Monitoring Critical Levels of Ozone in Remote Rocky Mountain Ecosystems and Exceedances of the National Ambient Air Quality Standard

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Ozone Parameters Related to Vegetation Response

Preferentially weights higher concentrations
 [requires hourly data]

- •Cumulative throughout growing season
- •Includes time periods when stomata are open [requires stomatal conductance data]

Ozone Metrics

- <u>Concentration</u> is the number of moles of ozone per unit volume of air.
- <u>Exposure</u> is the product of the concentration measured near the vegetation of interest and the length of time the vegetation is presumably exposed to the pollutant.
 [The integral of the instantaneous (or hourly) concentration over the time period of interest.]

from Musselman et al. 2006. Atmos Environ 40: 1869.

Ozone Metrics

- <u>Stomatal flux</u> is the rate of entry of ozone into the leaf.
- <u>Dose</u> is the total amount of pollutant absorbed through stomata over time. [cumulative stomatal flux]
- <u>Effective flux</u> is the balance between the stomatal flux and the leaf detoxification.
- <u>Effective dose</u> is the integral over time of effective flux.

[from Musselman et al. 2006. Atmos Environ 40: 1869.]

Ozone <u>Concentration</u> Metrics "Related" to Vegetation

P1: Maximum daily average

N100: Number of hourly concentration ≥100 ppb

4th8hrDM: 4th highest 8 hour daily maximum concentration

Ozone <u>Exposure</u> Metrics "Related" to Vegetation

AOT40: <u>a</u>ccumulated exposure <u>o</u>ver a <u>t</u>hreshold of <u>40</u> ppb SUM06: <u>sum</u> of all hourly concentrations at or above <u>60</u> ppb W126: sigmoidal weighted function, ppm-hrs $W_i = 1/[1 + 4403 \times e^{-(126 \times C_i)}]$

Critical Levels for Europe

 concentration, cumulative exposure or cumulative stomatal flux of atmospheric pollutants <u>above which</u> direct adverse effects on sensitive vegetation <u>may occur</u> according to present knowledge

Current European Air Quality Standards

- Exposure-based critical level: cumulative, threshold weighted
- Exposure-based VPD-modified critical level: cumulative, threshold weighted
- Flux-based critical level: cumulative stomatal flux [dose] [requires vegetation data]
- Not concentration based as in North America
- Not effective flux nor effective dose

Europe had used an exposure-based critical levels standard (AOT40) for more than two decades, and are now using a flux-based assessment.

The US, Canada, and Mexico have always used a concentration-based vegetation standard for ozone.

US EPA Staff in 1996 and again in 2006 recommended an exposure-based secondary standard for ozone.

In 1996 the EPA Administrator decided to stay with a concentration-based standard for ozone.

In 2010, the EPA Administrator decided to recommend an exposure-based secondary standard metric for ozone.

"Air Quality Management in the Unites States" National Research Council of the National Academy of Sciences, 2004. [www.nap.edu/catalog/10728.html]

"EPAs current practice for setting secondary standards for most criteria pollutants does not appear to be sufficiently protective of sensitive crops and ecosystems." "A major goal of the nation's AQM system in the coming decades should be to establish an appropriate research and monitoring program that can quantitatively document the links between air pollution and the structure and function of ecosystems and use that information to establish realistic standards and goals for the protection of ecosystems."

from "Air Quality Management in the Unites States" NRC Report (2004) [www.nap.edu/catalog/10728.html]

US O₃ Air Quality Standard

- NAAQS for ozone: concentration-based
- Evaluated every "5 yrs":
 1971, 1978, 1984, 1993, 1996, 2006, 2014
- Current NAAQS:
 - Primary: 0.075 ppb 4th highest 8-hr average
 - Secondary: same as Primary
- Proposed for 2010 [then delayed]:
 - Primary: 0.070 ppb 4th highest 8-hr average
 - Secondary: 13 ppm-hrs 3-month W126

Ozone Exposure Questions:

- Rural/Remote locations
- High elevation/Mountainous terrain
- Wilderness/Class I

Vegetation growing in these areas is likely at risk because:

- O_3 has been shown to be higher at higher elevation
- Air chemistry at remote sites favors O_3 persistence
- Snow cover at high elevation favors O_3 persistence
- Stomata of native plants in rural areas are often partially open at night when O₃ is present
- Plant defenses to O_3 are likely less at night







Sites 21 km apart











8-hr average findings:

- 60% of sites exceeded 75 ppb
- 75% of sites exceeded 70 ppb
- Values as high as 101.5 ppb
- 4th highest and highest almost the same
- Peaks during springtime and/or nighttime
- Most concentrations between 30-80 ppb

W126 findings:

- Very high values most sites exceed 13 ppm-hr
- 24-hr almost twice 12-hr values indicates high nighttime exposure
- Highest values (and N100s) at high elevation
- Springtime peaks
- Daytime W126 not related to elevation
- Nighttime W126 related to elevation

Conclusions:

- O_3 concentrations were at levels that would contribute to exceedance of the current primary and the proposed new secondary NAAQS at most sites.
- Few O_3 concentration were below 30 ppb or above 80 ppb.
- Mid-level O_3 concentrations were a primary contributor to the secondary standard exceedances.
- O_3 was persistent at night, particularly at higher elevations.
- There were significant year-to-year O_3 differences at each site.
- O_3 mixing ratios sometimes peaked in late spring and at high elevation sites (>3000 m), evidence of stratospheric intrusion.