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August 6, 2013

Air Quality at Devils Postpile National Monument

Abstract:
Ozone (O_3) and nitrogen oxides (NO_x = NO + NO_2) were measured at Devils Postpile National Monument during the summer of 2013. Data were recorded at two locations near the ranger station. Ozone concentrations were measured at both locations using portable 2B Technologies ozone monitors, and at one location, a 2B Technologies NO_x system was set up. During the summer, both locations measured similar ozone levels, and saw O_3 concentrations that were comparable to urban Central Valley locations. HYSPLIT back-trajectory modeling indicated that transport from the Central Valley was the main source for the ozone observed at DEPO. Very low NO and NO_2 levels indicated, in contrast, that local photochemical production at DEPO was insignificant.
Introduction:

Ozone ($O_3$), the principle component of photochemical smog, exists primarily in the two lowest layers of the atmosphere and can have either harmful or beneficial effects depending on which layer it resides in. In the stratosphere, the layer about 15 to 50 km above the earth (Seinfeld 6-7), ozone is involved in a photochemical process that prevents solar radiation of wavelengths less than or equal to 290 nm from reaching the surface of the earth (Sacks):

\[
O_2 (g) + \text{hv} \ (\leq 240 \text{nm}) \rightarrow 2O \ (g) \quad (1)
\]
\[
O \ (g) + O_2 (g) \rightarrow O_3 \quad (2)
\]
\[
O_3 (g) + \text{hv} \ (240 \text{nm} \leq \lambda \leq 290 \text{nm}) \rightarrow O_2 \ (g) + O \ (g) \quad (3)
\]

With these reactions, highly ultraviolet energetic radiation is prevented from reaching the surface of the earth. In this manner, stratospheric $O_3$ is highly beneficial. The layer that lies below the stratosphere, the troposphere, is the level where all life exists. In this region, ozone works as a strong oxidizing agent, and can be harmful to flora, fauna, and humans (Sacks). In the troposphere, $O_3$ is formed through a complicated process involving many different anthropogenic and biogenic reactants. The formation process can be summarized by:

\[
\text{VOC} + \text{NO}_x + \text{hv} \rightarrow O_3 + \text{Other Pollutants} \quad (4)
\]

Where VOC= Volatile organic compounds

Since $O_3$ is not directly emitted by pollution sources but is instead formed via later reactions, it is defined as a secondary pollutant. Because it is a secondary pollutant, changes in “ozone precursors” can lead to higher or lower levels of ozone. An example of an ozone precursor would be a volatile organic compound (VOC), like benzene ($C_6H_6$). One of the most important precursors is nitric oxide, which is produced by combustion. After being created in sources like automobiles, it is released into the atmosphere. NO is now free to interact with whatever it
encounters—the ground, water, or oxygen. If NO reacts with oxygen, it can contribute to O₃ formation via the following reactions:

\[
N_2 + O_2 \rightarrow 2NO \quad (5) \\
2NO (g) + O_2 (g) \rightarrow 2NO_2 (g) \quad (6) \\
NO_2 (g) + hv \rightarrow NO (g) + O (g) \quad (7) \\
O (g) + O_2 (g) \rightarrow O_3 (g) \quad (8)
\]

Because emissions of ozone precursors are typically associated with human activities, high levels of O₃ are frequently found in urban areas. At the same time, many locations with lower anthropogenic emissions still experience high ozone levels. This observation is usually explained by the fact that many of the precursors are dispersed from the location of origin to these remote locations via prevailing winds.

During the summer of 2013, O₃ was measured at Devils Postpile National Monument (DEPO), located on the western side of the Sierra Nevada Range at elevations between 2,200 and 2,500 meters. DEPO does not have high local concentrations of NO or NO₂, and thus, O₃ is not formed via equation (4) in significant amounts. However, during the summers of 2007 and 2008, O₃ measurements at DEPO indicated the presence of high O₃ values, some of which exceeded the National Ambient Air Quality Standards (NAAQS) set by the EPA. (The NAAQS states that for an 8 hour average ozone must not exceed 75 ppb (Bytnerowiz)). The goal of this study was to quantify O₃ levels at DEPO and assess the relative contributions of local production and long-
range transport.

