Conclusions Based on 3-Years of Tropospheric Ozone Measurements Co-located at AWS Sites

Mark W. Seefeldt

Cooperative Institute for Research in Environmental Sciences (CIRES) University of Colorado – Boulder

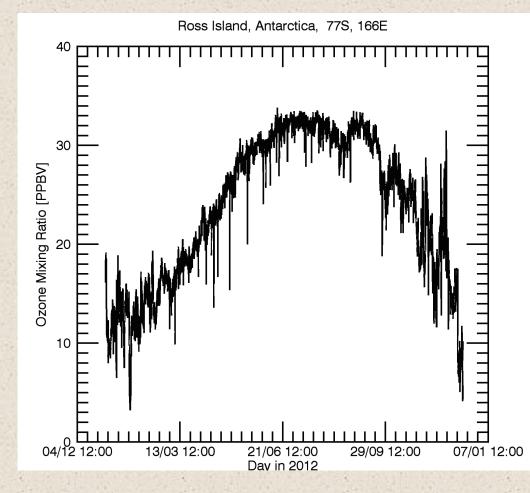
> Lars E. Kalnajs Laboratory for Atmospheric and Space Physics (LASP)

> > University of Colorado – Boulder

Allison M. Burg Department of Engineering – Physics – Systems Providence College

Annual Cycle of Tropospheric Ozone

• There is an annual pattern to ozone levels in the Ross Island region with a seasonal maximum (34-38 ppb) in late August and the minimum (10-16 ppb) in mid-summer (Dec.-Jan.)

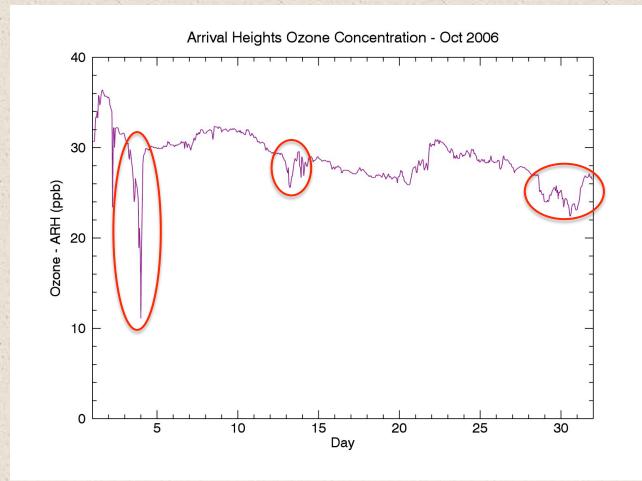


Annual Cycle of Tropospheric Ozone

- During the summer months the ozone concentration is around 10-20 ppb
- During the fall months there is a steady recovery in the concentration of ozone leveling off during the winter months at approximately 36 ppb
- Starting with the polar sunrise, there is a progressive decrease in the ozone concentration, eventually reaching summer levels
- This same general pattern is observed every year with some yearto-year variability

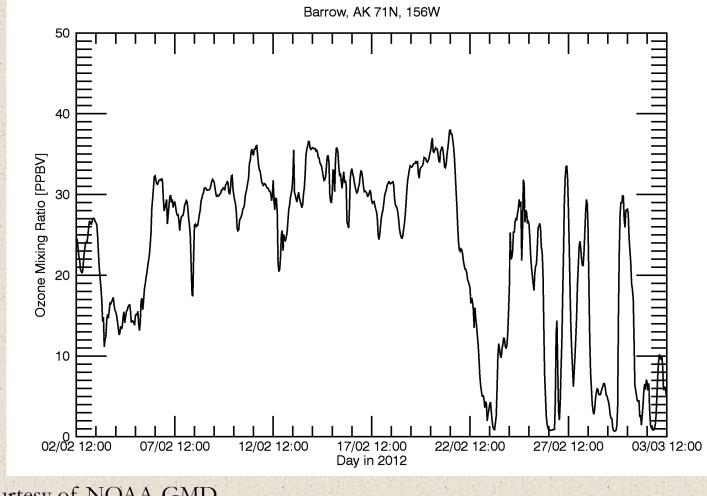
Annual Cycle of Tropospheric Ozone

• The speculation was that the spring time decrease was a caused by episodic ozone depletion events (ODEs), similar to what has been revealed in studies from the Arctic.



