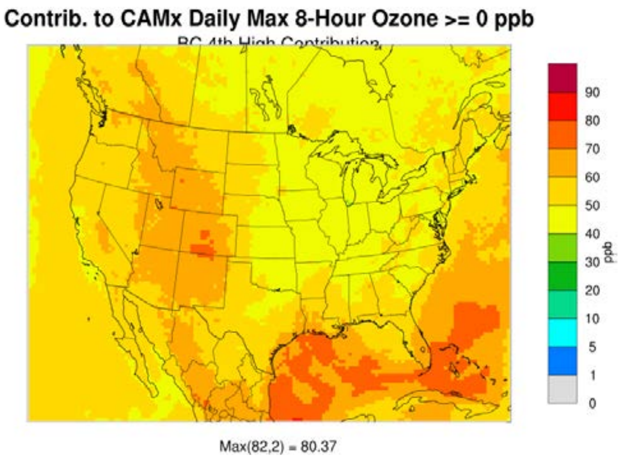


Modeling Domain

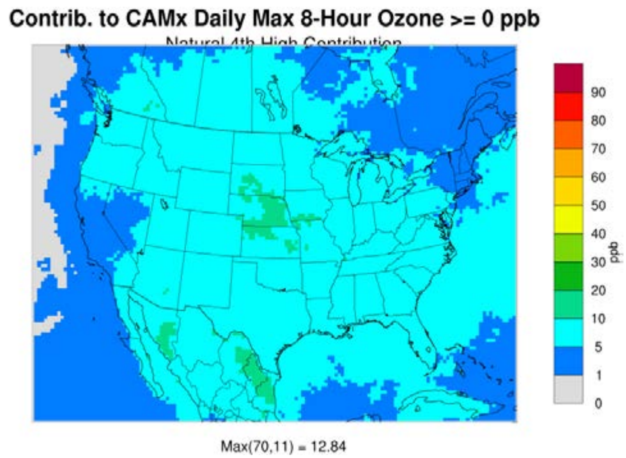
- All project materials at: http://www.wrapair2.org/WestJumpAQMS.aspx

“Other Sources” Max Contrib. 4th High DMAX8 Ozone

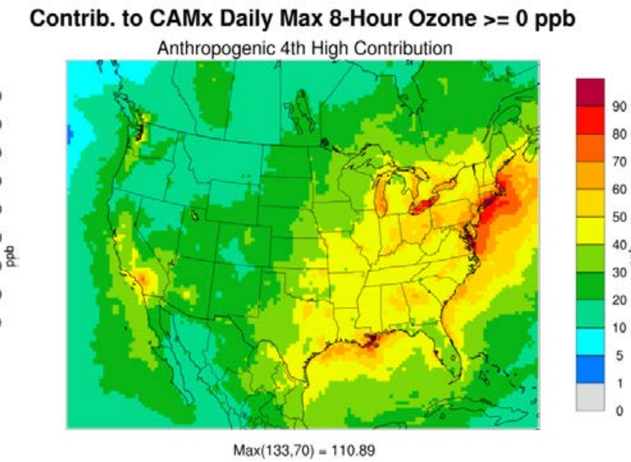
Boundary Conditions

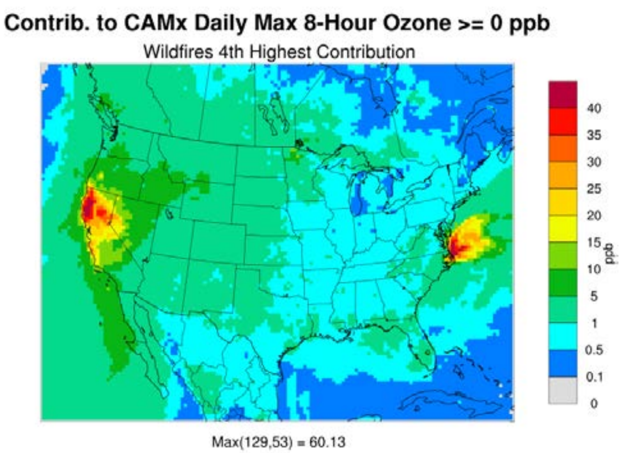


Natural

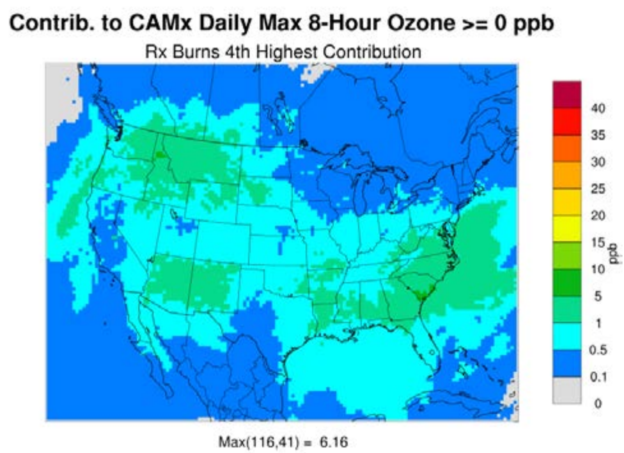


Anthropogenic

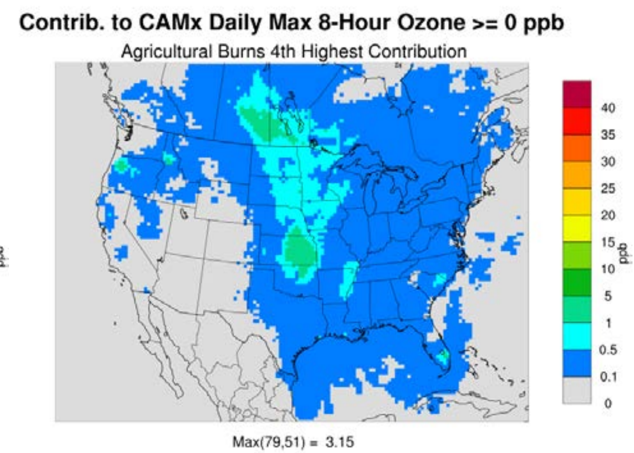




Wildfire

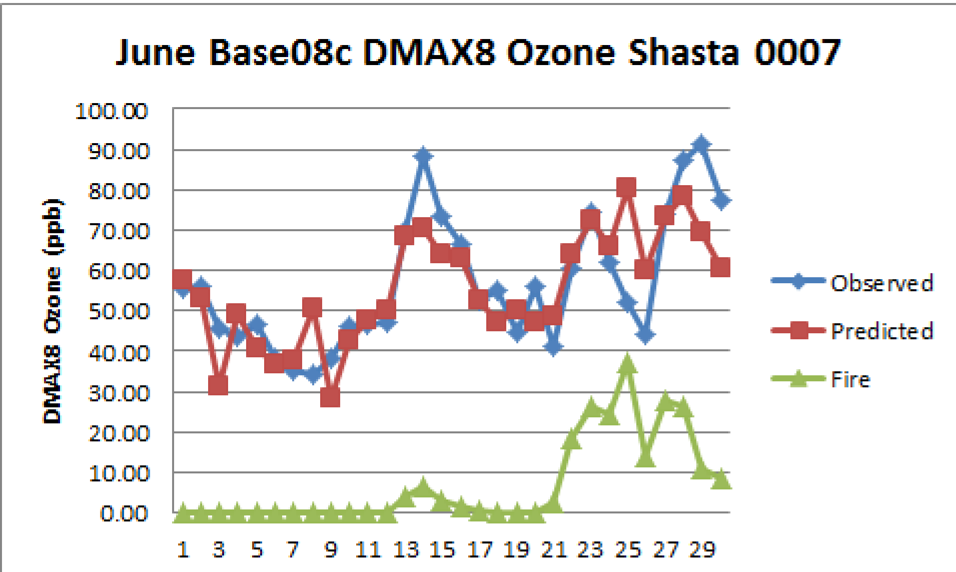


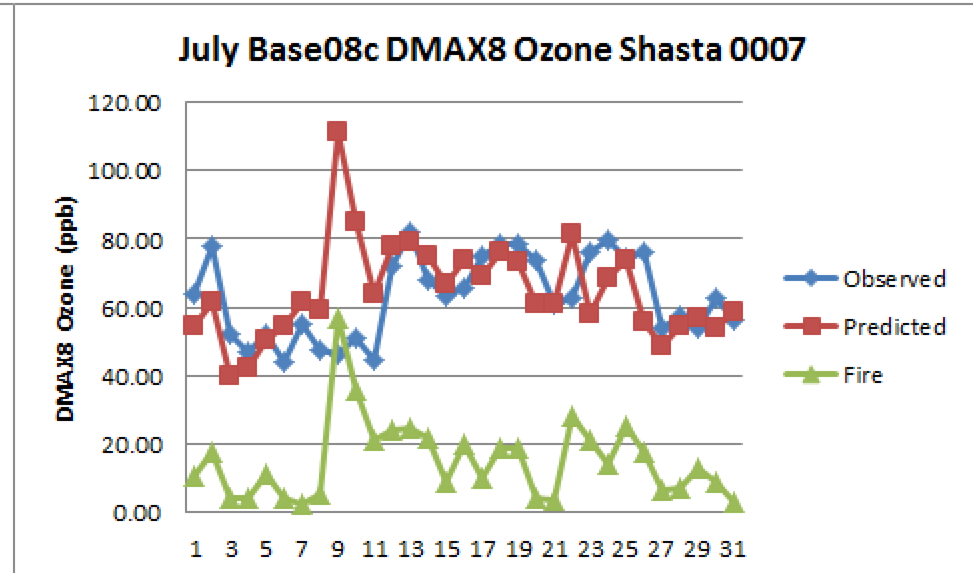
Prescribed Fire

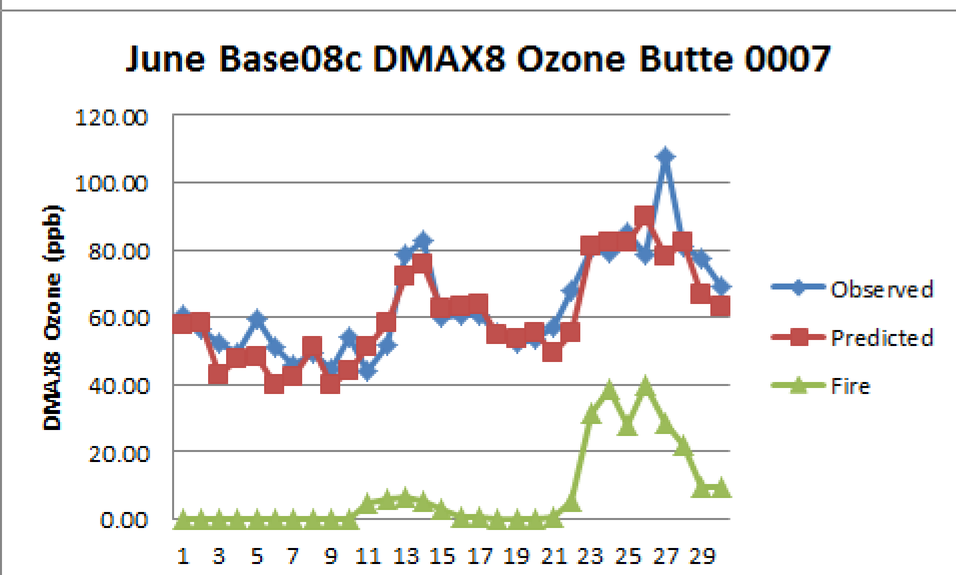


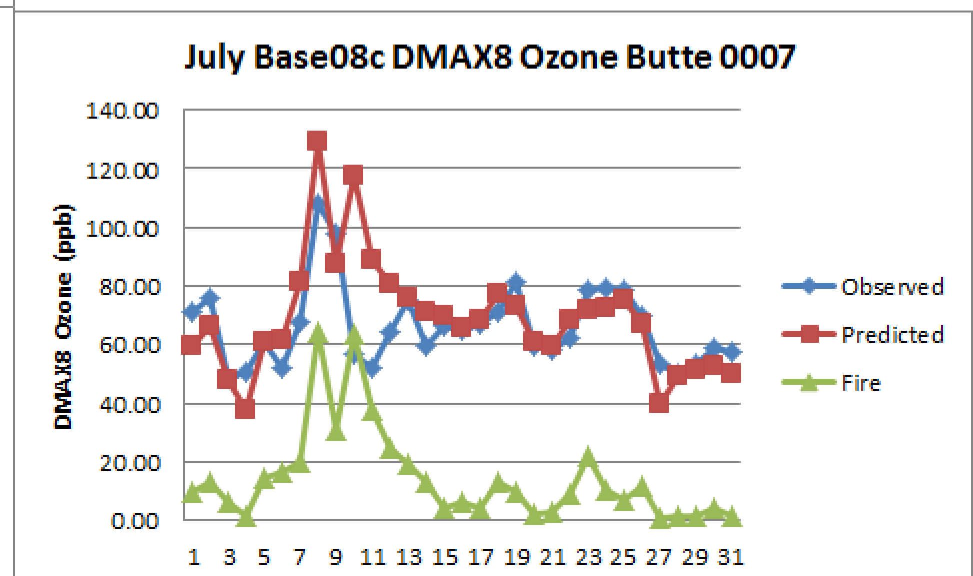
Agricultural Fire

Northern California Wildfires June-July 2008

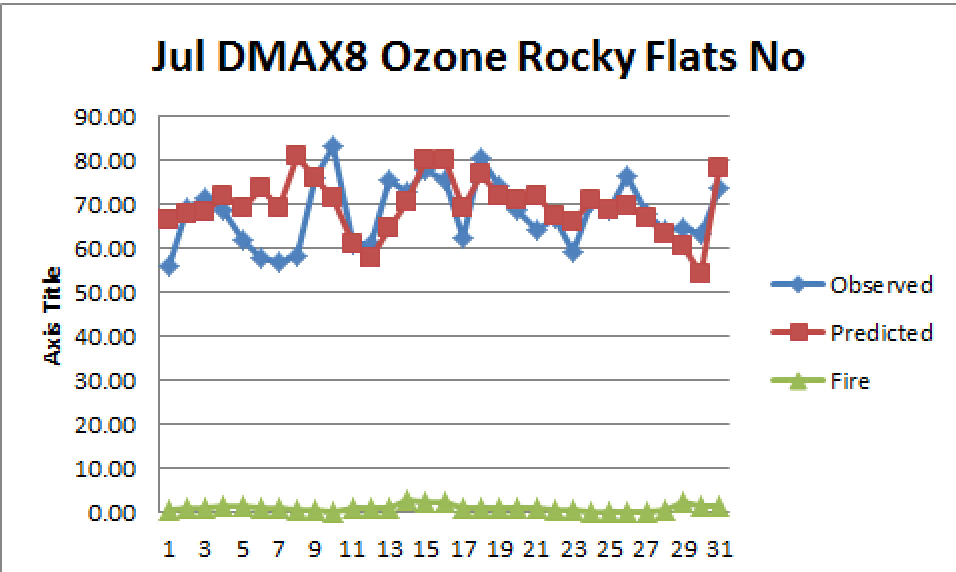


