Using GEOS-Chem alongside observations from Mount Bachelor to understand the relationship between Peroxyacetyl Nitrate (PAN) and Ozone during Spring 2008

Overview

Because of concerns of increasing O₃ in the western U.S., possibly from Asian emissions (Jaffe and Ray, 2007), it is necessary to understand the transport and chemistry of O₃ and PAN. Models show a range of O₃ impacts associated with long range transport (LRT) (Zhang et al 2008; Fiore et al 2008; Reidmiller et al. 2009). The goals of this work are to: 1) simulate PAN at Mount Bachelor (MBO) to understand O₃ production during LRT, 2) understand year to year variability of observed PAN and O₃, 3) identify the sources of PAN to the NE Pacific, and 4) evaluate the ability of GEOS-Chem to capture PAN at MBO, and by extension to understand its ability to capture sources of O₃.

A suite of gas phase and aerosol measurements were made during spring 2008 at MBO (2763 masl). Here we focus on observations of PAN for 3 April to 18 June 2008. During two periods of elevated PAN (17-19 April and 12-13 May), backward trajectory calculations indicate that the air spent time in the Asian boundary layer prior to reaching MBO. A third period of elevated PAN associated with North American air was also observed.

In the context of our broader goals, we use GEOS-Chem to interpret the events of interest in three ways. We first explore how the observed relationship between PAN and O₃ at MBO reflects the plume subsidence temperature. Next we trace the Asian plumes across the Pacific to identify synoptic regimes that support both trans-Pacific transport and subsidence in the eastern Pacific. Finally, we show a case study where the model was integral in identifying the origin of a week-long period of elevated PAN.

1. Location of Mount Bachelor (~2.7 km, ~730 hPa). Photos of the mountain and the summit lift building where the instruments are housed.

2. Information about the GEOS-Chem Simulation:
   - Model: Model version v8-03-03. Full chemistry simulation.
   - GEOS-5 meteorological fields at 2.5 degrees latitude by 2.5 degrees longitude.
   - Emissions: FLAMBE daily biomass burning emissions (revised in March 2009).
   - Sigma-levels 9-16 are roughly equivalent to 874 – 732 hPa.

3. How well did GEOS-Chem capture observed variations in CO, PAN, and O₃ at Mount Bachelor?
   Observed and simulated CO, PAN, and O₃ at Mt. Bachelor for spring 2008. The first two colored boxes represent the two periods of strong Asian influence. The third box encompasses the period of prolonged North American continental influence. The data in the three boxes will be discussed in detail in the following sections.

4. How does temperature in a subsiding air mass impact NOx partitioning and subsequent O₃ production in a descending plume?
   The observed relationship between PAN and O₃ varied with subsidence temperature in the 3 April - 15 May plume. We used in situ chairlift soundings to identify subsiding periods when our summit station was free from boundary layer influence.

5. All plumes do not follow the same path across the Pacific. What types of synoptic regimes support subsidence over the eastern Pacific?
   Here we show the GEOS-Chem simulated plume pathway across the Pacific alongside the mean synoptic state during subsidence for both the April 17-18 and May 12-13 plumes.

6. Can GEOS-Chem identify the source(s) of the week-long period of elevated PAN observed during May?
   A period of elevated PAN (median = 290 pptv) was observed 23-25 May. Aside from periods of elevated CO (~140 ppbv) on 25 May, CO remained < 140 ppbv. O₃ ranged from 38-54 ppbv.

Seasonally unique trajectories indicate the air arriving at MBO 26-28 May traveled from Hudson Bay, through the Manitoba boundary layer and then west along the Canadian – U.S. border. Fires were observed in the Dakotas, Manitoba and SE Saskatchewan 20 – 26 May. Note strong northwesterly subsiding flow from the Gulf of Alaska to the Pacific Northwest. The plume traveled over the great circle, moving from southern Russia to Oregon in ~4 days.

PAN and CO observed on 17 April. GEOS-Chem simulates the two Asian pollution plumes on April 17th and May 12th. However the model simulates higher mixing ratios of PAN and CO than were observed at Mt. Bachelor during the second event.

There is better agreement between the measurements of CO, O₃, and PAN and GEOS-Chem in May than in April (see attached tables for details). Why?

GEOS-Chem simulates the two Asian pollution plumes on April 17th - 18th and May 12th - 13th. However the model simulates higher mixing ratios of CO and PAN than were observed at Mt. Bachelor during the second event. The model also captures the week-long period of elevated PAN (median = 290 ppbv).

15-17 April Average 700 mb Height

15-17 April Average 700 mb Vector Winds

15-17 April Average 700 mb Height

15-17 April Average 700 mb Vector Winds

Below: GEOS-Chem captures this transition well, showing an increasing PAN/HNO₃ ratio during this time period of decreasing air mass temperatures. (Note timing is slightly later and event extends longer in the model.)

PAN (pptv)
CO (ppbv)
O₃ (ppbv)

GEOS-Chem Level 9 - 16
Mt. Bachelor

GEOS-Chem Level 9 - 16
Mt. Bachelor

Above: Chemical parameters observed during the mid-April elevated PAN event at MBO. Note that the relationship between O₃ and PAN differed during the morning periods. We used the difference between hourly average peak O₃ and PAN mixing ratios during each four “pure” free troposphere influenced period to derive a O₃ production efficiency per unit of PAN decomposed of 45 ± 10 mol mol⁻¹. This calculation assumes that the plume is well-mixed and the same plume type was sampled throughout the event. Second we assume that the NO₃ in the warming plume is in steady state between the source from PAN decomposition and the loss from NO₃ oxidation to HNO₃.

10-12 May Average 700 mb Height

10-12 May Average 700 mb Vector Winds

The synoptic state surrounding this plume is similar to the climatological mean during this period. This plume took a more southern path across the Pacific.

10-12 May Average 700 mb Height

10-12 May Average 700 mb Vector Winds

Source region for PAN observed during early part of event.

Source region for PAN observed during latter part of event. GEOS-Chem does not support an Arctic contribution to observed PAN at MBO.

April 17-18 plume:

May 22-23 plume:

Source region for PAN observed during early part of event.

Source region for PAN observed during latter part of event. GEOS-Chem does not support an Arctic contribution to observed PAN at MBO.