Dramatic Arctic ODE

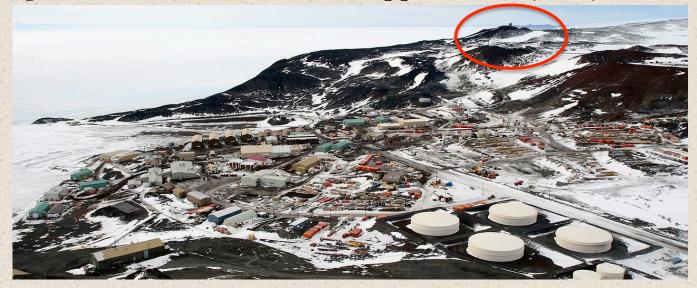
• The ODEs in the Arctic are dramatic, clearly defined, and oftentimes going to near 0 ppb



Courtesy of NOAA-GMD

Arrival Heights - Ozone Observations

 NOAA ESRL has had an ozone instrument located at Arrival Heights (McMurdo Station) for approximately 15 years



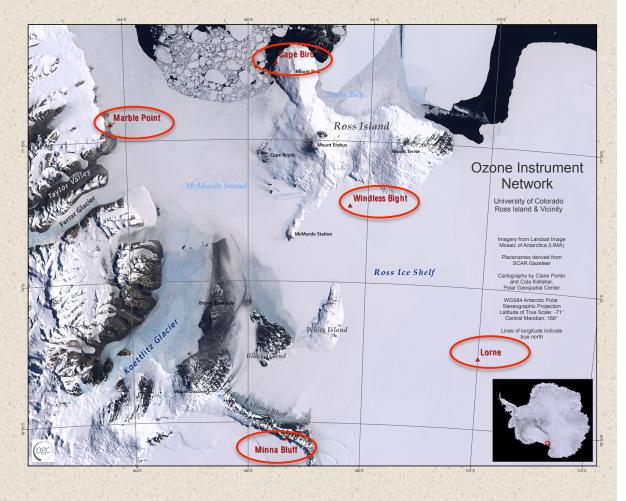
• The observations have the benefit of being long-term and reasonably maintained although they also have limitations due to the location (above the ice surface, near anthropogenic sources)

http://www.esrl.noaa.gov/gmd/dv/data/

Near-Surface Tropospheric Ozone Sensors

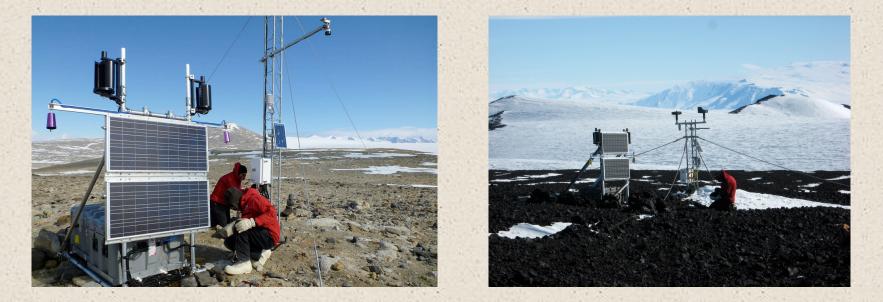
- Five near-surface ozone sensors were installed at automatic weather station sites (AWS) during the 2011-12 field season
- The sensors

 operated year-round
 with the intent to
 answer questions
 regarding the annual
 cycle of ozone in
 the Ross Island
 region



Near-Surface Tropospheric Ozone Sensors

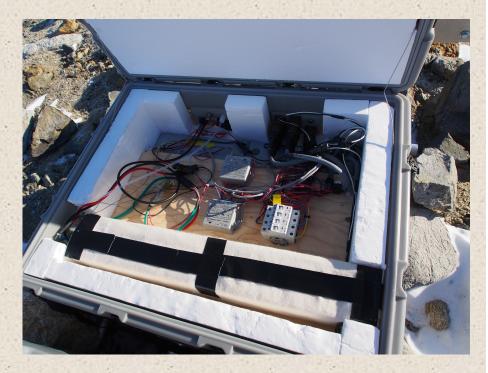
• The sensors were co-located at AWS sites to provide the corresponding meteorological observations



- The selected AWS sites were based on identifying meteorologically and chemically diverse locations
- The ozone sensors are low-power for year round operation and the data was transmitted in real-time

Ozone Instrument Detail

- In-house designed and built ozone instruments
- UV absorption technique, based on a custom UV-LED source
- Power consumption ~ 4W for continuous measurements / 1 – 2W for reduced 1 – 2 measurements per hour
- Operates down to -55C, measurements down to -38C



Ozone Instrument Review

- Sensors operated well during the first summer, but experienced mechanical failures of pumps during late winter
 - Surprisingly this was more likely due to blowing volcanic grit than cold temperatures.
- Service visit in late 2012 updated pumps, added filters to remove grit. Instruments operated nominally for the next year.



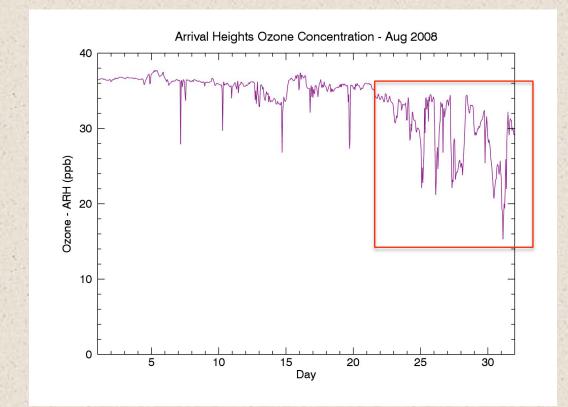
Ozone Instrument Review

- Started to question data integrity during the second winter. Issues likely due to contamination of grit filters or contamination of optical system.
- Overall, the engineering and infrastructure performed well, largely uninterrupted power supply and reliable communications via iridium.



ODEs in the Ross Island region

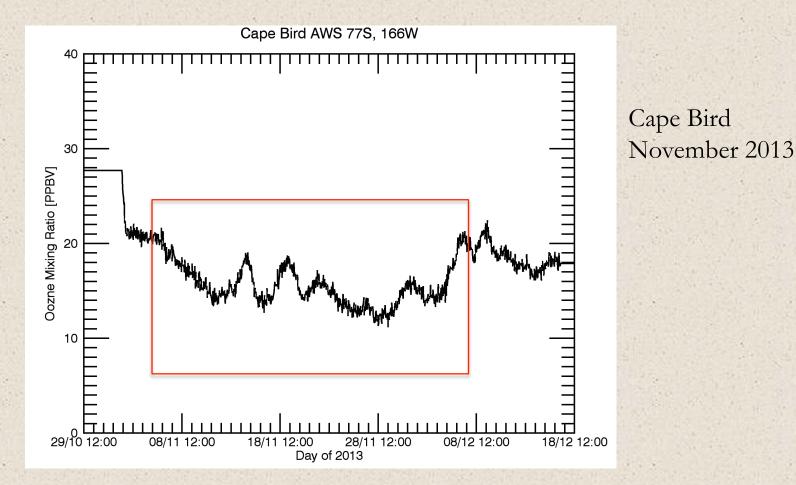
- In contrast to the Arctic, the Ross Island region ODEs are less severe and more difficult to identify
- The best cases decrease in ozone is approximately 8-18 ppb and it never comes close to 0 ppb



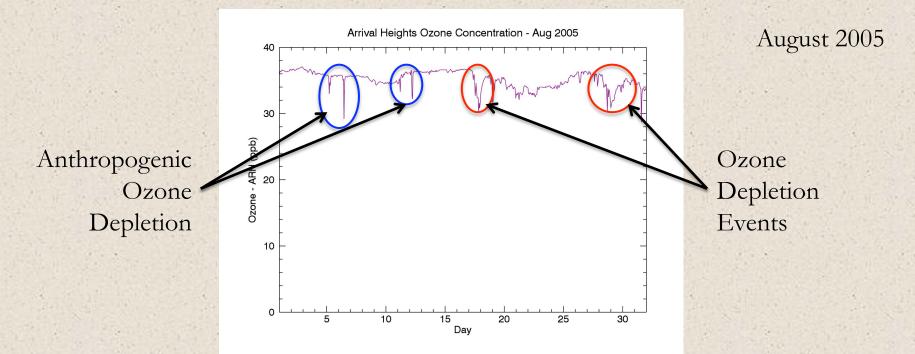
August 2008

ODEs in the Ross Island region

• The Cape Bird ozone sensor shows an ODE that is approximately 8-10 ppb extending over 24 hours