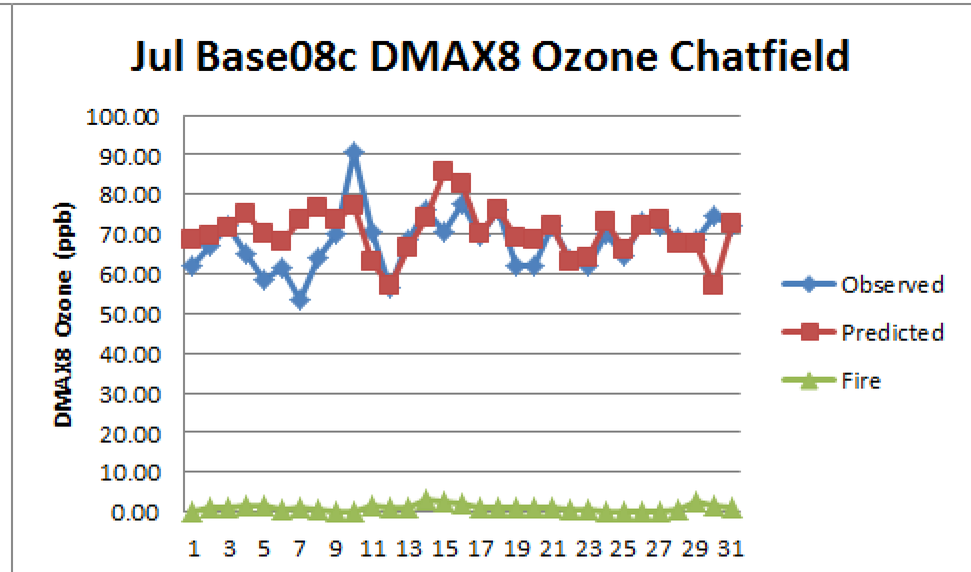


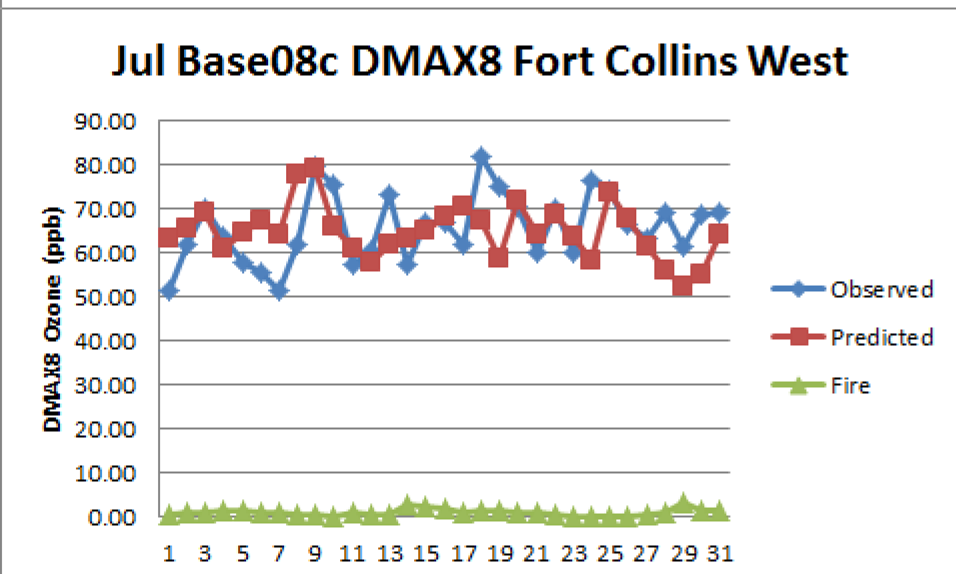


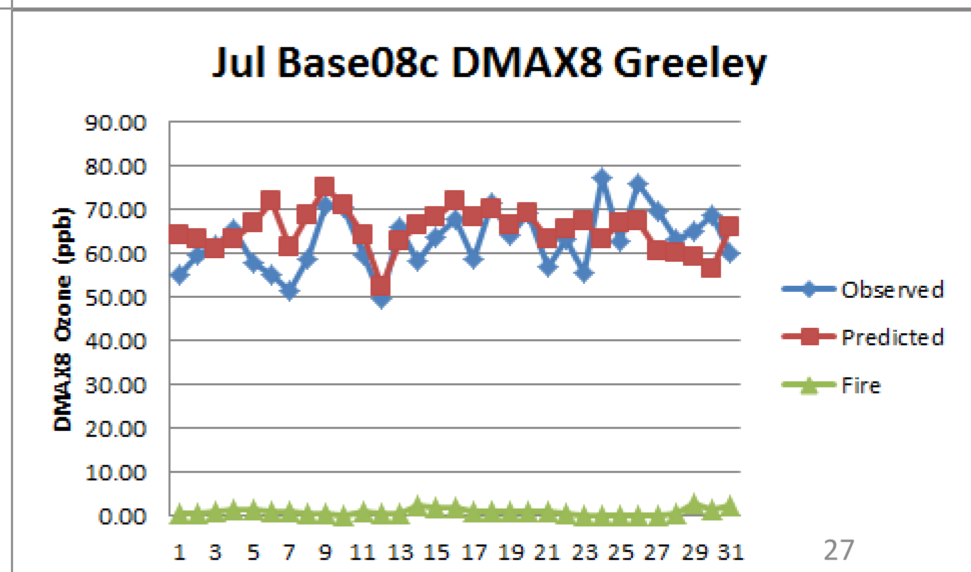


Denver Ozone Monitors July 2008



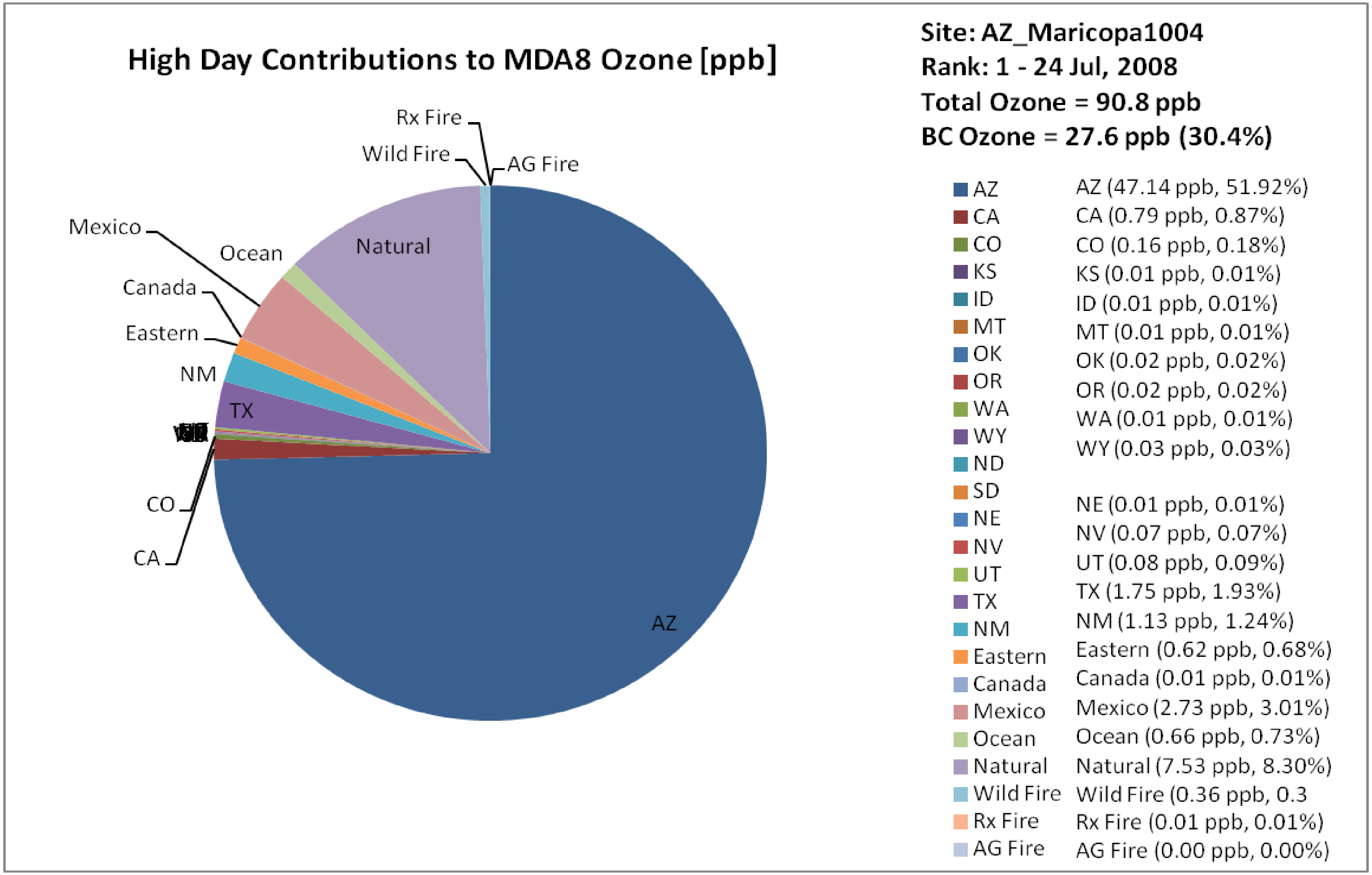






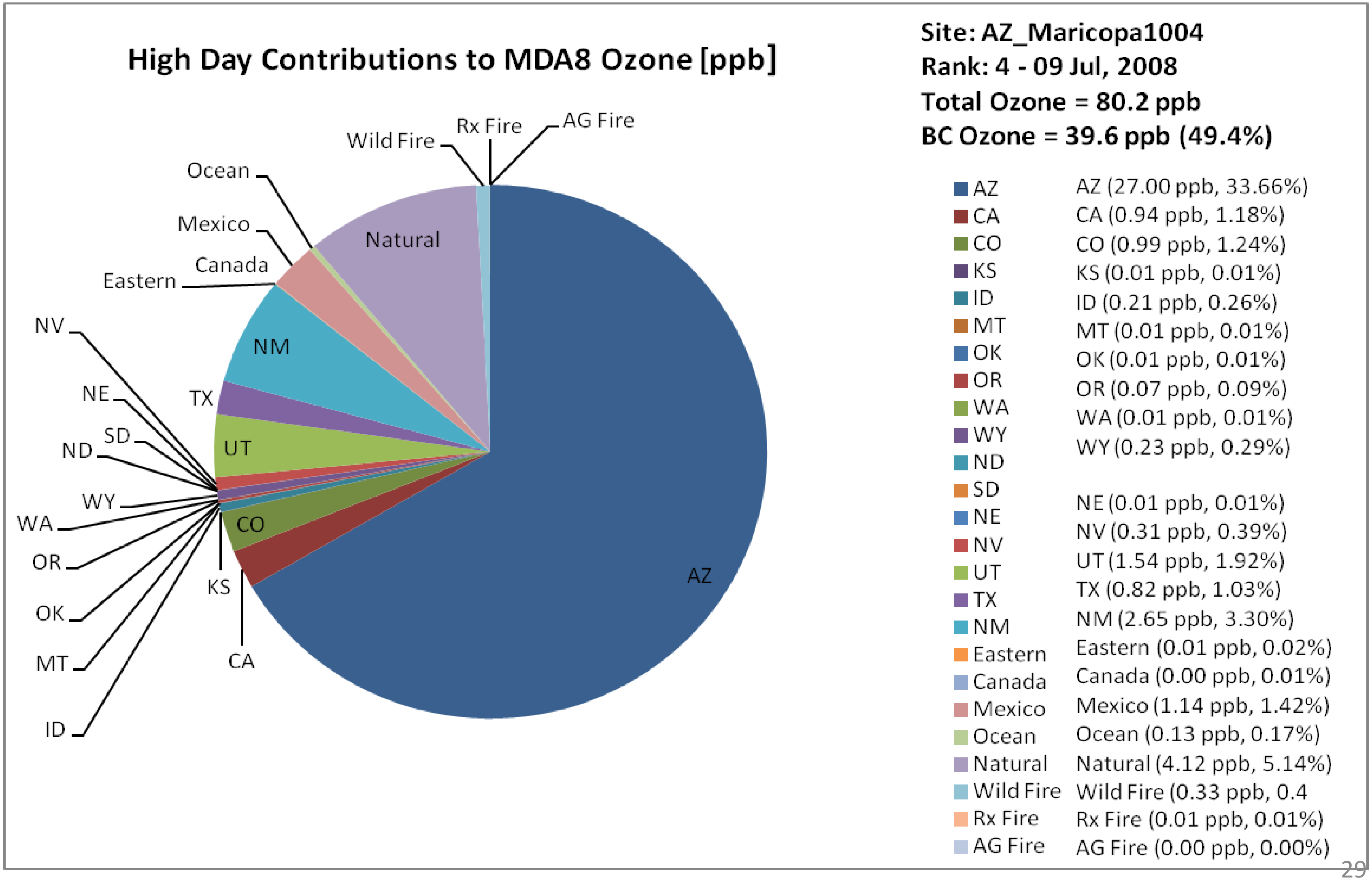
State Contributions to Modeled 10 Highest DMAX8 Ozone Days (from WestJumpAQMS Appendix B)

Highest Modeled DMAX8 Day @ North Phoenix, AZ site



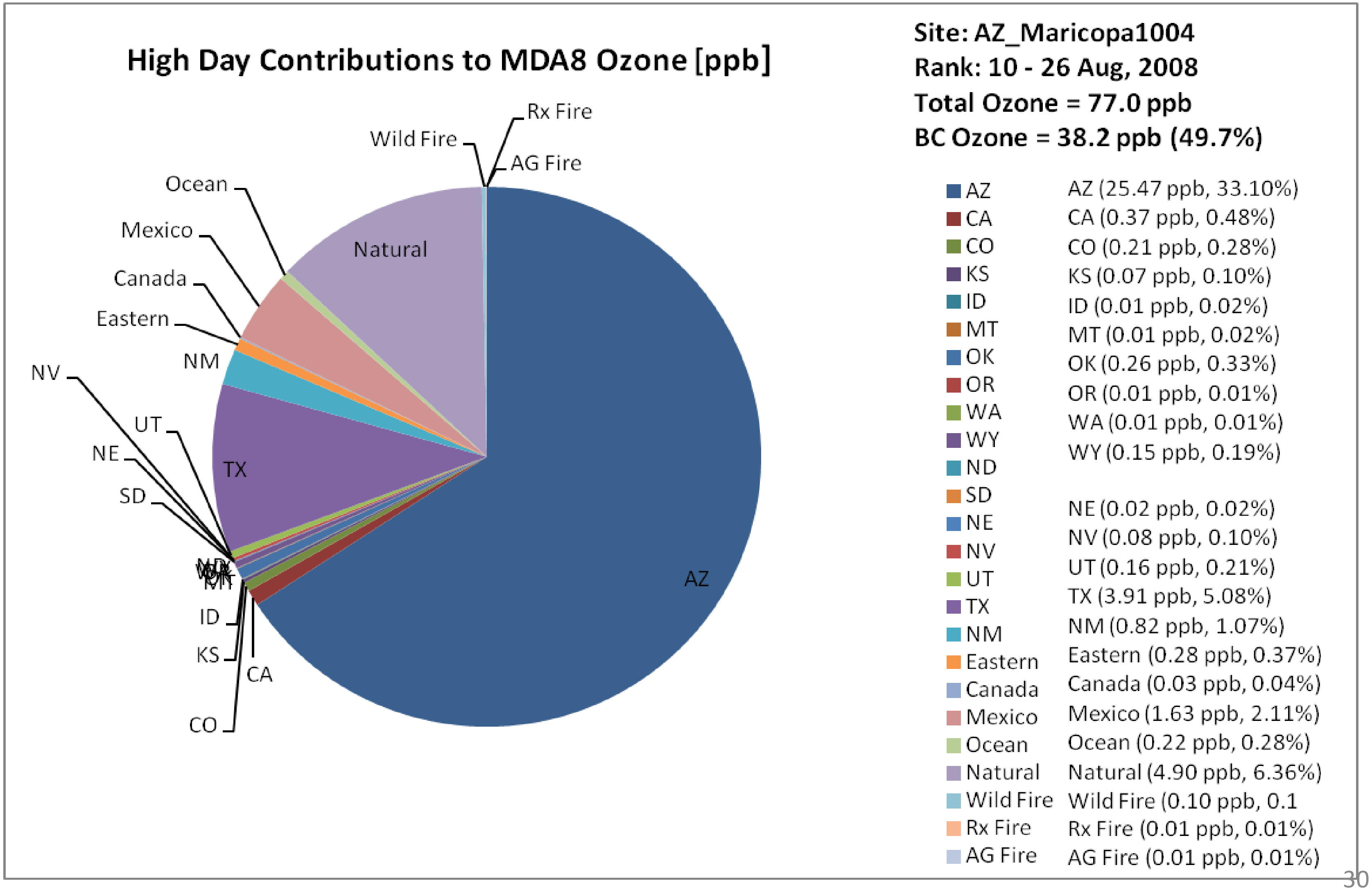
State Contributions to Modeled 10 Highest DMAX8 Ozone Days (from WestJumpAQMS Appendix B)

4th Highest Modeled DMAX8 Day @ North Phoenix, AZ site



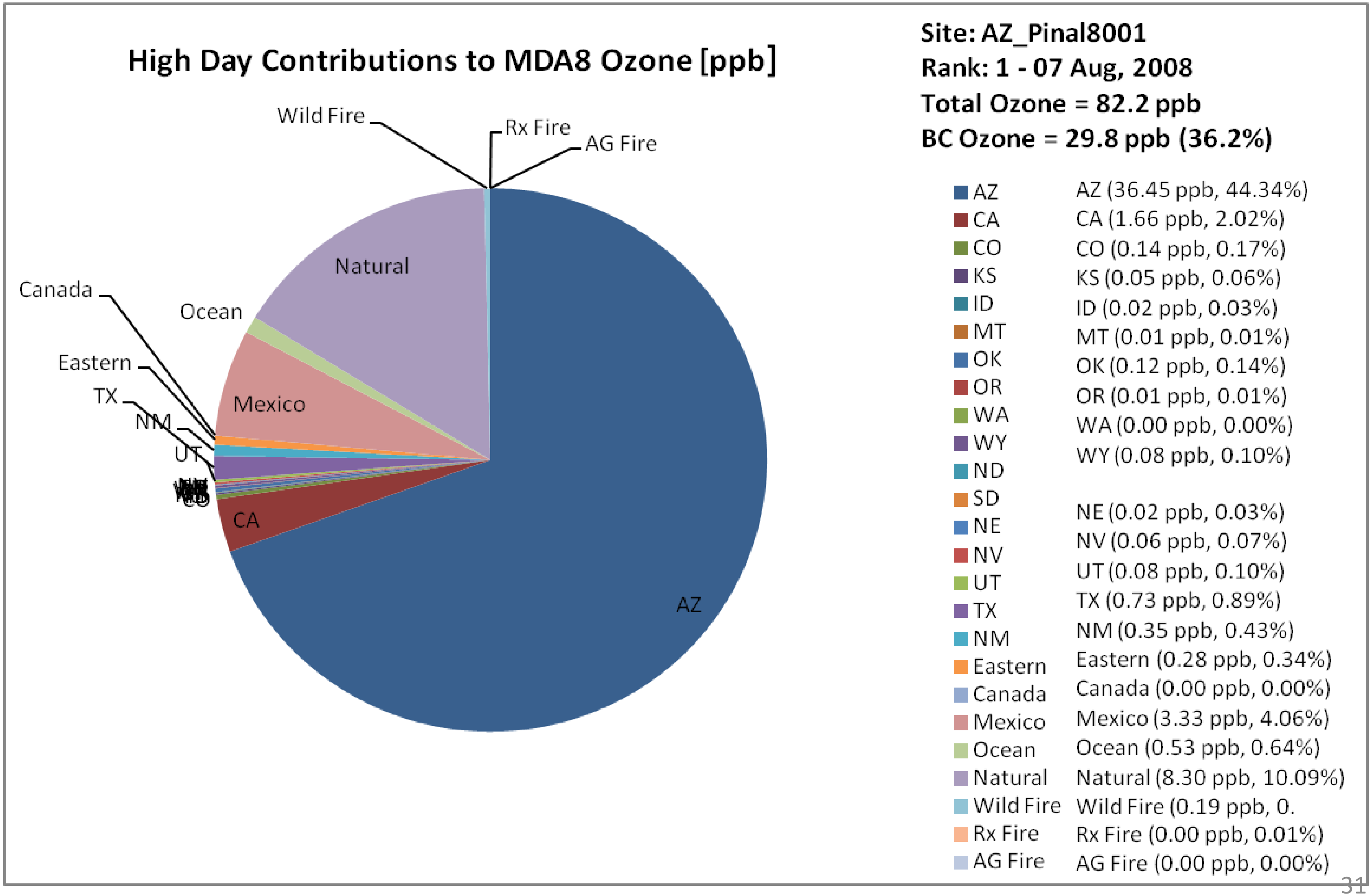
State Contributions to Modeled 10 Highest DMAX8 Ozone Days (from WestJumpAQMS Appendix B)

10th Highest Modeled DMAX8 Day @ North Phoenix, AZ site



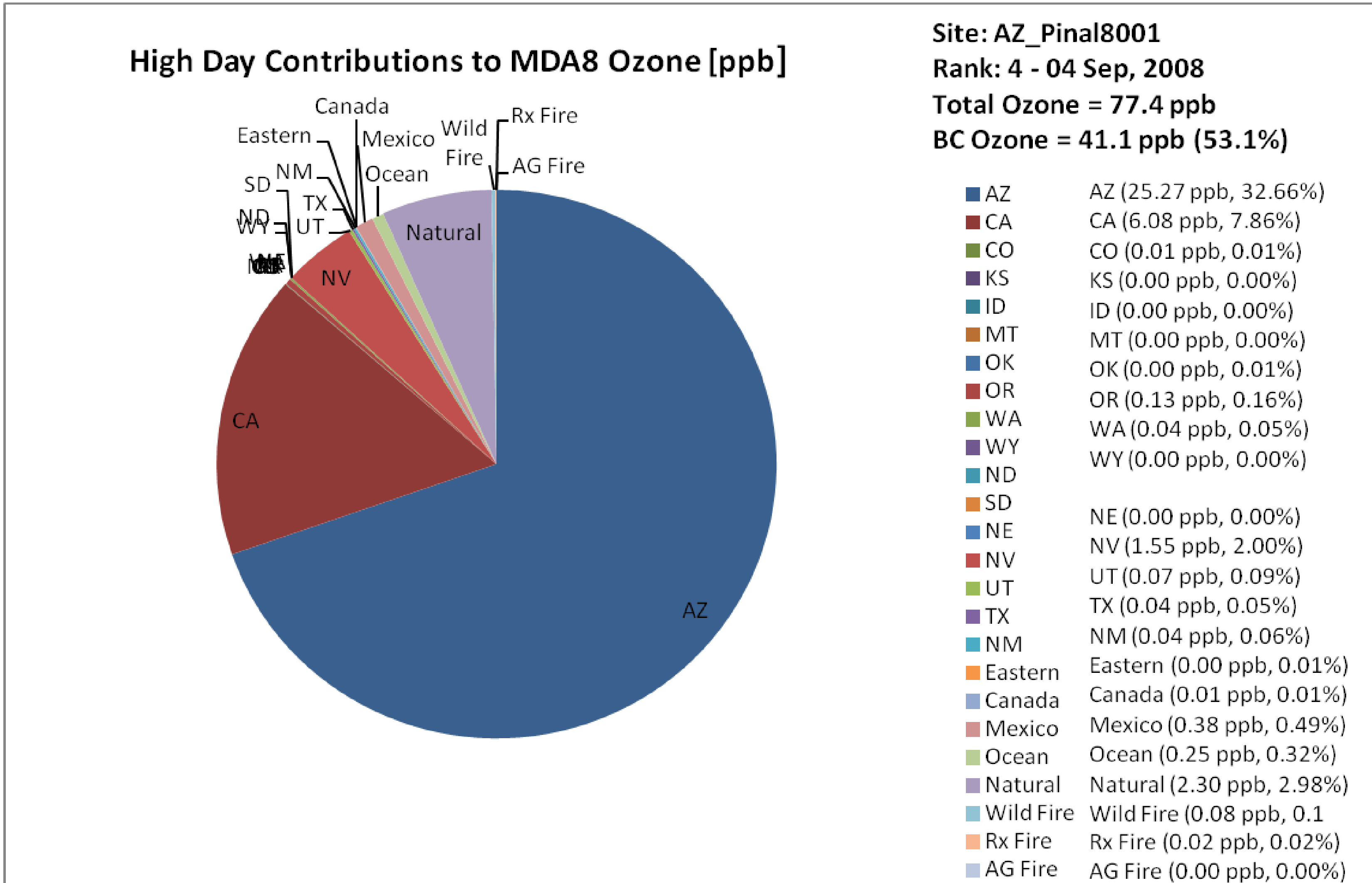
State Contributions to Modeled 10 Highest DMAX8 Ozone Days (from WestJumpAQMS Appendix B)

Highest Modeled DMAX8 Day at Queen Valley, AZ site



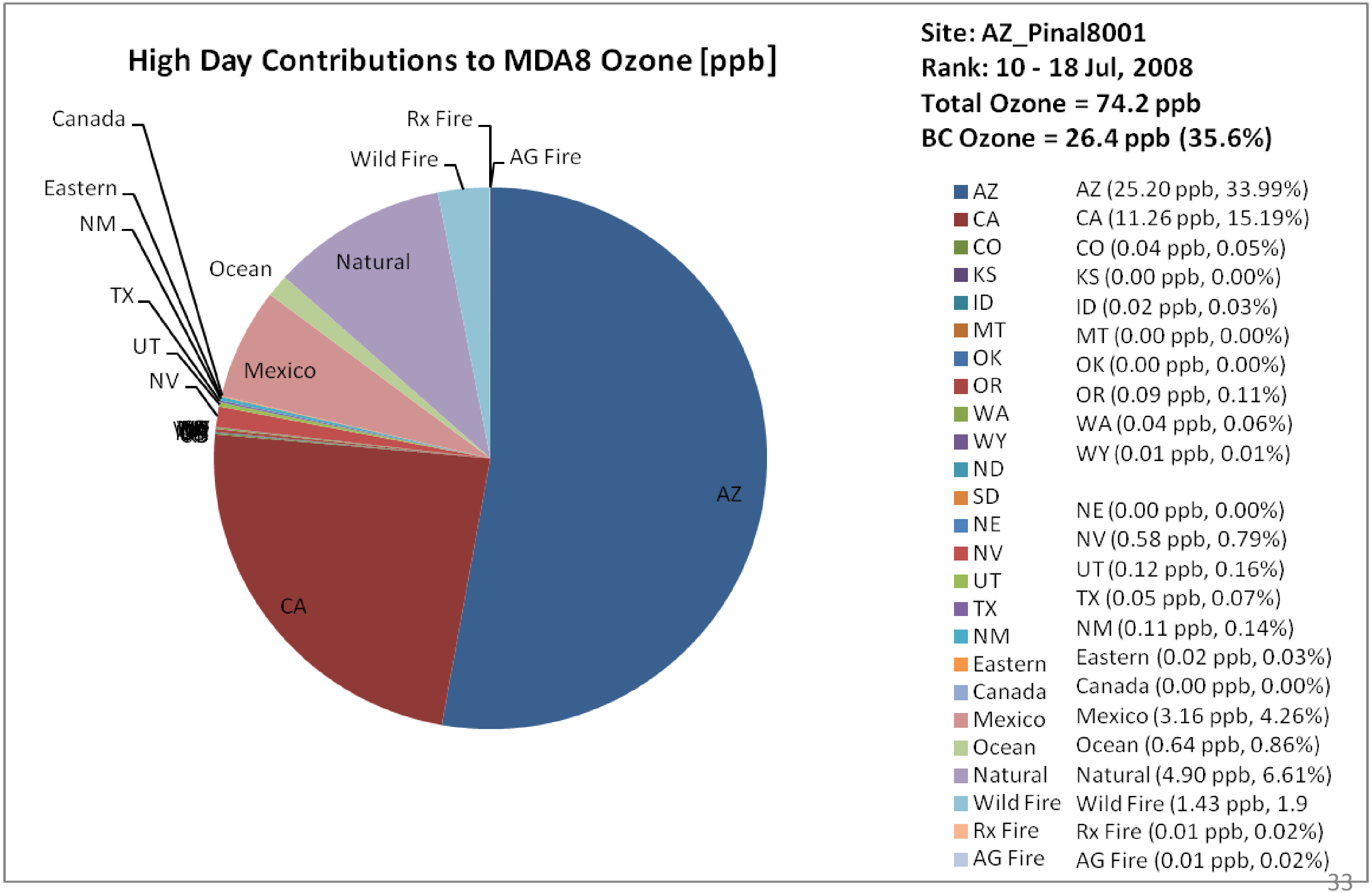
State Contributions to Modeled 10 Highest DMAX8 Ozone Days (from WestJumpAQMS Appendix B)

4th Highest Modeled DMAX8 Day at Queen Valley, AZ site



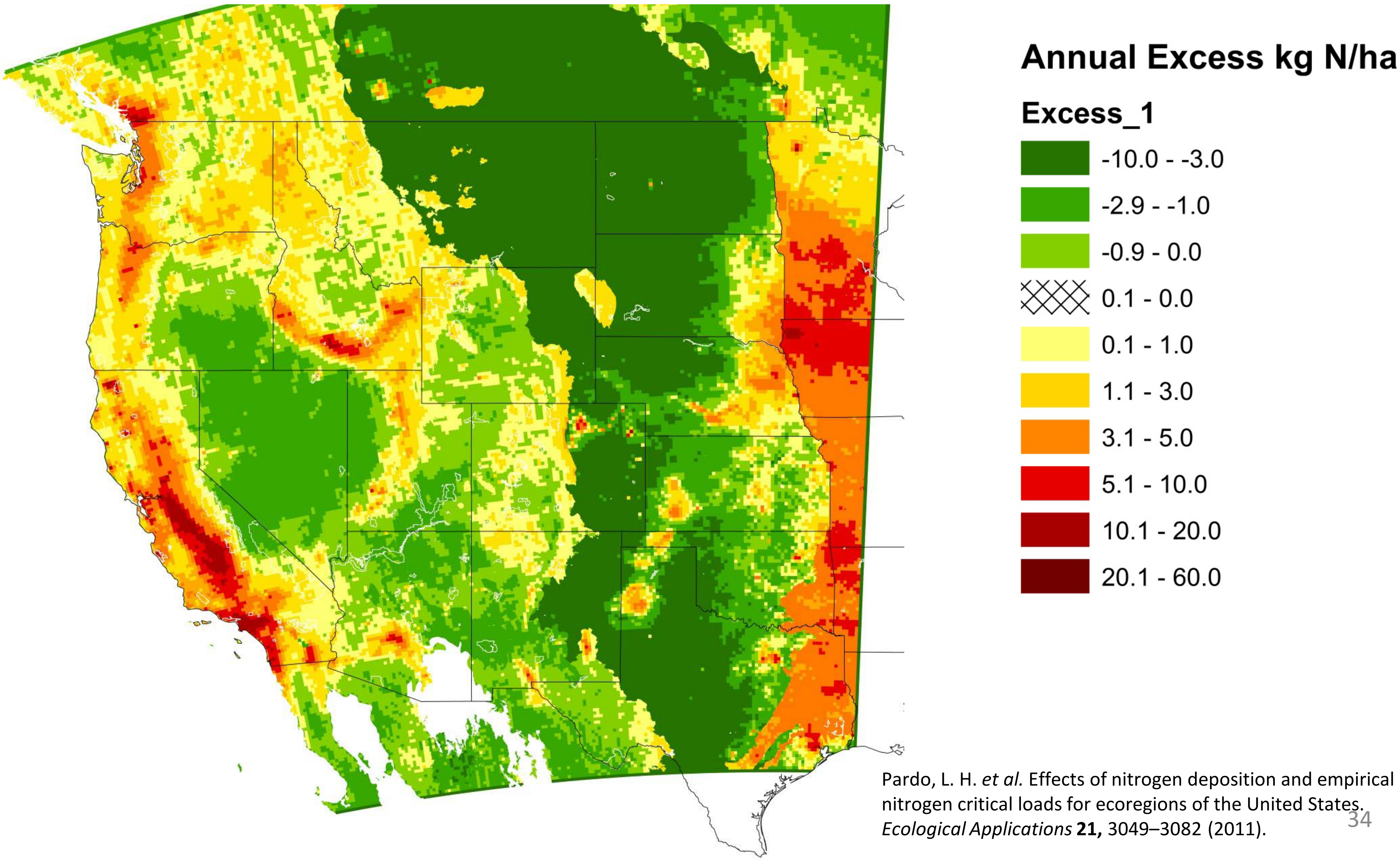
State Contributions to Modeled 10 Highest DMAX8 Ozone Days (from WestJumpAQMS Appendix B)

10th Highest Modeled DMAX8 Day at Queen Valley, AZ site



Nitrogen Deposition Excess

Total Modeled Nitrogen Wet & Dry Deposition (all species) - Critical Load



Pardo, L. H. *et al.* Effects of nitrogen deposition and empirical nitrogen critical loads for ecoregions of the United States. *Ecological Applications* **21,** 3049–3082 (2011).

Total Modeled Nitrogen Deposition Includes:

- Organic Nitrogen Species: PAN, RNO_3 (model chemistry includes organic N formed from biogenic VOCs)
- Dry Deposition Other Oxidized Nitrogen: NO, NO_2, N_2O_5, HONO, HO_2NO_2
- Dry Deposition Ammonia (NH_3)
- Wet Deposition Other Oxidized Nitrogen: NO, NO_2, N_2O_5, HONO, HO_2NO_2
- Dry Deposition of Nitric Acid (HNO_3)
- Particulate Nitrate (NO_3^-): Wet and dry
- Particulate Ammonium (NH_4^+): Wet and dry

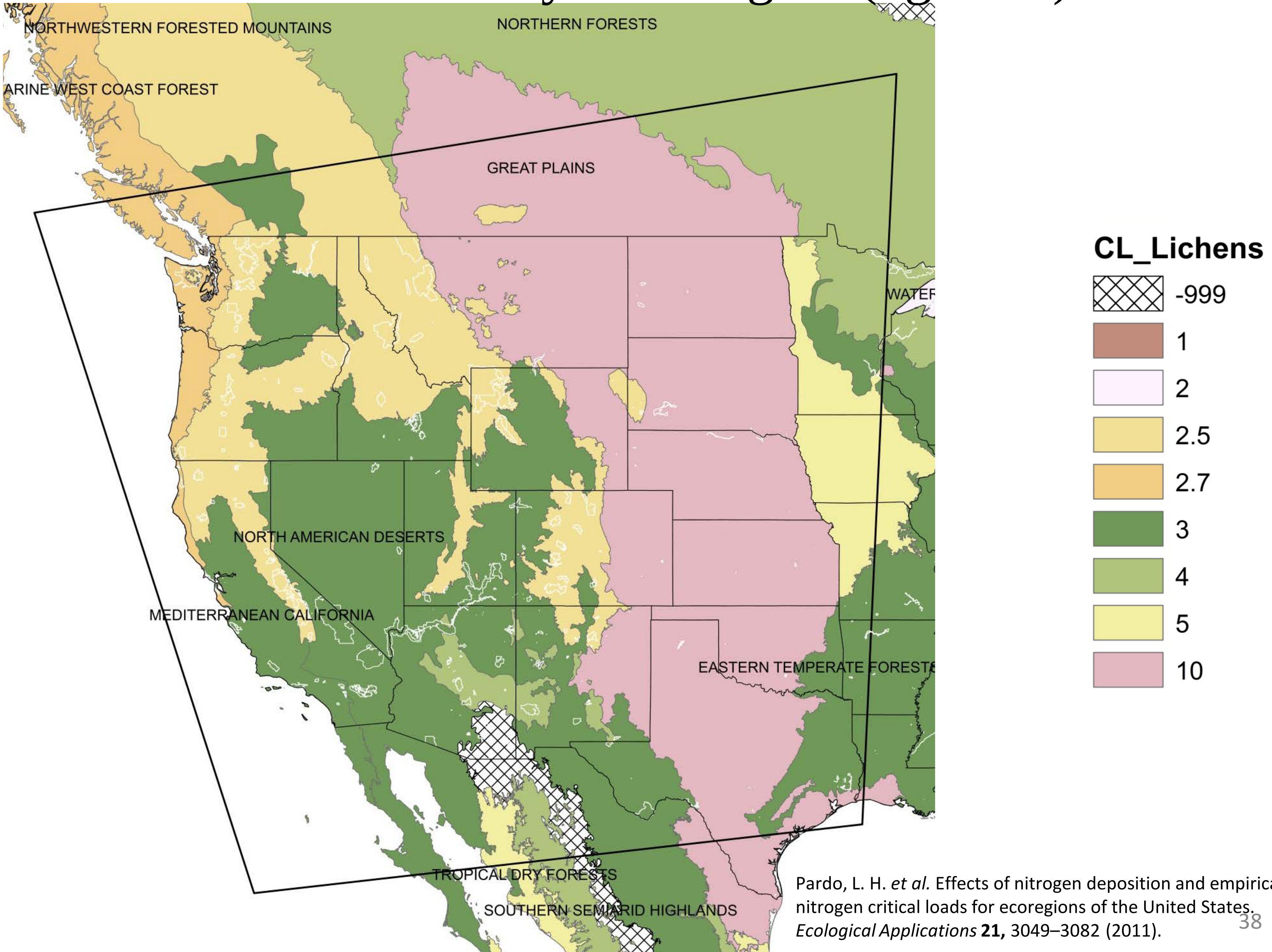
Total Measured Nitrogen Deposition Includes:

- ~~Organic Nitrogen Species: PAN, RNO_3 (model chemistry includes organic N formed from biogenic VOCs)~~
- ~~Dry Deposition Other Oxidized Nitrogen: NO, NO_2, N_2O_5, HONO, HO_2NO_2~~
- ~~Dry Deposition Ammonia (NH_3)~~
- Wet Deposition Other Oxidized Nitrogen: NO, NO_2, N_2O_5, HONO, HO_2NO_2
- Dry Deposition of Nitric Acid (HNO_3)
- Particulate Nitrate (NO_3^-): Wet and dry
- Particulate Ammonium (NH_4^+): Wet and dry

Nitrogen deposition measurement data is incomplete

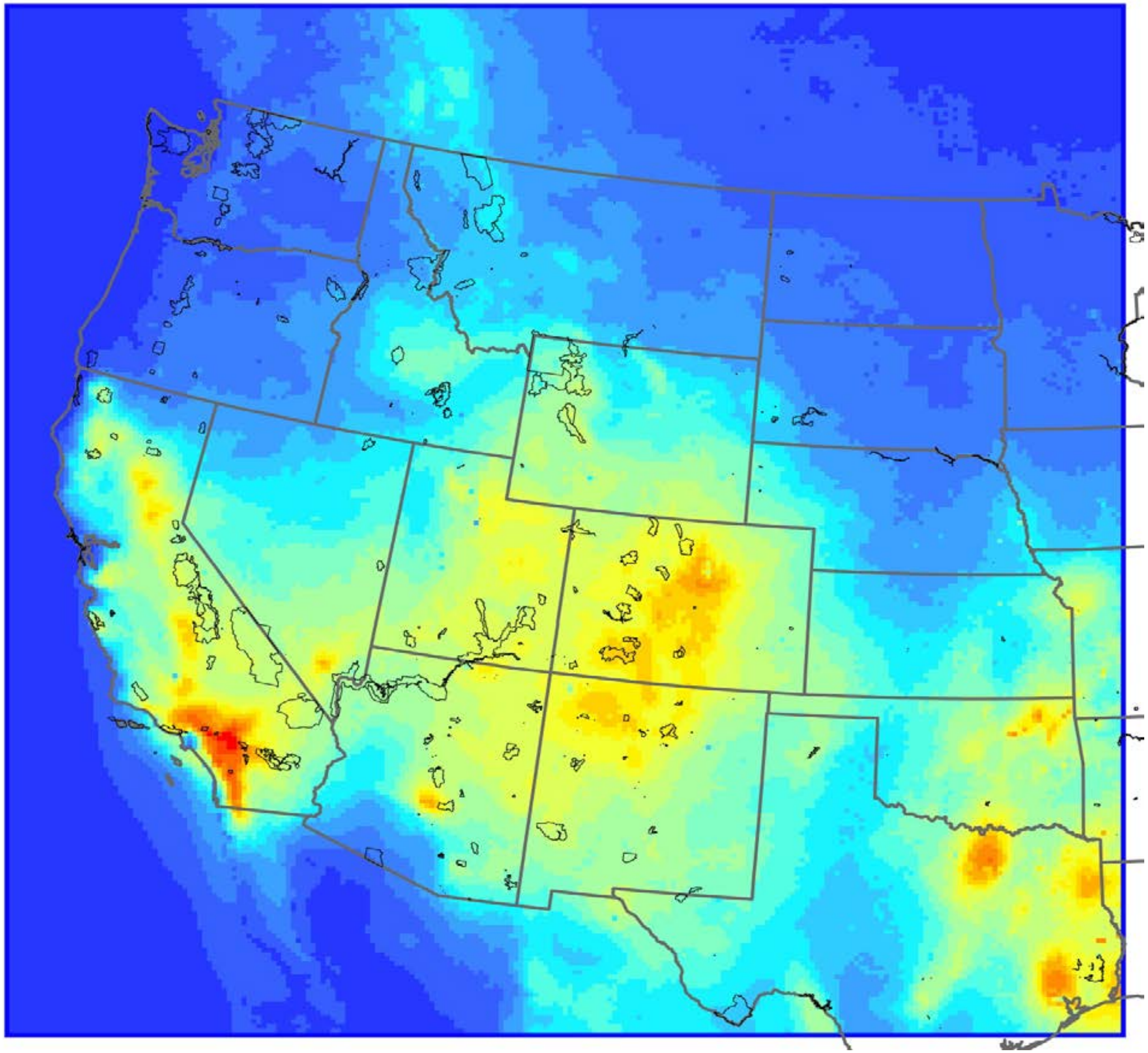
- Chemical Transport Models (e.g., CAMx) capture the bulk of total Nitrogen Deposition (although CAMx is missing reduced organic nitrogen and includes limited oxidized organic nitrogen – both expected to be small)
- Many Critical Load values are estimated using measurement data, some with scaling factors to account for “missing” N, others incorporate modeling data, still others leave data as is with caveats
- Efforts to close this gap continue, including the creation, in 2010, and subsequent expansion of the Ammonia Monitoring Network (AMoN)

Critical Load by Eco-Region (kg N/ha)



Pardo, L. H. *et al.* Effects of nitrogen deposition and empirical nitrogen critical loads for ecoregions of the United States. *Ecological Applications* **21,** 3049–3082 (2011).

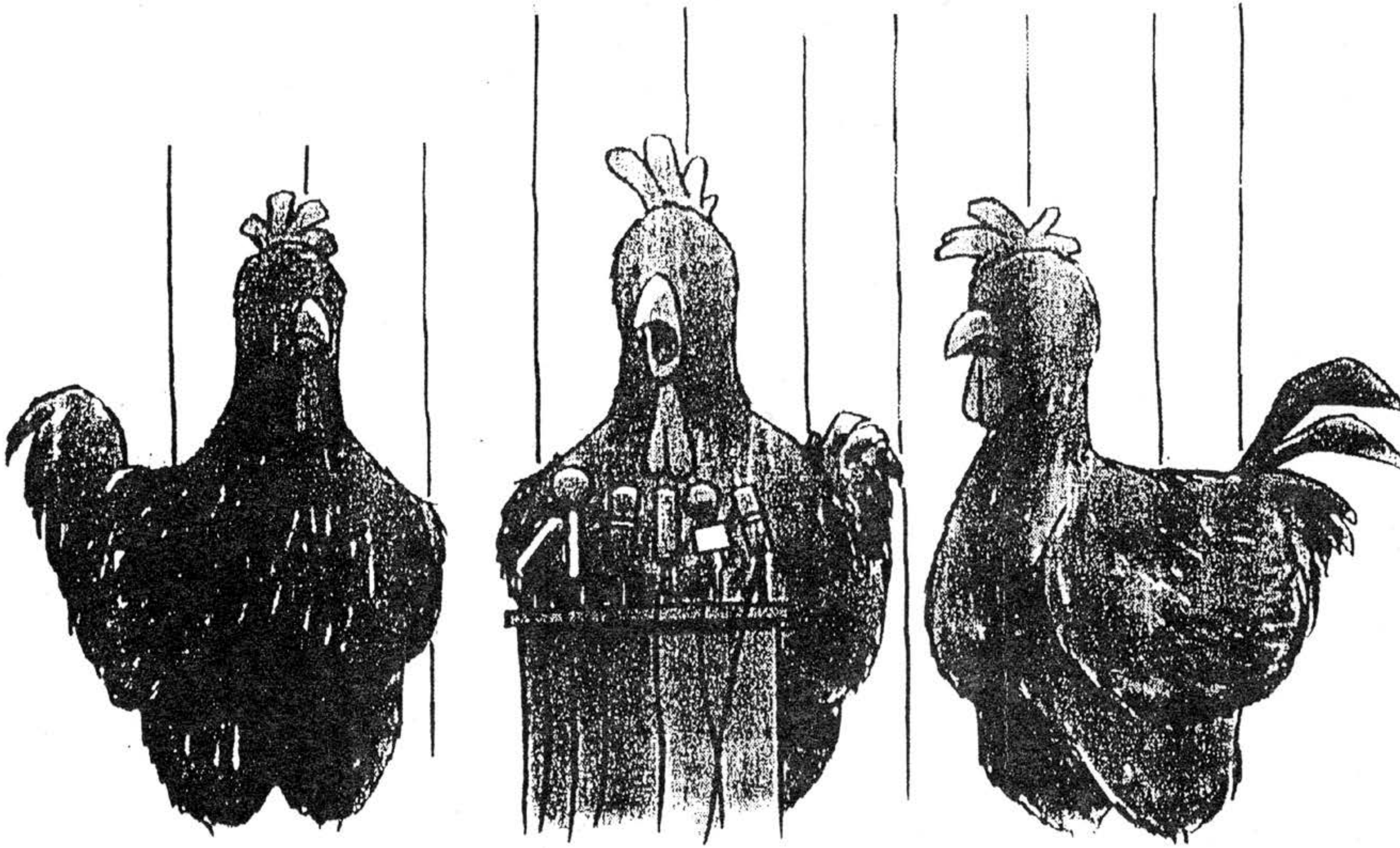
WestJumpAQMS Maximum Ozone Season W126 (ppm-hrs)



Max W126 (ppm-hrs)