**Experimental Set Up and Procedures:**

Measurements of O$_3$ and NO$_x$ (=NO + NO$_2$) were conducted June 6 to August 19. To collect the ozone data, two portable 2B Technologies model 202 ozone monitors were set up at two locations within DEPO. The first site was the Meadow site (37.6293° N, 119.0848° W), located in a grassy meadow next to the middle fork of the San Joaquin River; the Flag site, was located a few hundred meters away (37.6299° N, 119.0846° W), next to the Flag pole near the shuttle bus drop-off. At both locations, the ozone monitor was enclosed in a tough plastic box, and at the Meadow site, the equipment was provided with a 12-volt battery to provide power, and a solar panel to recharge the battery (Figure 1). The Flag location was powered using locals AC power. The monitors measure O$_3$ by drawing air through a Teflon tube into an optical cell that (Figure 2), and used Beers Law to quantify how much light of wavelength 254 nm was absorbed. Using this information, the monitor calculated the ambient concentration of O$_3$. This process is repeated every ten seconds, and five minute averages were recorded inside the internal memory. Later, the five minute averages were converted into hourly averages. At the Flag location, additional monitors were also set-up to measure NO and NO$_2$. The set up to collect these data used two instruments that interacted in tandem (For more detailed information on how the equipment functioned please go to the 2B Technologies website and look up the information on models 401 and 410). At regular intervals during the summer, the data were downloaded from the monitors to a Toughbook computer using HyperTerminal software. Once downloaded, Excel and JMP software were used to analyze the data.
Sampling inlet (upper left) and solar panel. The ozone monitor and the battery reside inside the plastic enclosure

**Results:**

*Trends Between the two sites:*

Figure 3, displays the concentration of ozone in parts per billion (ppb) as a function of the fractional day of year (Julian), for both the Flag and Meadow sites. In most cases, the differences between the two sites are so small as to be negligible. However, at night, the Meadow site has systematically lower O₃ values than the Flag.

This trend is believed to reflect the different surface cover at each location. The Meadow
is surrounded by grass, while the Flag is on top of rocky soil and gravel (Figure 4). Comparing the two surfaces, grass is more capable of acting as an ozone sink—it can react with O₃, and remove it from the air. By contrast, when O₃ hits the ground at the Flag site, it is less likely to react with the rocks and dirt more.

Figure 3:

**Meadow and Flag Concentrations**

The hourly data for each location are plotted as a function of fractional day of year. The “peaks” represent the daylight hours and the “dips” correspond to pre-dawn minima.
Results for NO and NO₂

The levels of NO and NO₂ measured at DEPO were very low, with observed concentrations rarely exceeding 5 ppb (Figure 5). These levels are essentially baseline scatter because the 2B monitor has a detection limit of about 4 to 5 ppb. The amount of NO that is present, is therefore not high enough to have a significant impact on the concentration of O₃. These levels also help explain why the Flag location does not have ozone concentrations significantly larger than the Meadow, despite being positioned closer to occasional car and bus traffic. The precursors involved in the production of ozone, NO and NO₂, are so low at the Flag site that there is no opportunity for enhanced photochemical production of O₃.
Figure 5

The NO and NOx hourly concentrations as a function of fractional day of year.

**Diurnal Cycles for Ozone:**

For periods when both the Flag and the Meadow site recorded valid data, the data were grouped by hour and averaged; the resulting information was then plotted as a diurnal graph (Figure 6). This graph displays the diurnal pattern for both locations. Both locations follow a very consistent diurnal pattern. Between the hours of 18:00 and 5:00 PST, the O₃ concentrations go down, and during the hours of 6:00-17:00 PST, the O₃ concentrations rise. This pattern follows the standard rules for O₃ formation. From 6:00-10:00 hours PST, there is a rapid rise in ozone. During this time a downward mixing of ozone rich air from aloft causes a rapid rise in ozone (due to the break-up of the temperature inversion from the night before. Then between the
hours of 11:00-17:00 hours PST, there is a gradual increase in O₃ because there is local formation of O₃ and upslope transport of O₃ up the San Joaquin drainage from the Central Valley. Next, between the hours of 18:00-23:00 PST, the ozone levels rapidly decrease because after sunset the photochemical processes that produce O₃ shut down because of a lack of sunlight. Lastly, from the hours of 0:00-6:00 PST, there is a steady decrease in ozone because of the formation of a temperature inversion above the sampling site and dry deposition. This occurs when the air near the surface of the earth is not being heated as much as the air above, and thus, the air near the surface no longer mixed upwards towards the free troposphere. This trapped the O₃ produced during the hours of 6:00-17:00 near the surface of the earth. The trapped O₃ is now forced to interact with the grass at the Meadow, or the ground at the Flag. This dry deposition causes the O₃ concentrations to decrease.
The graph shows the average hourly concentrations of O₃ that each location experienced.

**Ozone and Rain:**

As stated above, the diurnal pattern displayed by the DEPO data is usually very consistent. However, on some occasions, the expected diurnal pattern is not observed (Figure 7). On fractional days 175 to 176, the O₃ concentrations no longer follow the pattern established on the other days. The reason for this deviation from the norm becomes apparent when accumulated precipitation values are plotted on top of the O₃ concentrations (Figure 8).