There are also difficulties in distinguishing between anthropogenic and natural depletion events



ODEs in the Ross Island region

- Anthropogenic ozone depletion is observed year round
- ODEs are primarily during the austral spring (Aug. Nov.)

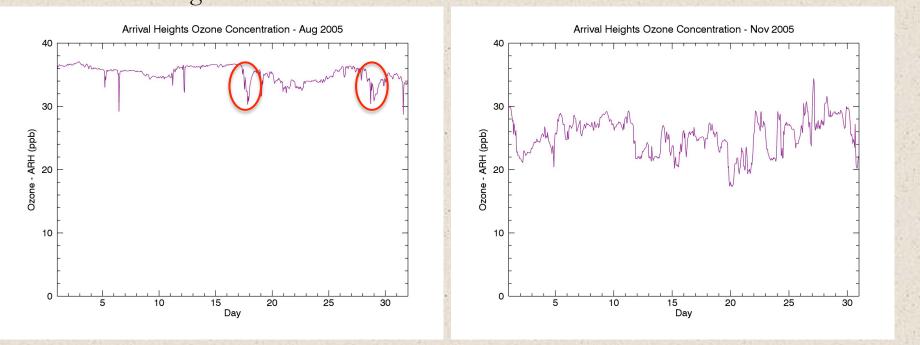
Defining an ODE

- The result is that it is very difficult to clearly define what is an ODE in the Ross Island region
- A method to objectively identify and classify ODEs has been elusive
 - Algorithms to flag ODEs based on the magnitude of a decrease in ozone in a given moving window of time was

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Arrival Heights - ozone observations - year:
 Initial o3 drop: 3.0 (ppb) in less than:
                                            6 (hrs)
 Ending o3 increase: 2.0 (ppb) in less than: 6 (hrs)
 o3 max-min threshold 8.0 (ppb)
                                   Remove pollution (<=): 6(hrs)
2003
    9 17 22 35.1
                     2003 9 18 5 21.4
                                          13.7
                                                 7
2003 10 2 3 32.1
                     2003 10 3 3 23.0
                                           9.1
                                                24
                                        8.9
2003 11 14 8 35.3
                     2003 11 14 18 26.4
                                                10
2003 11 25 4 30.6 2003 11 25 16 19.8
                                        10.8 12
2003 12 9 24 32.4 2003 12 10 18 22.0
                                       10.4
                                                18
2003 12 12 23 24.0 2003 12 19 11 13.7
                                          10.3 156
2003 12 29 24 24.6
                     2003 12 30 17 14.7
                                           9.9
                                                17
```

Defining an ODE

- The best results have come from manually sorting through monthly plots of ozone
 - Results in a subjective and non-definitive climatology
 - By late spring (~ Nov.), the variability in ozone makes identification of ODEs very difficult
 August 2005 November 2005



Defining an ODE

- Based on this rough subjective definition, with objective guidelines, the ODEs are less frequent and less severe than previously thought.
- Based on the Arrival Heights observations, there are approximately 3-7 ODE per year, with some years not having any
- The ODEs are approximately 8-18 ppb in magnitude
- Even the most certain events are far less dramatic than observed in the Arctic

Ozone Depletion Events (ODE)

- Transport-Controlled rapid at onset, significant ozone loss,
 often occurs with rapid wind speed / direction changes
 - Horizontal advection of an ozone depleted air mass
 - Changes in the boundary layer depth
- Chemically-Controlled ODE more gradual and not as intense
 - The ozone depletion chemistry is occurring locally

Simpson et al. (2007)

Meteorology Data

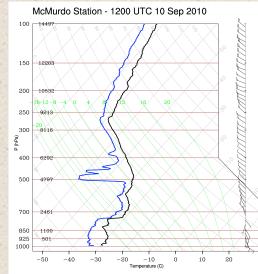
Automatic Weather Stations:

- University of Wisconsin AWS sites have been operating in the Ross Island region since about 1980
- There are currently 10 AWS sites operating in the Ross Island region

McMurdo Radiosondes:

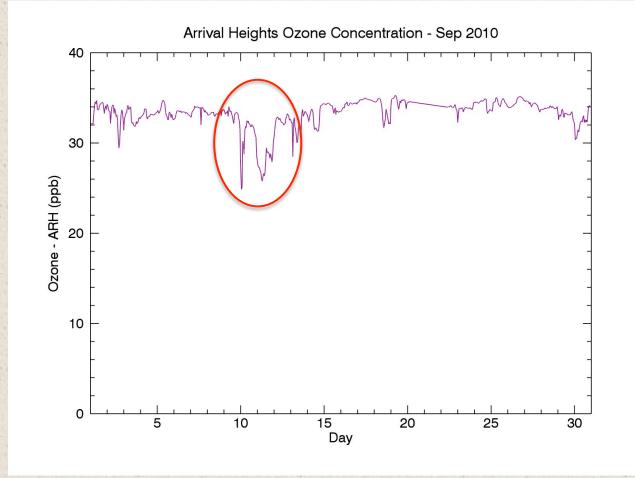
 Radisondes are launched typically at 00 UTC during the winter and 00 and 12 UTC during the summer



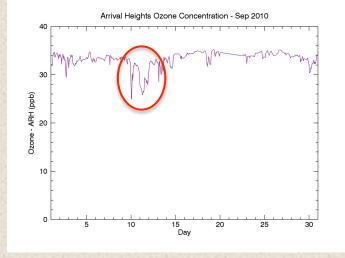


Meteorological Connections

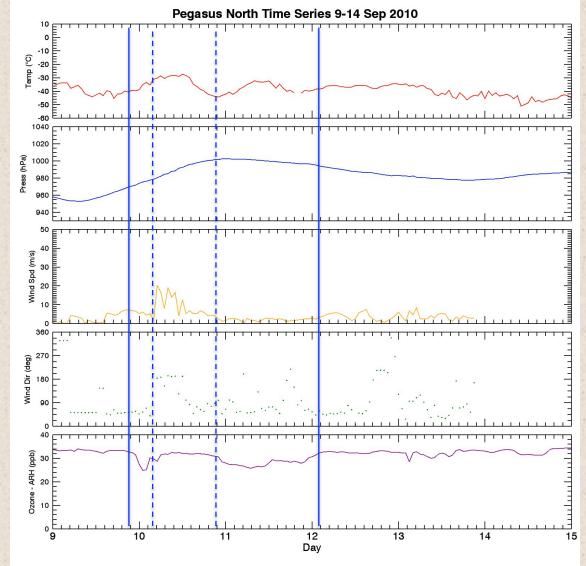
 Changes in atmospheric conditions (wind direction, BL depth) may result in multiple spikes from a "single event"



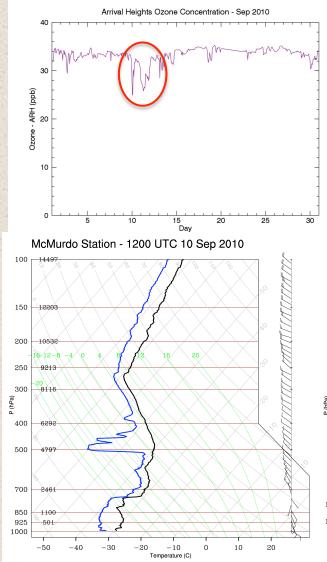
Case Study: September 2010



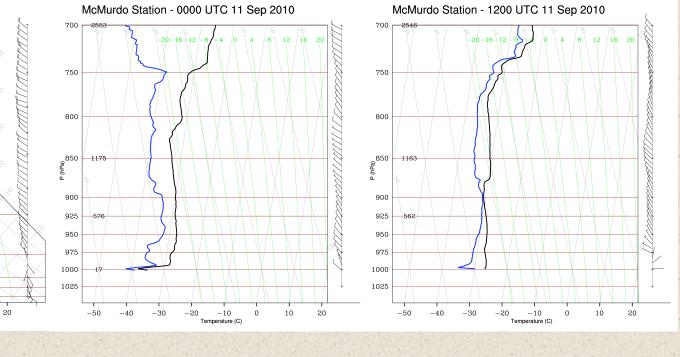