BC_w126

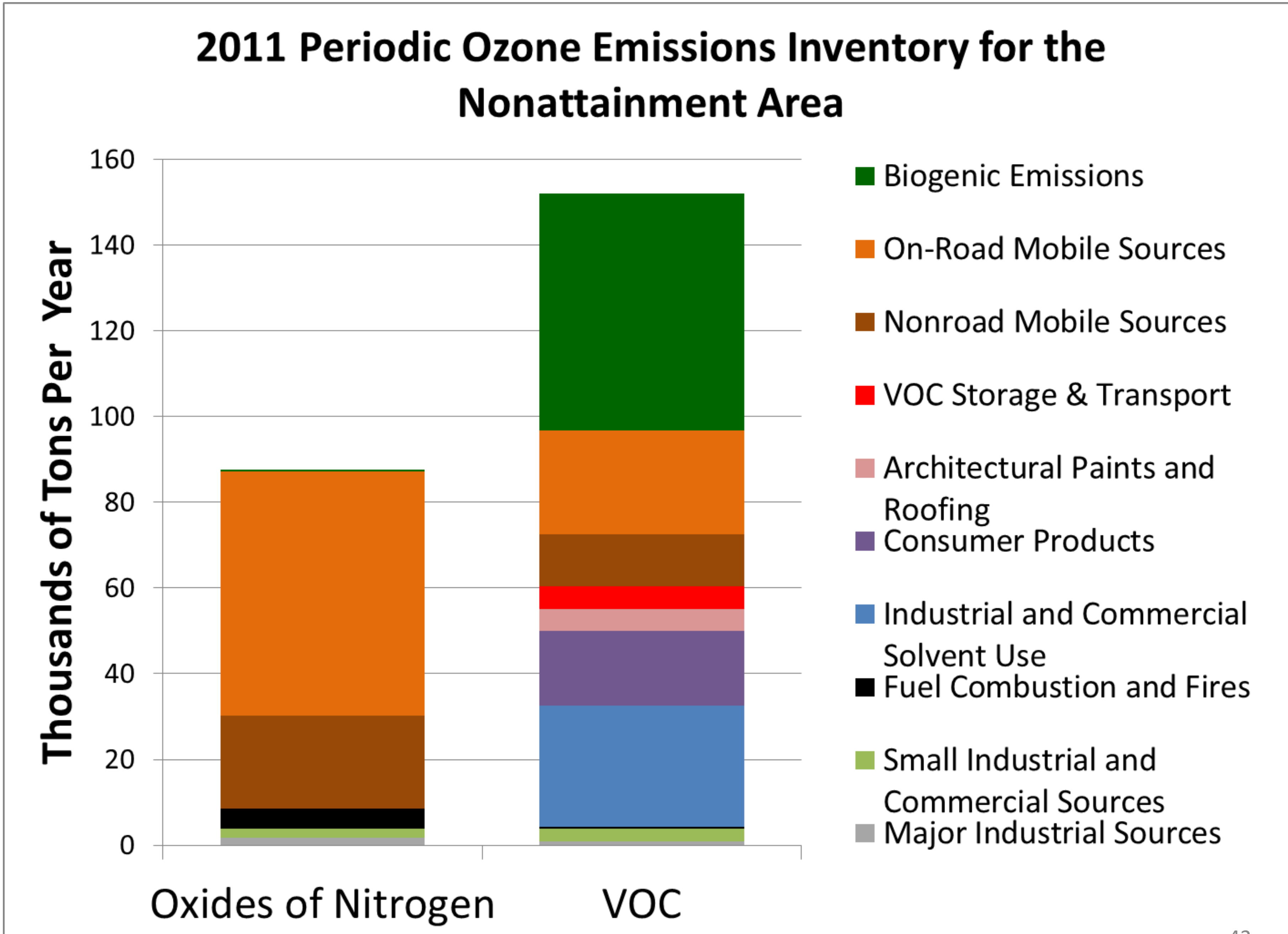
0.0
0.1 - 3.0
3.1 - 5.0
5.1 - 7.0
7.1 - 9.0
9.1 - 10.5
10.6 - 12.0
12.1 - 13.5
13.6 - 15.0
15.1 - 17.0
17.1 - 19.0
19.1 - 21.0
21.1 - 23.0
23.1 - 25.0
25.1 - 27.0
27.1 - 30.0
30.1 - 35.0
35.1 - 40.0
40.1 - 45.0
45.1 - 50.0



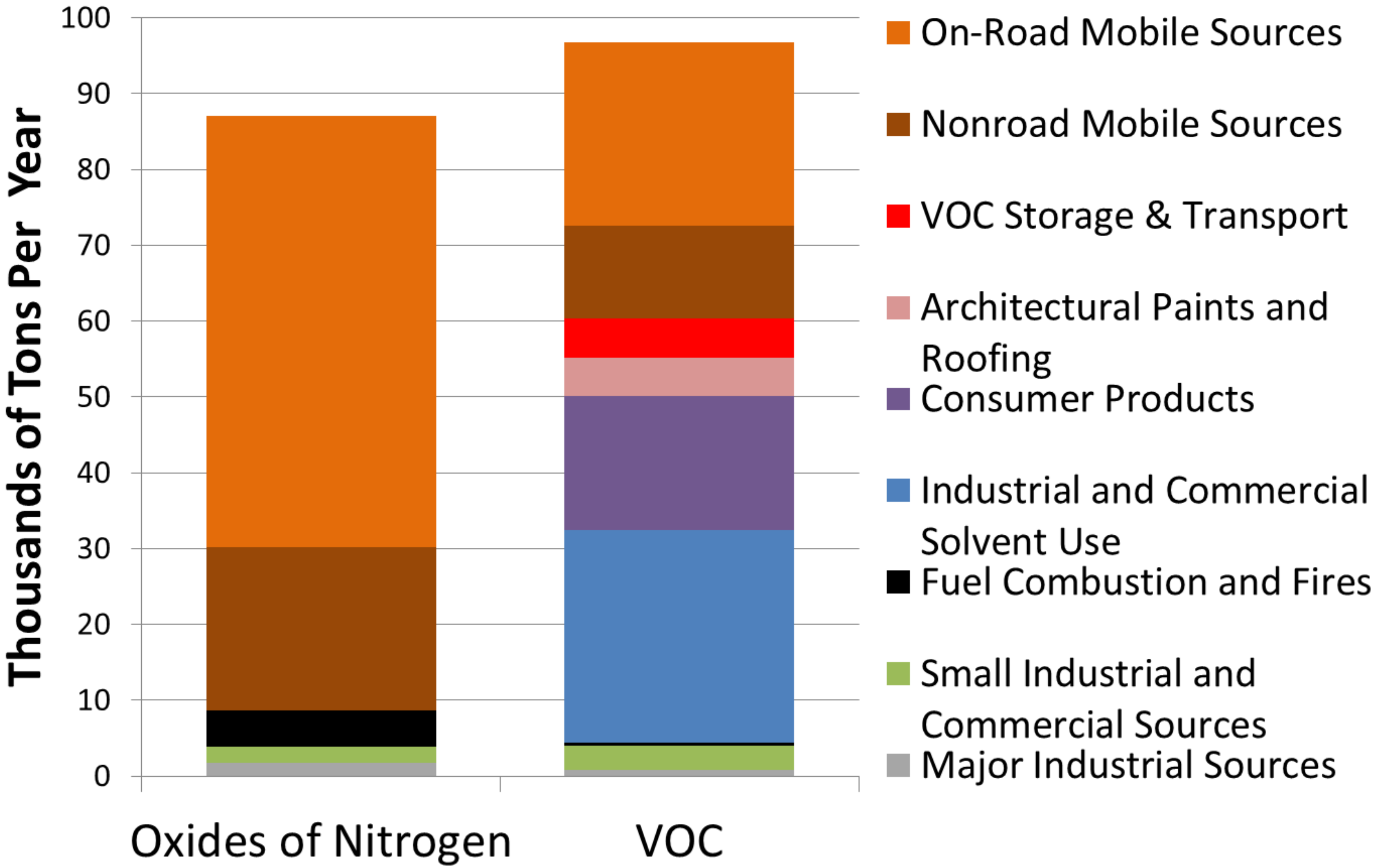
"Until our experts fully study the object in question, we cannot confirm or deny Ms. Penny's claim that the sky is falling."

Ozone Precursor Pollutants and Their Sources

- In the metro Phoenix area, sources of these pollutants include automobiles, gas-powered motors, and many smaller sources:
  - Gas stations
  - Consumer products
  - Solvents used in paint shops and finishing operations
  - wherever natural gas, gasoline, diesel fuel, kerosene, and oil are combusted
- Precursor behavior and characteristics
  - Timing of activity
  - Practices
  - Behavior


2011 Periodic Ozone Emissions Inventory for the Nonattainment Area
Thousands of Tons Per Year
160
140
120
100
80
60
40
20
0
Oxides of Nitrogen
VOC
Biogenic Emissions
On-Road Mobile Sources
Nonroad Mobile Sources
VOC Storage & Transport
Architectural Paints and Roofing
Consumer Products
Industrial and Commercial Solvent Use
Fuel Combustion and Fires
Small Industrial and Commercial Sources
Major Industrial Sources

2011 Periodic Ozone Anthropogenic Emissions Inventory for the Nonattainment Area

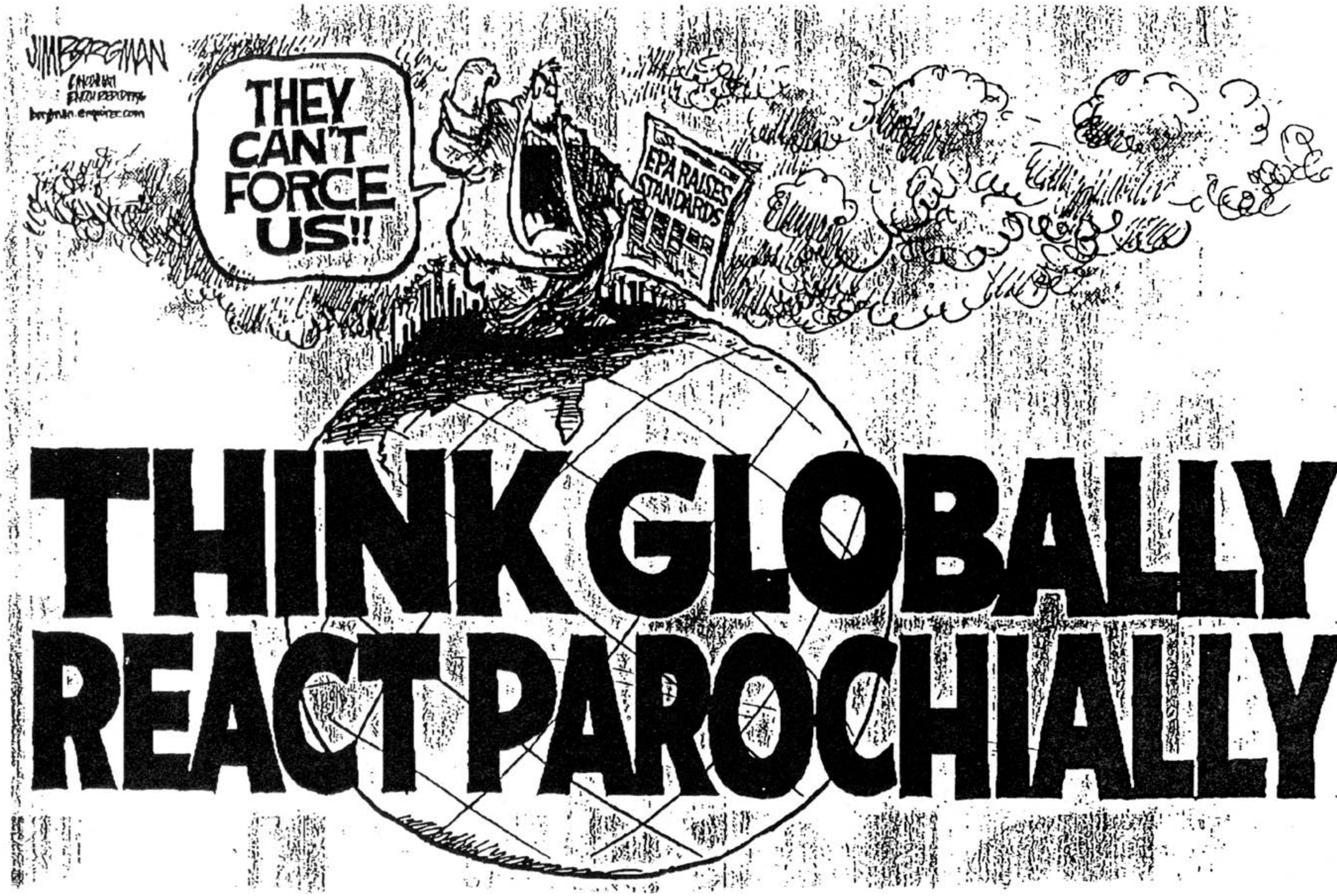


Evolution of EPA National Ozone Standard 1971-2008

Year	Primary/ Secondary	Indicator	Averaging Time	Level (ppm)	Form
1971	Same	Total photo-chemical oxidants	1-hour	0.08	Not to be exceeded more than one hour per year
1979	Same	Ozone	1-hour	0.12	Effectively, no more than 3 exceedance days over a 3-year period
1997	Same	Ozone	8-hour	0.08	Annual fourth-highest daily max 8-hr concentration, averaged over 3 years
2008	Same	Ozone	8-hour	0.075	Annual fourth-highest daily max 8-hr concentration, averaged over 3 years

Future EPA National Ozone Standard

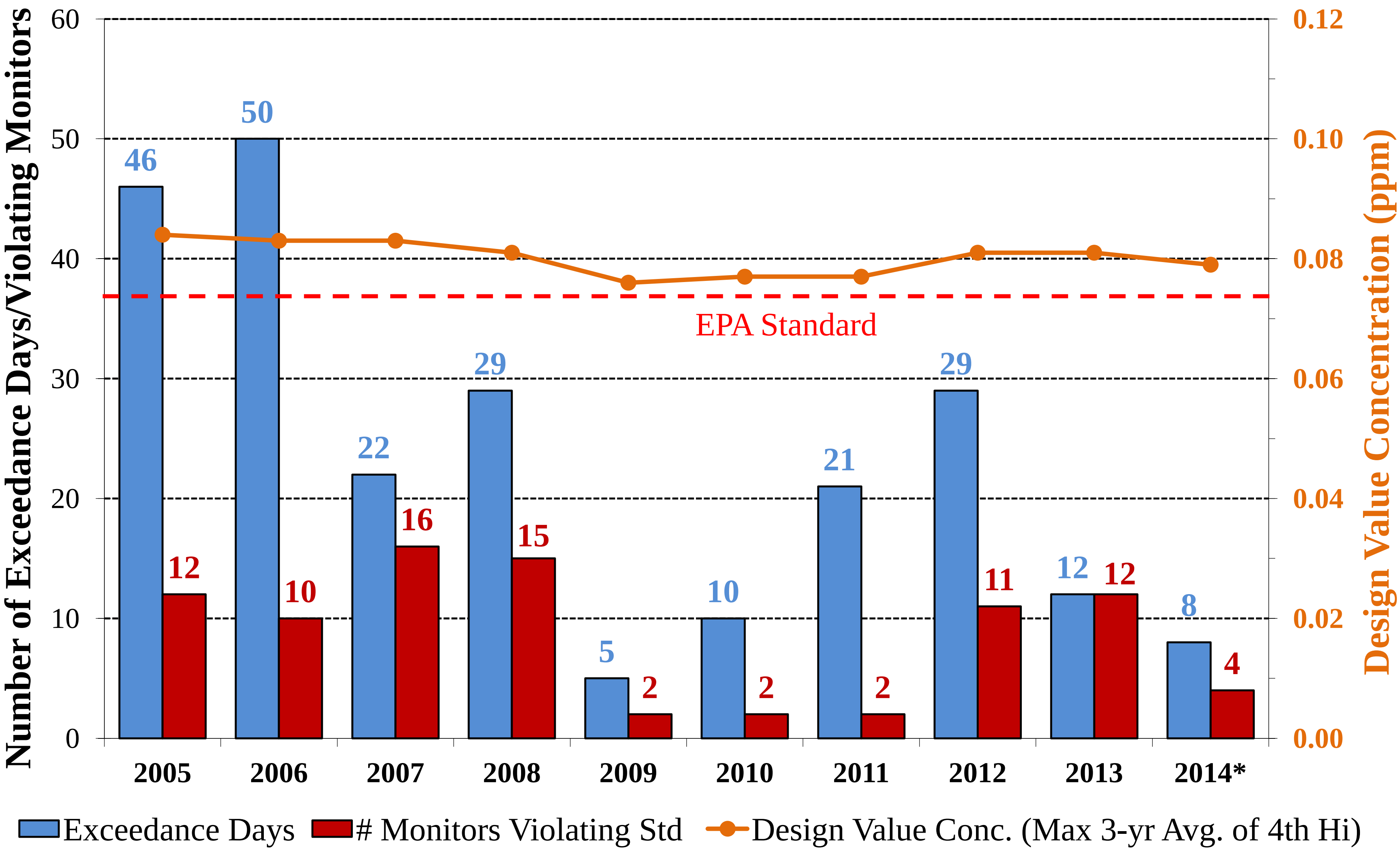
- Court-ordered deadlines
  - EPA (re)considering revised Ozone health standard in a range of 60 to 70 ppb
  - EPA also considering a secondary Ozone standard for ecosystem protection
    - Growing season / daylight hours-weighted cumulative metric


JIMBORGMAN
THEY CAN'T FORCE US!!
EPA RAISES STANDARDS
THINK GLOBALLY
REACT PAROCHIALLY

Compliance with EPA National Ozone Standard

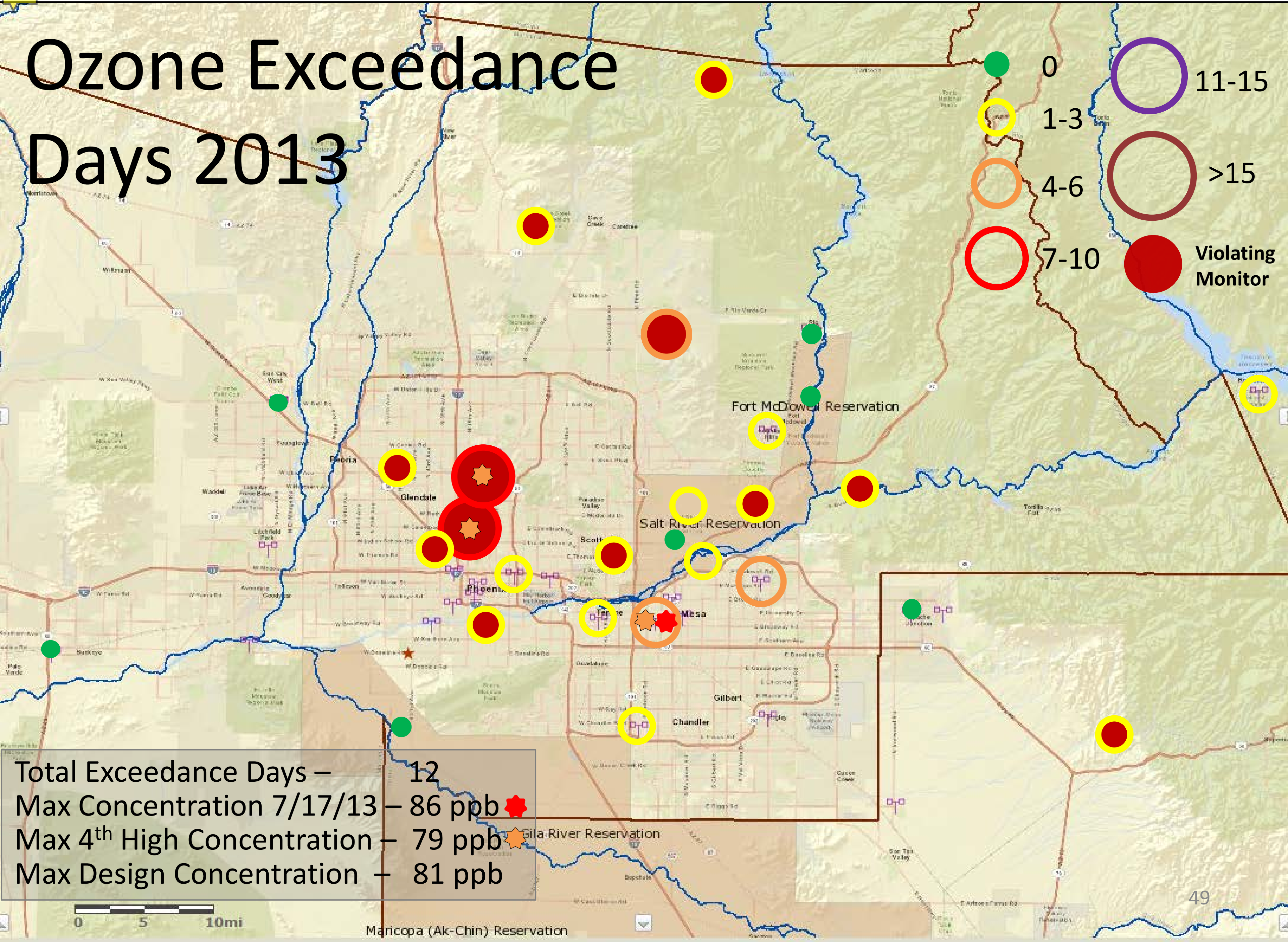
- Measured at ground station sites, highest 8-hour average each day
  - 4th highest values each year are averaged over 3-year periods to determine compliance (e.g., 2009-11, 2010-12, 2011-13)
  - Statistic is called a "Design Value" for that site for that time period
  - 3-year average of the 4th highest measured values is used to prevent flip-flopping in and out of attainment

8-hour Average Ambient Ozone Compliance Based on 2008 Federal Standard, Phoenix Nonattainment Area, 2005 – 2014*



*2014 data are preliminary through 8/31/14 and do not include tribal monitors.

Ozone Exceedance Days 2013



Total Exceedance Days – 12
Max Concentration 7/17/13 – 86 ppb
Max 4th High Concentration – 79 ppb
Max Design Concentration – 81 ppb

Summary

- Ozone is most the complicated air pollution problem in metro Phoenix
  - Chemistry
  - Meteorology
  - Sources
  - Persistent, long-term challenge
  - Standard becoming more stringent
- Public health problem
  - Also affects ecosystems and plant health