

# SEMINAR

## Redefining odd oxygen: a new budget diagnostic for tropospheric ozone

**Kelvin Bates**

NOAA Climate & Global Change and  
Harvard University Center for the Environment Postdoctoral Fellow

Tropospheric ozone, an important atmospheric oxidant and greenhouse gas, can be produced within the troposphere by photochemical oxidation of volatile organic compounds (VOCs) and CO in the presence of nitrogen oxide radicals ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ) or transported from the stratosphere, where it is produced by  $\text{O}_2$  photolysis. Global 3-D chemical transport models (CTMs) resolving the coupling between chemistry and transport have become standard tools for developing an understanding of the factors controlling tropospheric ozone, but the chemical cycling between ozone and various chemical species presents a difficulty in tracking ozone and quantifying ozone budgets in the models. Models define for this purpose an "odd oxygen" ( $\text{O}_x$ ) chemical family, including ozone and the species with which it cycles, as the relevant quantity for computing the ozone budget. However, different models use various definitions of the  $\text{O}_x$  family, leading to ambiguities in model intercomparisons, and the definitions commonly used have prominent theoretical deficiencies. For example, a major  $\text{O}_x$  loss in all definitions is the  $\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$  reaction, where  $\text{O}(^1\text{D})$  is produced by ozone photolysis. But this may not be an actual loss, because the resulting hydrogen oxide ( $\text{HO}_x$ ) radicals regenerate ozone in the presence of nitrogen oxides.

We propose an expanded definition of the odd oxygen family,  $\text{O}_y = \text{O}_x + \text{O}_z$ , to include both  $\text{O}_x$  and an additional subfamily,  $\text{O}_z$ , consisting of  $\text{HO}_x$  and its reservoirs. In the  $\text{O}_y$  framework, the primary sources of tropospheric ozone are transport from the stratosphere and production of  $\text{O}_z$ , mainly by photolysis of carbonyls, while sinks include deposition and conversion to  $\text{O}_2$  and  $\text{H}_2\text{O}$ . The  $\text{O}(^1\text{D}) + \text{H}_2\text{O}$  reaction conserves  $\text{O}_y$  and drives the conversion of  $\text{O}_x$  to  $\text{O}_z$ , and reactions of NO with peroxy radicals act as an amplifier on the cycling from  $\text{O}_z$  to  $\text{O}_x$ , rather than a primary source of odd oxygen. We incorporate this new accounting into the GEOS-Chem model and show how it implies a longer lifetime of ozone and greater contribution of stratospheric input as a source of tropospheric ozone, and can also be used to "tag" ozone by source. Using  $\text{O}_y$  in model intercomparisons may help to resolve the large discrepancies in tropospheric ozone budgets.

**Monday, March 18, 2019, 3:30 p.m**

Refreshments 3:15 p.m

NCAR Foothills Laboratory

3450 Mitchell Lane, Boulder, CO 80301

FL2-1022, large seminar room

Live webcast: <http://ucarconnect.ucar.edu/live>

For more information please contact Bonnie Slagel, [bonnie@ucar.edu](mailto:bonnie@ucar.edu), phone 303-497-8318.