- An ozone depleted air mass is advected into the region
- There is an immediate recovery when the wind shifts from the south
- As the wind shifts back to the NE the ozone depletion is observed again



Case Study: September 2010



- The initial depletion has deep boundary layer
- After the winds shift back to the NE the ozone at Arrival Heights remains high due to the inversion
- The inversion is removed and the ozone depleted air returns to Arrival Heights



Meteorological Connections

- In looking at the collected ODEs, there are some consistent corresponding meteorology observations
- However there is no definite pattern and explanation. We can't explain what is happening with this apparent correlation:
 - Is the boundary layer mixing ozone depleted air to the surface?
 - Is there long-range transport of ozone depleted air detected in the observations?
 - Is the snow mixed and elevated due to the winds resulting in activating the chemistry?

Conclusions – ODEs:

- ODEs, while difficult to define, are less frequent and much less dramatic than seen in the Arctic and previously thought for the Ross Island Region
- It is difficult to explain the overall seasonal cycle of ozone based on the observation of ODE's in the Ross Island region
- This means that we are either not observing the ozone in the correct area – the regions where the ODEs are occurring, or the depletion does not occur as an event driven process but it is instead a large scale slow depletion
- Therefore, it is difficult to explain the seasonal cycle of ozone in Antarctica due to a superposition of ODEs

Conclusions – Instrumentation:

- Additional autonomous atmospheric observations can be made at co-located AWS sites but there are caveats
 - The power systems, freewave/Iridium communications, and additional infrastructure was successful
 - Without the ability to recalibrate, longer term chemical measurements loose certainty as the instruments age
 - There are limitations to the lifetime of mechanical parts under Antarctic conditions

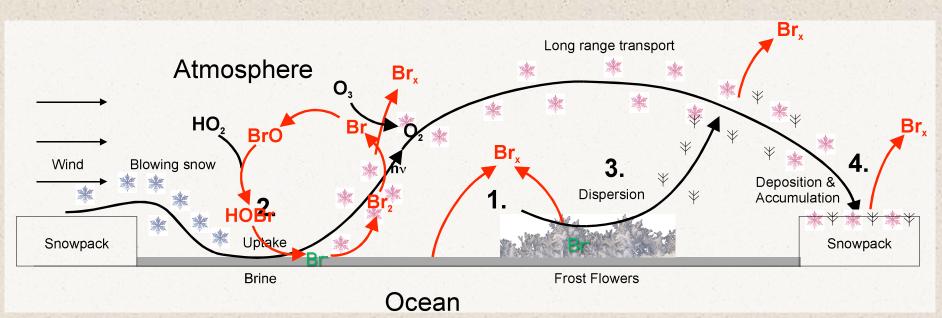
Meteorology: Mark Seefeldt mark.seefeldt@colorado.edu

Atmospheric Chemistry / Instrumentation: Lars Kalnajs lars.kalnajs@colorado.edu

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Possible Release Mechanisms for Reactive Bromine



- 1. Direct release of reactive bromine from brine and frost flowers
- 2. Uptake of brine by blowing snow and subsequent release of reactive bromine
- 3. Dispersion of saline frost flowers and subsequent release of reactive bromine
- 4. Deposition and accumulation of snow and ice crystals with high salinity on the snowpack and subsequent bromine release

Ozone Depletion Events (ODE)

- The depletion of ozone from the surface to about 100-400 m
- Salts are transported from ocean and oxidized to become reactive halogen species
- In the Antarctic the ODEs are frequent during the austral spring (Aug. – Nov.) with the return of sunlight

Simpson et al. (2007)

 $2 \times (Br + O_3 \twoheadrightarrow BrO + O_2)$ BrO + BrO \Rightarrow Br₂ + O₂ Br₂ + $hv \Rightarrow 2Br$

Net: $2O_3 \rightarrow 3O_2$