Looking at Figure 8, when more rain accumulated, the O₃ concentrations decreased. The explanation for this is twofold. One, O₃ is soluble in water. At 25 degrees Celsius, about 109 mg
of O₃ can dissolve in one liter of water (“Ozone Solubility”). When it rains, some of the gas-phase ozone is absorbed by the rain water. Two, because it is raining, there is more cloud coverage, with this coverage there is less solar radiation available to promote reactions 6-8, and less O₃ is formed.
Hourly averages for the Flag and Meadow locations.
When the accumulated amount of rain increases, the ambient O$_3$ concentrations show a sharp decrease.
**Back Trajectories Calculations:**

Back Trajectories were calculated for the three highest and four lowest hourly ozone measurements using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model, which provided by the Air Resource Laboratory website, operated by the National Oceanographic and Atmospheric Administration (Draxler). The highest ozone measurements analyzed with HYSPLIT are displayed in Table 1. (The trajectories for the lowest ozone measurements were not included—they displayed the same general pathways as the highest days). For each back trajectory, the Flag GPS coordinates were used to conduct the calculation. Back Trajectories run with Meadow GPS coordinates yielded the same results because of the limited spatial resolution of the HYSPLIT model.

<table>
<thead>
<tr>
<th>Table 1: Back Trajectories Dates and Ozone Values</th>
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<tr>
<td>6/9/2013</td>
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<tr>
<td>6/15/2013</td>
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<td>7/4/2013</td>
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Each trajectory went back in time 72 hours, and EDAS 40 km weather data were used to create the trajectories. In the trajectories, each triangle or square represents a 6 hour interval, and the red line represents the path at 500 meters above ground level and the blue line represents the path at 1000 meters above ground level. After the trajectories were calculated, each was studied to determine if each trajectory shared a common path. It was observed that although the point of origin for the parcels of air were different on each day, before reacting DEPO, all of the trajectories passed through the Central Valley. Each trajectory followed a path that lead through most, if not all, of these counties: San Joaquin, Stanislaus, Merced, Fresno, Madera, Mariposa, Tuolumne, and Calaveras (Figure 10).

These Central Valley regions are known to be quite polluted and when concurrent O₃ measurements for these locations (e.g. Jerseydale, Merced) are plotted with the O₃ measurements from DEPO, one can see that they are comparable (Figure 11). The measurements from these locations have the similar diurnal and day to day changes as DEPO. Though it is interesting to note that contrary to what is expected, locations within the Bay Area (e.g. Hayward) experience ozone concentrations lower than levels at DEPO. Locations that are thought to have very high ozone concentrations, in fact have lower levels that a national park. Moreover, although the concentrations follow the same pattern there is no consistent transport-induced time shift in the O₃ data for any of the urban locations compared to DEPO. All of the locations have peak hours and low hours at the same time of the day.

The fact that the Meadow and Flag data follow the same daily pattern as the urban sites
makes it impossible to identify which urban location might be impacting the O₃ the most. The pattern only shows that the path that the wind follows to reach DEPO allows it to nearly always pick up polluted Central Valley air and transport it up the San Joaquin River Drainage to DEPO.

Figure 10: HYSPLIT Back Trajectories

- **June 9, 2013**

- **July 4, 2013**
The figure above is the data collected at the Meadow and Flag sites compared with one location in the bay area (Hayward) and two locations in the Central Valley.
**Windroses:**

To verify the general results from the back trajectories, the wind direction and speed for the DEPO Meadow site were put into wind rose diagrams for the month of June and July (Figure 13). In the diagrams, the direction of the wind is shown outside of the circle. The frequency with which the wind went in this direction is shown by the length of the bar, and the colors within the bar display the speed of the wind in MPH.

![Windrose diagrams for June and July](image)

The wind rose data were consistent with the back-trajectories findings. Both windroses indicate that for most of the time, the wind came from the west and the southwest.

**Conclusion:**

Devils Postpile National Monument had higher than average ozone concentrations when compared with more urban locations—the concentrations were larger than some Bay Area locations and comparable to Central Valley locations. Though DEPO did have comparably high concentrations of ozone, the location displayed an average diurnal pattern for the summer. Furthermore, DEPO experienced low levels of NO and NO₂, which confirmed that most of the
ozone produced at DEPO was not due to local photochemical production. Moreover, by having two separate locations at DEPO, the Meadow location and the Flag location, the variations in how different surface coverage can act as an ozone sink were seen. The wet grass of the Meadow was better able to remove ozone than the rocky ground of the Flag location. Lastly, the effect of rain on the concentrations of ozone was also seen during the observation period. When it rained, two factors—the solubility of O₃ in water and the reduced solar irradiance—worked to reduce ambient levels of O₃.
References:


