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THE INTERMOUNTAIN WEST AND EPA OZONE STANDARDS

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Abstract

Ozone data sets were collected at Storm Peak Laboratory (SPL), a high elevation site located in northwest Colorado, from 1999 to 2018. Through an analysis of these data sets a number of high ozone events were discovered. Multiple case studies indicate that wildfires, Asian ozone transport, and stratospheric ozone intrusions are commonly associated with these ozone events. These factors observed at SPL are considered throughout much of the Intermountain West (IMW). Data also indicates that ozone concentrations throughout remote locations of the IMW appear to be quite variable. This study highlights baseline ozone at SPL and the factors which are causing it to steadily increase over time.

Introduction

The United States Environmental Protection Agency (EPA) was created for the purpose of protecting human health and the environment. In 1963 The Clean Air Act was enacted by congress which required the EPA to set standards against harmful pollutants found in the air we breathe (EPA 2015). These are called the National Ambient Air Quality Standards (NAAQS), and ozone is one of the six principle pollutants examined. Ozone was selected by the EPA because it is a main source of oxidizing hydroxyl radicals, and a health hazard to people and various ecosystems (Fowler et al. 2008). Currently the NAAQS for ozone state that the fourth-highest annual maximum daily average 8-hour ozone concentrations must be 70 parts per billion by volume (ppbv) or below, averaged over 3 years (EPA 2015). NAAQS are the same for the entirety of the United States despite each region's unique challenges.

The challenges facing the Intermountain West's ability to stay within EPA ozone standards are many. Ozone is generally considered a big city problem, however the factors which this study will discuss tend to affect Class I Areas disproportionally. Class I areas are International Parks, National Wilderness Areas that exceed 5000 acres, National Memorial Parks that exceed 6000 acres, and National Parks that exceed 6000 acres (Rodriguez et al. 2009). Many high elevation wilderness areas have historically been oases of clean air, however, visibility and air quality throughout remote locations of the IMW are deteriorating.

The goal of this research project is to identify reasons why high elevation IMW sites are seeing an increase in ozone concentrations, and to what magnitude. Upon conducting a literature review on the subject it was determined that wildfires, Asian ozone transport, stratospheric intrusion, and increased oil and natural gas development were four major contributing factors in

IMW ozone concentrations. The site used to collect data for the study was not in close proximity to oil and natural gas development and therefore this factor was eliminated.

While many research projects have been focused on urban ozone, and its corresponding health effects, there has been considerably less research conducted on ozone throughout ever-changing high elevation regions such as the IMW. A more complete understanding of both anthropogenic and natural ozone impacts throughout the IMW can lead to improved policy decisions and abatement techniques.

Background

As a starting point, it is important to understand how tropospheric ozone forms. There are three main ingredients, known as precursors, in ozone formation: The presence of volatile organic compounds (VOCs), oxides of nitrogen (NO_X), and ultraviolet radiation from sunlight which ultimately "bakes" these ingredients together (Carter et al. 2012). Eventually ozone is destroyed by reactions involving photolysis and water vapor (Monks et al. 2009). Due to sunlight's important role in ozone formation we tend to see higher ozone concentrations throughout the summer months.

During the summer, in highly populated urban areas, hourly ozone averages can exceed 150 ppbv. In contrast, wintertime ozone concentrations in the US are normally in the range of 30-50 ppbv (Schnell et al. 2009). While summer-time conditions cultivate the highest levels of ozone for most locations, remote IMW basins experience ozone concentrations as high as 166 ppbv in the middle of winter (Rappenglück et al. 2014). SPL is a mountaintop site and the datasets collected were not able to look at this phenomenon directly. While this is true, these factors are vastly important to surrounding IMW locations and a brief mention is merited.

Some oil and gas production sites in the IMW are massive. The Jonah, Pinedale Anticline (JAP) field in Wyoming's Upper Green River Basin produces 2 billion cubic feet of natural gas per day. In order to produce natural gas on this scale, drilling rigs and pipeline compressors operate 24h per day running on diesel and natural-gas engines. (Schnell et al. 2009). NO_X and VOCs are released in the production of natural gas which leads to exceptionally high photochemical ozone production when combined with inversion events. On February 22, 2008 hourly average ozone concentrations at JPA increased from 37 ppbv to 120 ppbv in just 4 hours (Schnell et al. 2009).

Low-temperature ozone formations are highly likely in other regions of the world with similar meteorological conditions, terrain, and fuel extraction (Schnell et al. 2009). Inversion conditions, along with the oil and natural gas industry, can make it difficult for the IMW to stay within EPA ozone standards. Thankfully this is mainly a problem during winter months as increased day length and stronger solar radiation help to reduce inversions. Unfortunately there is a much more wide spread challenge the IMW is facing during the spring.

The Earth as a whole has experienced an increase in ozone concentrations starting in the late 1800s (Cooper et al. 2010). While this is the case, North America has actually seen a decrease in domestic emissions since the 1980s (Cooper et al. 2010). One might expect an improvement in ozone concentrations, however springtime surface ozone continues to rise in western North America. A major contributor to this increase comes to us all the way from Asia.

East Asia has the fastest growing emissions, including ozone precursor emissions, much of which is exported to the Western US (Baylon et al. 2016). Asian NO_X emissions increased by 44% during 2001-2006 while similar ozone precursor emissions decreased by more than a third across Europe and the USA from 1985-2008 (Cooper et al. 2010). A study conducted by the EPA

showed that US domestic anthropogenic emissions of NO_X, CO, and VOCs have decreased from 1990 to 2010 by 49%, 58%, and 44% respectively (EPA 2012). Asian emissions can make their way to the western US and occasionally cause ozone concentrations to rise above 70 ppbv. In fact, ozone produced from Asian emissions accounts for at least 16% of tropospheric ozone in the northeastern Pacific during spring (Jaeglé et al. 2003).

East Asian ozone transportation to North America is most pronounced during spring months. During this time of year winds from the North Pacific Ocean are the strongest. It has also been observed that approximately half of all ozone transported from Asia to North America is produced in Asia while the rest is produced in the upper troposphere during trans-Pacific transport (Zhang et al. 2008). The amount of ozone observed from this process is also steadily intensifying at a rate of around 0.41 ppbv/yr (Cooper et al. 2012).

As summer approaches, ozone levels naturally rise due to increased incident solar radiation. Areas with high population tend to see the greatest ozone concentrations in conjunction with anthropogenic emissions. While the IMW has a relatively low population, when compared with much of the US, wildfires are common and produce many of the same ozone precursors.

The IMW is changing as the climate system warms. Snowpack is decreasing which leads to more arid land (Mote et al. 2005). This has a large impact on wildfires, and it is expected that average area burned per year will increase four times per degree C of warming (Solomon et al. 2011). 93% of large fires in the IMW occur in June, July and August (Knapp 1998). These wildfires produce CO, NO_X, and VOCs which often lead to unhealthy ozone concentrations (Val Martin et al. 2006).

The final challenge considered is stratospheric intrusion, or stratosphere-to-troposphere transport (STT). The IMW experiences stratospheric intrusion when air masses originating near the tropopause are transported downward to the surface. These events often cause ozone observations to increase by 20-40 ppbv (Lin et al. 2012).

The primary mechanism for transporting stratospheric ozone to the mid and lower troposphere is the dry airstream of midlatitude cyclones (Stohl et al. 2003). The IMW is located at the end of the North Pacific midlatitude storm track which leads to more frequent STT reaching below 700 hPa (Sprenger et al 2003). These STT events typically occur in cold dry conditions during late winter and early spring (Lin et al 2012). This is most likely due to peak ozone abundance at the tropopause, stronger surface heating leading to turbulent mixing, a longer ozone lifetime compared to summer, and an increase in storms (Lin et al. 2012).

The EPA does have guidelines for extreme stratospheric ozone intrusion. They state that air quality monitoring data influenced by an extreme stratospheric ozone intrusion may be excluded from regulator determinations related to violations of the NAAQS for ground level ozone (EPA 2015). The challenging part is identifying these events in real time. The EPA uses the GOES-Chem model to estimate background ozone when determining policy, unfortunately, GOES-Chem does not do well in remote mountain sites in spring and consistently underestimates ozone from deep STT events (Emery et al. 2012).

It was determined that in high-elevation IMW sites, during springtime, stratospheric ozone has a greater impact than all ozone produced from Asian and North American anthropogenic emissions (Lin et al. 2012). Certain climate models forecast STT events to become more frequent under future climate scenarios (Zeng et al. 2010). It is expected that stratospheric ozone recovery along with accelerated circulation in a warmer climate would cause more stratospheric ozone to mix down to the surface (Zeng et al. 2010).

Storm Peak Laboratory

The main resource used in conducting this study was ozone concentration data recorded from SPL. SPL is located at an elevation of 3208 meters on top of Steamboat Springs ski resort in Colorado. The laboratory is on the Continental Divide and a north-south mountain rage which provides a clear upwind fetch. This site is also unique in producing transitions from free tropospheric air to boundary layer air nearly every day. This high elevation site is a great candidate for studying wildfires, stratospheric intrusion, and Asian ozone transport events.

Instrumentation

The instrument used to measure ozone concentrations from January 1999 through April 2013 is called a Dasibi Ozone Monitor (Dasibi Environmental Corp., Glendale, CA). This instrument measures within a range of 0.001-1.000 ppm, includes an automatic zero, span test, and records data every 5 minutes. The instrument was calibrated every 6 months and the UV lamp was replaced any time a degraded signal was detected.

In October 2006 this instrument was replaced by the Model 49*i* Ozone Analyzer (Thermo Fisher Scientific., Waltham, MA). The Model 49*i* Ozone Analyzer is an upgrade from the Dasibi Ozone Monitor with a range of 0 to 200 ppm and a 20 second response time. It also provides higher resolution data by recording ozone every minute rather than every five minutes. Like the Dasibi Ozone Monitor, this instrument was calibrated every 6 months and the UV lamp was replace when necessary.

A UV lamp is vital to these instruments measuring ozone. They operate on the principle that ozone absorbs UV light at a wavelength of 254 nm. More UV light will be absorbed with higher concentrations of ozone. The Beer-Lambert Law depicts how the Model 49*i* Ozone Analyzer uses a UV lamp to determine ozone concentration:

$$\frac{I}{I_0} = e^{-KLC}$$

I = UV light intensity
I_0 = UV light intensity without ozone
K = 308 cm^{-1} (the absorption coefficient)
L = 38 cm (the length of the cell)
C = Ozone concentration

Another instrument used was the TSI integrating nephelometer (model 3563, St. Paul, Minnesota). This nephelometer can measure total light scattering (7-170°) by aerosol particle, and the conditions inside the nephelometer such as temperature and pressure. To determine how much light is being scattered, the nephelometer draws in air and a halogen lamp illuminates the sample. The light scattering coefficient (σ_{sp}) is ultimately determined which tells us about the density and reflectivity of the aerosols. This information is useful in identifying wildfire events.

The SPL Ozone Record and Baseline Ozone

To discover the impact of wildfires, Asian ozone transport, and stratospheric intrusion in the IMW it was first necessary to check the data set for errors. The system used in January 1999 through April 2013 did not contain flagged data and therefore a manual quality assessment was required. The standard implemented was to eliminate any data points which were negative, and any which were above 200 ppbv. 200 ppbv is unrealistically high for SPL high ozone events.

The ozone measurements taken by the system implemented in April 2013 contained flagged data and a resolution five times greater than the previous system. Flagged data was eliminated and the remaining data was again checked manually. Having completed this process, the dataset was ready work with.

Baseline ozone is the velvet backdrop which allows high ozone events to stand out. SPL's baseline ozone was calculated to be 42.79 ppbv. This concentration was discovered by removing values above 75 ppbv, and averaging nighttime ozone (22:00 - 3:00 MST). Ozone concentrations above 75 ppbv were eliminated in order to avoid the influence of stratospheric intrusion events. Approximately half of the years (1999-2018) did not contain a single data point of nighttime ozone above 75 ppbv. The other years had between 10 and 200 minutes of nighttime ozone above 75 ppbv. High ozone events at night near SPL are rare. Eliminating nighttime stratospheric intrusion events in this manner had a low impact on the baseline ozone value of 42.79 ppbv.

Figure 1 shows how baseline ozone has changed each year. Other ozone trends of interest include daily ozone averages for each month (figure 2), average ozone per day throughout the year (figure 3), and total diurnal averages (figure 4).

Wildfires

Wildfires are a leading cause of unhealthy ozone concentrations at SPL. In order to determine if a spike in ozone was directly correlated to wildfire two resources were implemented; nephelometer data and the National Oceanic and Atmospheric Administration (NOAA) Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT).

Along with NO_X and VOC's, wildfires produce an abundance of aerosols. Nephelometers can detect these aerosols by looking at total light scattering from particles. For this study, nephelometer data sets were collected with a 1 Hz sample rate and recorded as 1 min averages. The component used for this study was the aerosol light scattering coefficient at all available wavelengths and a 1 hour resolution. SPL's Nephelometer rarely exceeds 40% relative humidity and therefore a heater is not required.

During summer at SPL, light scattering coefficients (σ_{sp}) above 40 Mm^{-1} are assumed to be the result of wildfires (Hallar et al. 2015). An example of a nephelometer highlighting a wildfire event can be seen in figure 5. While this technique is useful in linking ozone spikes to wildfires which are not well documented, HYSPLIT adds value in cases dealing with major wildfires.

HYSPLIT is a form of backward trajectory modeling. The latitude and longitude of a given ozone instrument can be given to the model followed by the desired global data assimilation system, altitude information, and a specified amount of time the model should run. Upon completing this process, HYSPLIT will map the path of air parcels ending at the

coordinates of the ozone sensor. This effectually indicates where the air being sampled came from.

On September 5th 2017, SPL recorded ozone concentrations above 100 ppbv. These dangerous concentrations were connected to the Deep Creek Fire which started on September 4th 2017. To help explain the extent to which this fire influenced SPL, the North American Mesoscale Forecast System (NAM) HYSPLIT was implemented. The fire was relatively close to SPL and therefore 4 hour back trajectories were sufficient. The Deep Creek Fire was to the west of SPL and the model indicated that the winds were generally out of the northwest (Figure 6). This helps to explain the extreme ozone concentrations seen at SPL around this time (Figure 7).

While analyzing the SPL ozone record it was apparent that the highest concentrations were associated with wildfires. These fires were most common from June to September, and a number of them caused ozone to spike above 100 ppbv.

Asian Ozone Transport

A study conducted by Obrist, et al. in 2008 focused on Asian ozone transport of gaseous elemental mercury (GEM) at SPL. Their study found that ozone from Asia was positively correlated with GEM from Asia. To further verify this, ozone levels at Mount Bachelor Observatory were examined. Under most conditions, Asian ozone transport events at Mount Bachelor affect SPL within a day or two. On April 3rd 2007 GEM levels at Mount Bachelor were elevated, and ozone was 70 ppbv. Similar concentrations were seen at SPL on April 4th-5th 2007 (Obrist et al. 2008).

The dates highlight by Obrist et al. for elevated GEM (specifically March 17th 2007 through April 10th 2007) were explored by this study. By looking at known Asian transport events, the magnitude of increased ozone from this phenomenon can be discovered. The most pronounced spike in GEM was on April 4th (Figure 8), and this was associated with an ozone increase between 15 ppbv and 20 ppbv (Figure 9).

Asian ozone transport appears to be taking place throughout much of the spring, but to a lesser degree. An increase of more than 15 ppbv at SPL, directly from Asian ozone, appears to be uncommon. As previously noted, weather conditions play a major role in how much Asian ozone gets pulled down from the upper troposphere to the surface. The degree to which Asian transport can elevate ozone concentrations at SPL is significant and higher than anticipated. With Asian ozone transport increasing each year (Cooper et al. 2012), this will have a more substantial impact in the near future.

Stratospheric Intrusion

The location and altitude of SPL make it especially susceptible to stratospheric ozone. In order to connect an ozone spike at SPL to stratospheric air, a way to look at the dynamic tropopause was needed. To help identify the height of the dynamic tropopause, the program Integrated Data Viewer (IDV) was used. In IDV a time can be selected and the height of the dynamic tropopause is mapped throughout the globe.

Days with elevated ozone at SPL were later explored in IDV. Many of these days saw a decrease in the height of the dynamic tropopause, or even a stratospheric fold. Stratospheric folds, or stratospheric air folding under tropospheric air, were generally associated with higher

ozone concentrations than were lower dynamic tropopause events. Stratospheric air, mixing to the surface, frequently caused ozone concentrations to increase by more than 20 ppbv. Many stratospheric intrusions lead to ozone concentrations above 70 ppbv in the spring and summer. One case study is depicted with ozone concentrations on April 21st 2016 (figure 10) and the associated height of the dynamic tropopause (figure 11).

Conclusions

Ozone concentrations throughout remote locations of the IMW are much more variable then one might think. Even the most pristine IMW high elevation sites reach unhealthy ozone levels multiple times throughout the year. From this study it appears that: wildfires cause the most extreme ozone concentrations, Asian ozone transport has the greatest impact on steadily increasing baseline ozone from year to year, and stratospheric intrusion events lead to the most frequent ozone spikes. There were occasionally elevated ozone events which could not be explained by any of these three things.

Understanding high elevation ozone is critical for policy makers and those designing abatement techniques. Ultimately, this knowledge can be used to more fully protect the health of humans and the environment. Understanding the nature of wildfires, Asian ozone transport, and stratospheric intrusions can also lead to better air quality forecasts. Advancements in these areas could have a significant and positive impact on the IMW.

Future research should continue on this subject by analyzing other causes of elevated ozone. It should also be noted that a changing climate impacts the frequency of wildfires and stratospheric intrusions. The amount of ozone coming from East Asia is also expected to change over time. With these things in mind, it is crucial to continue studying the magnitude to which these factors increase high elevation IMW ozone.

Figures

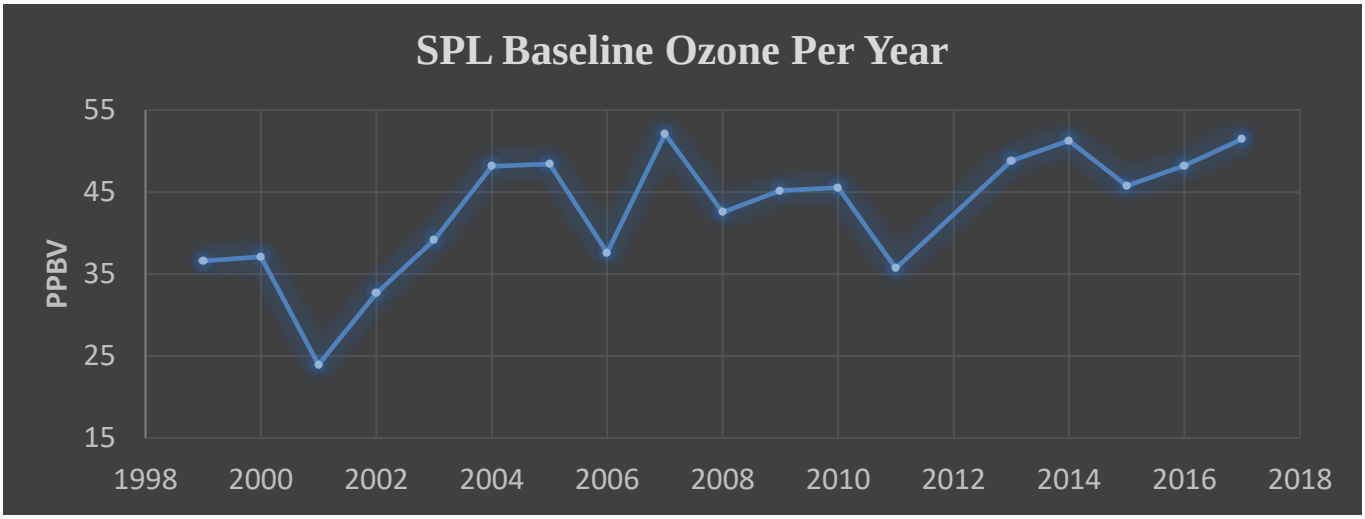

Figure 1*: Baseline ozone at SPL calculated by removing values above 75 ppbv, and averaging nighttime ozone (22:00 - 3:00 MST). Ozone concentrations above 75 ppbv were eliminated in order to avoid the influence of stratospheric intrusion events. This shows that baseline ozone is currently increasing and that there is significant ozone variation from year to year.*

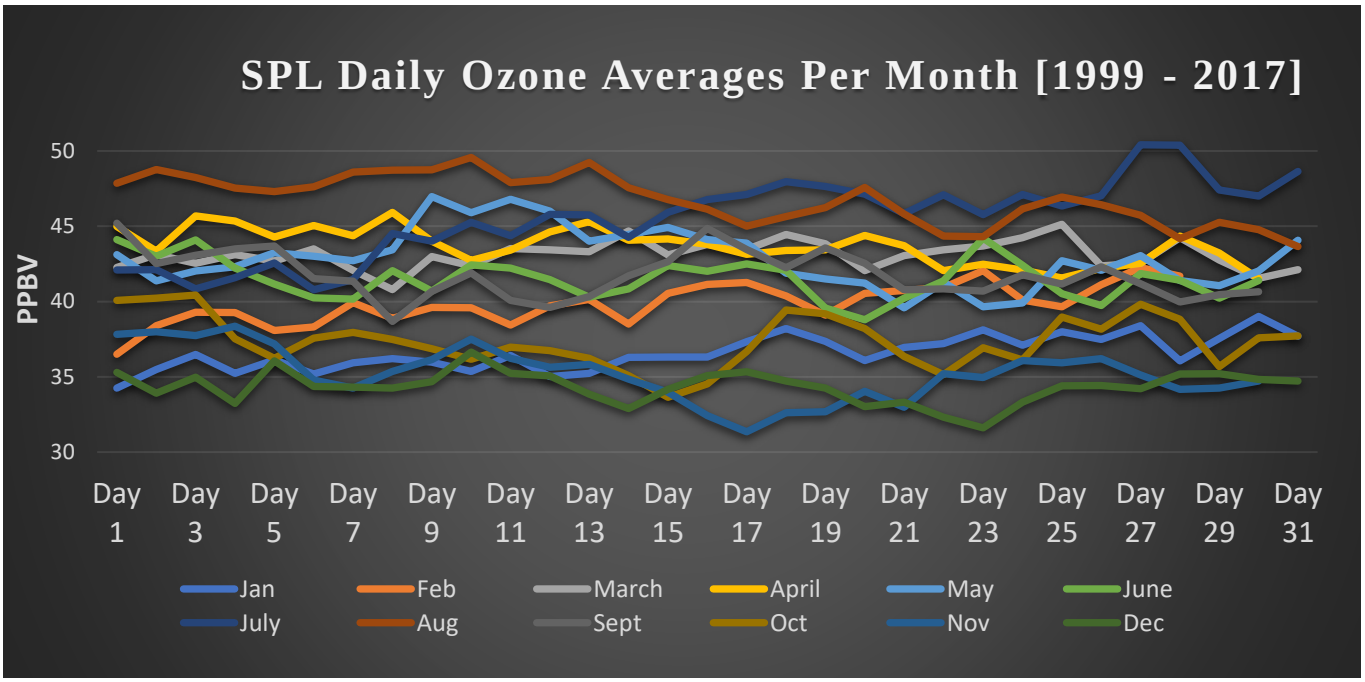

Figure 2: *This graph was produced by calculating the total average of each day of the month to creating a graph with 28-31 points. This process was then repeated for each month and the information was integrated into a single graph. A trend is shown for each month in terms of which months: increase in ozone, decrease in ozone, or have little variation. High ozone events were not eliminated in producing this graph.*

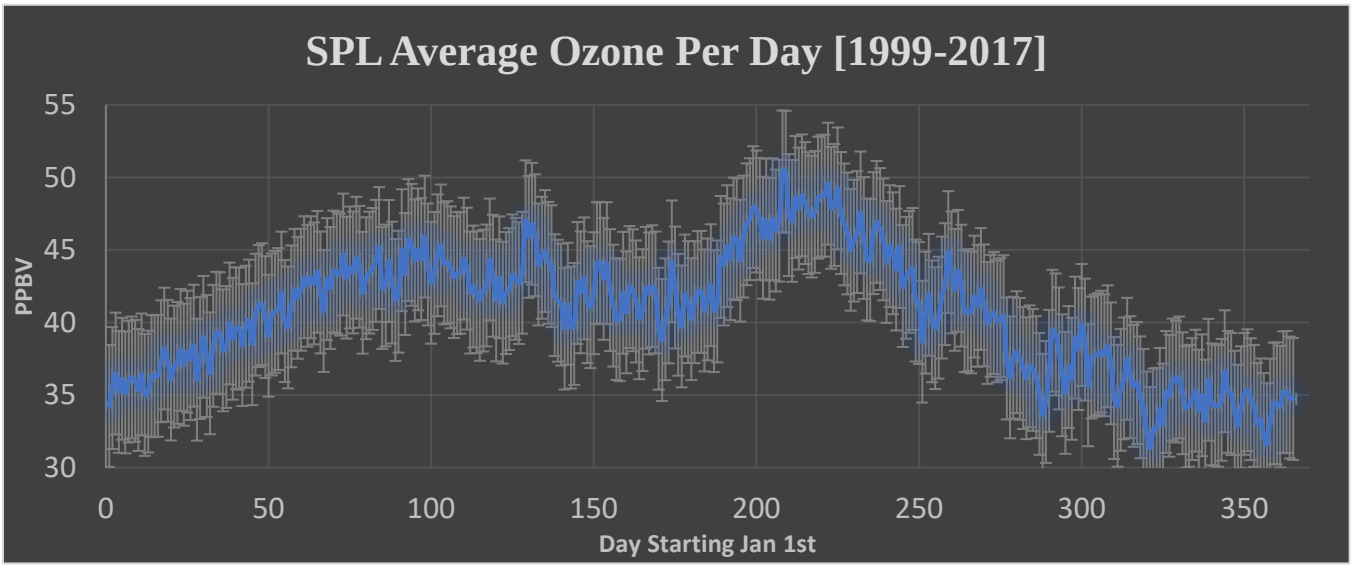

Figure 3: *This graph was produced by calculating the average ozone on January 1st and then averaging that with the January 1st of each available year. This was then repeated through all 365 days (skipping leap days), to produce a single line graph. Standard deviation was also calculated and implemented. Notice how ozone changes throughout a given year with a maximum in summer.*

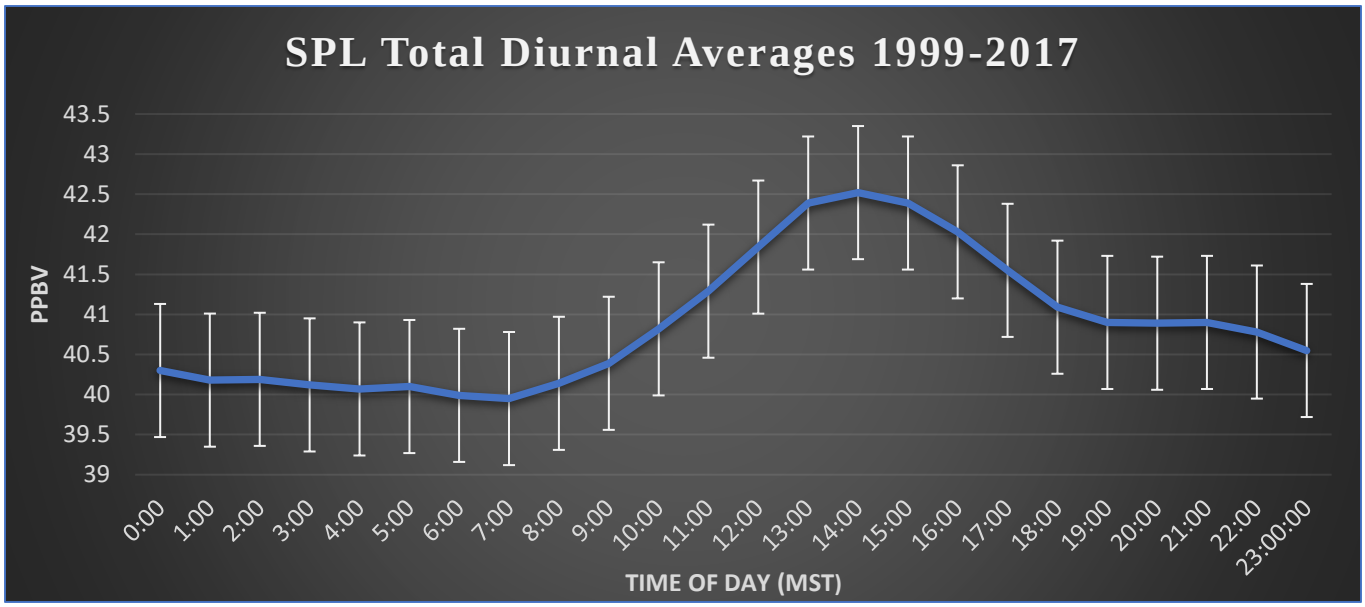

Figure 4: *This was produced by calculating the average for the '0' hour for each day of the year over all available years of data. The process was repeated for each hour up through '23'. The resulting graph is a simple 24 data points including standard deviation. This is helpful in visualizing how much ozone really changes from hour to hour. An ozone minimum is recorded at 7:00 with an average max near hour 14:00. The y-axis is formatted such that the diurnal variation seems significant, however, there is only an average difference of 2.5 ppbv from the minimum value to the maximum. During non-summer months the variation is relatively small which acts to waters down the total diurnal average.*

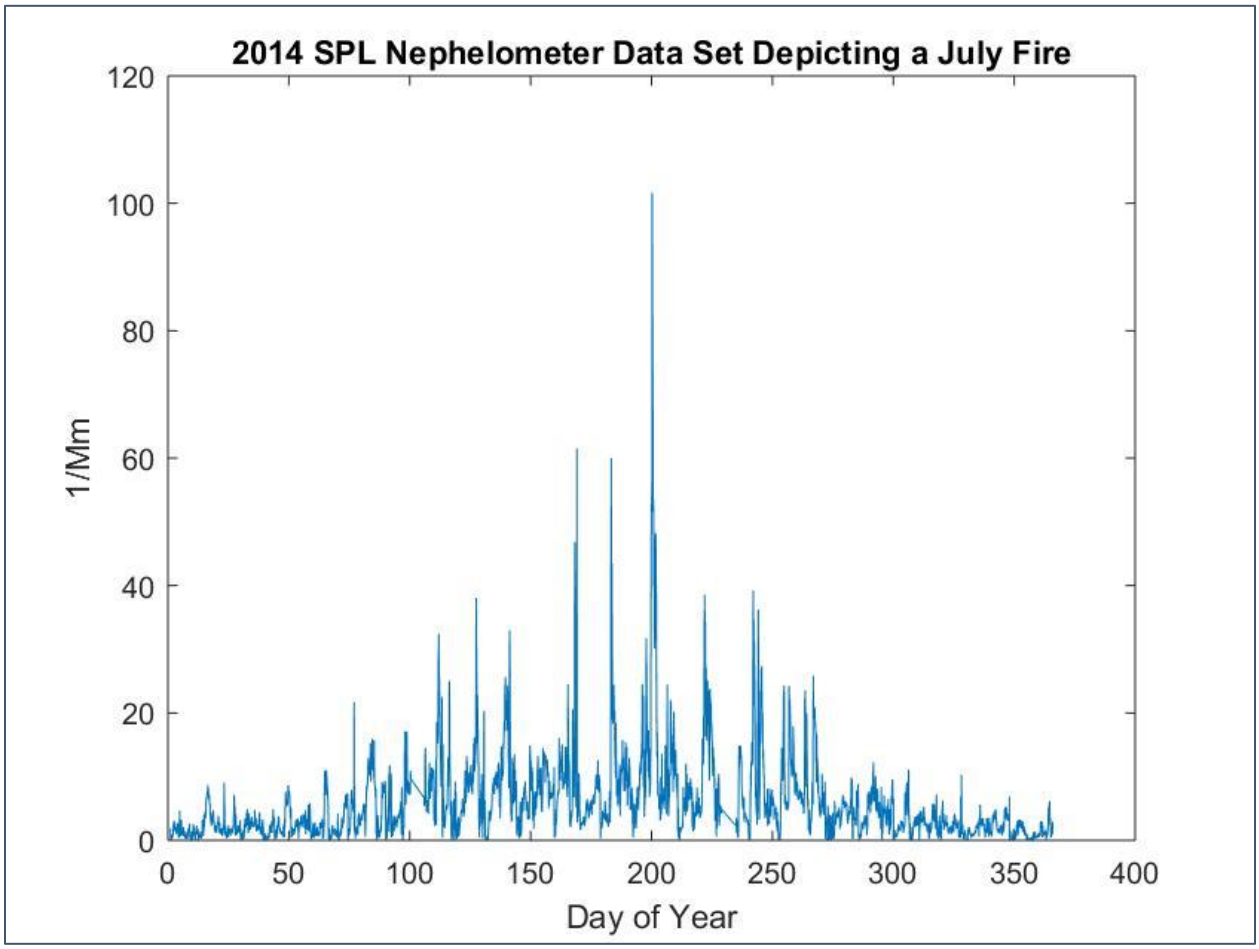

Figure 5: *Nephelometer data sets were collected with a 1 Hz sample rate and recorded in 1 min averages. The component used for this study was the aerosol light scattering coefficient at a 1 hour resolution. The graph was produced in Matrix Laboratory (MATLAB), and nephelometer data used was taken from http://ebas.nilu.no/. A wildfire event is shown on day 200 or July 19th 2014. This correlated with an ozone spike at SPL.*

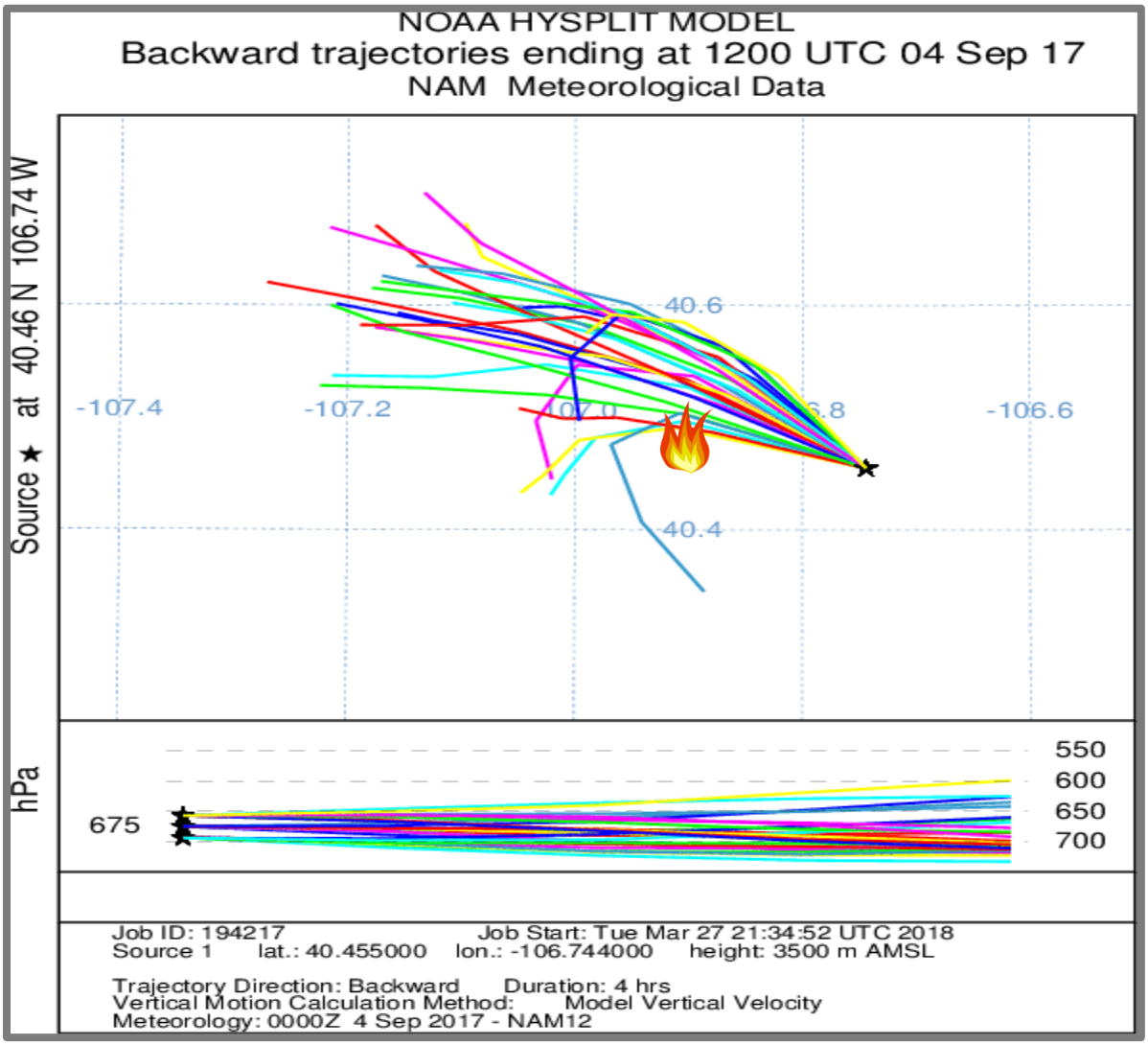

Figure 6: *HYSPLIT showing backwards air trajectories ending at SPL. The fire symbol indicates the location of the Deep Creek Fire which started the previous day. With trajectories such as these, we would expect NO_X and VOCs from the fire to increase ozone at SPL. All information, such as altitude, can be found within the image.*

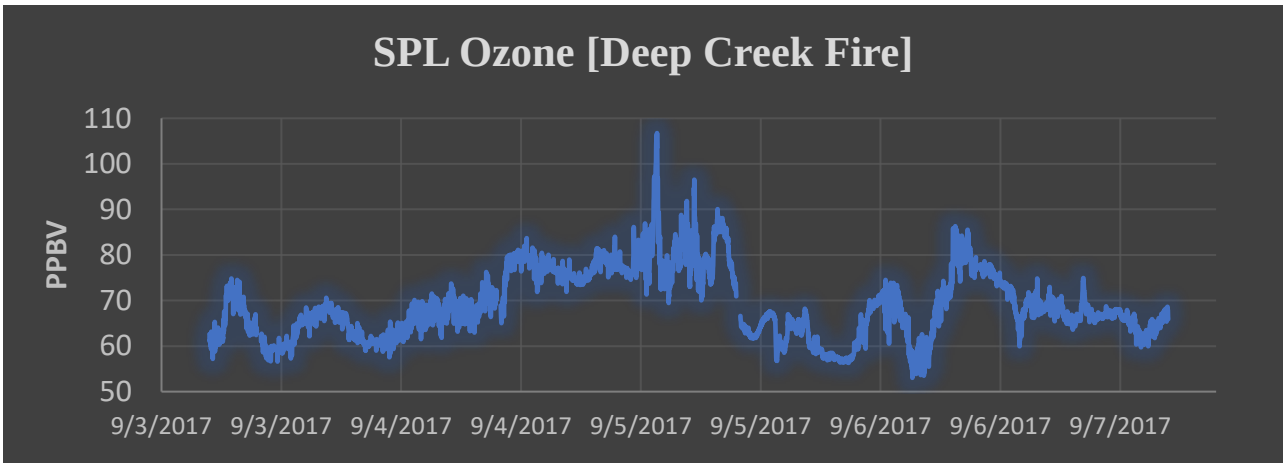

Figure 7: *Ozone concentrations at SPL. The fire was reported on September 4th near Deep Creek, Colorado and resulted in extreme ozone concentrations on September 5th. Note that baseline ozone for SPL was calculated at 42.79 ppbv, and the EPA ozone standard is 70 ppbv. Time shown is in MST.*

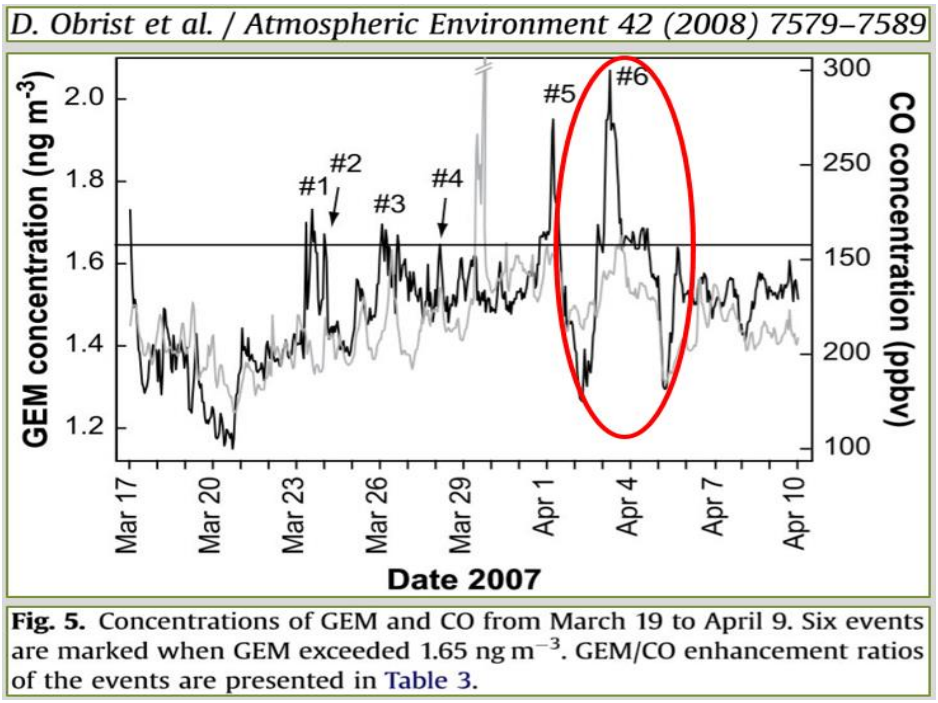

Figure 8: *Taken directly from Obrist et al. The red ring was drawn on to highlight the GEM concentrations which relate to the Ozone graph in figure 9.*

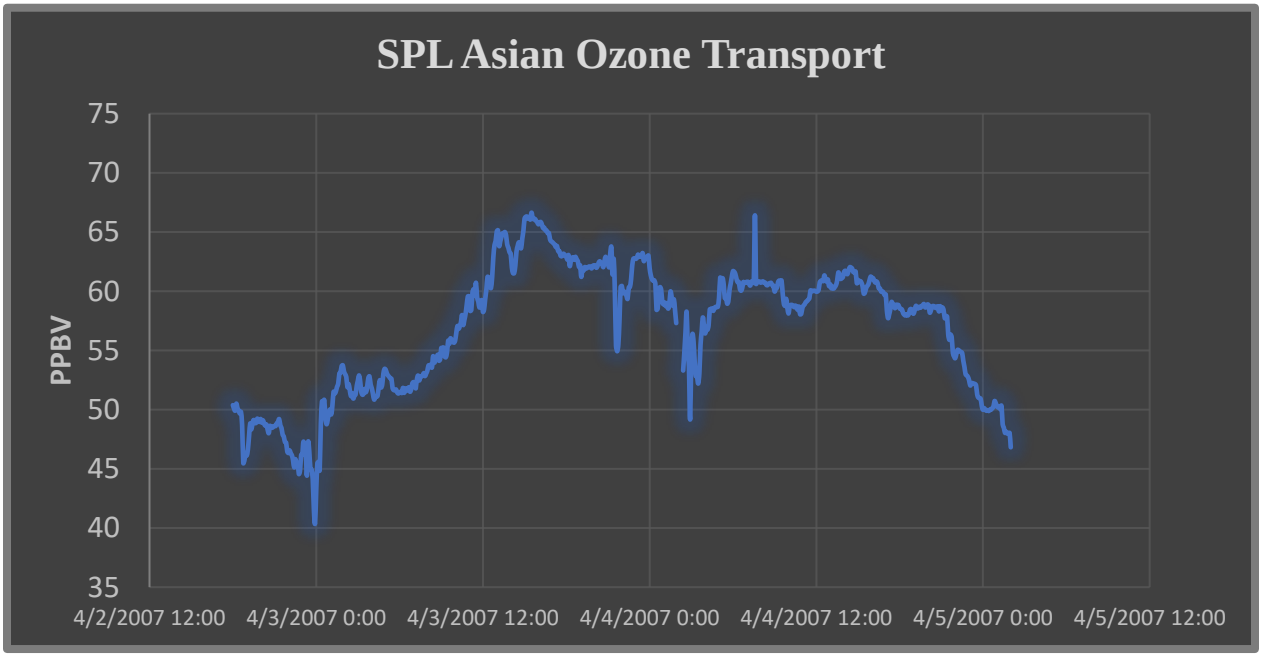

Figure 9: *Ozone spike directly correlated with Asian Transport. A diurnal increase in ozone is part of the initial rise, however, ozone stays elevated through the night of the 4th. 65 ppbv is well above baseline ozone. Time shown is in MST.*

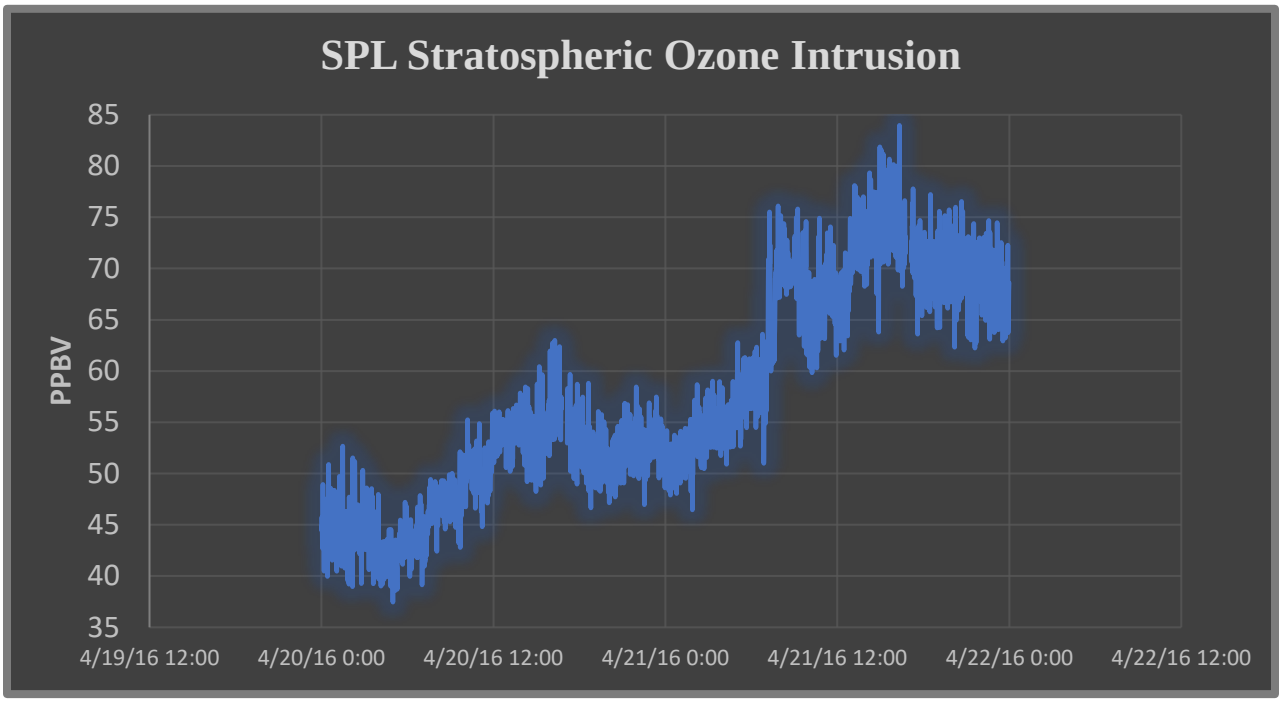

Figure 10: *Again, a part of the initial rise in ozone concentration is connected to normal diurnal cycles. We do note however that ozone during the morning of the 21st is about 10 ppbv higher than the morning of the 20th. Ozone raises rapidly throughout the day on the 21st due to stratospheric intrusion. Time shown is in MST.*

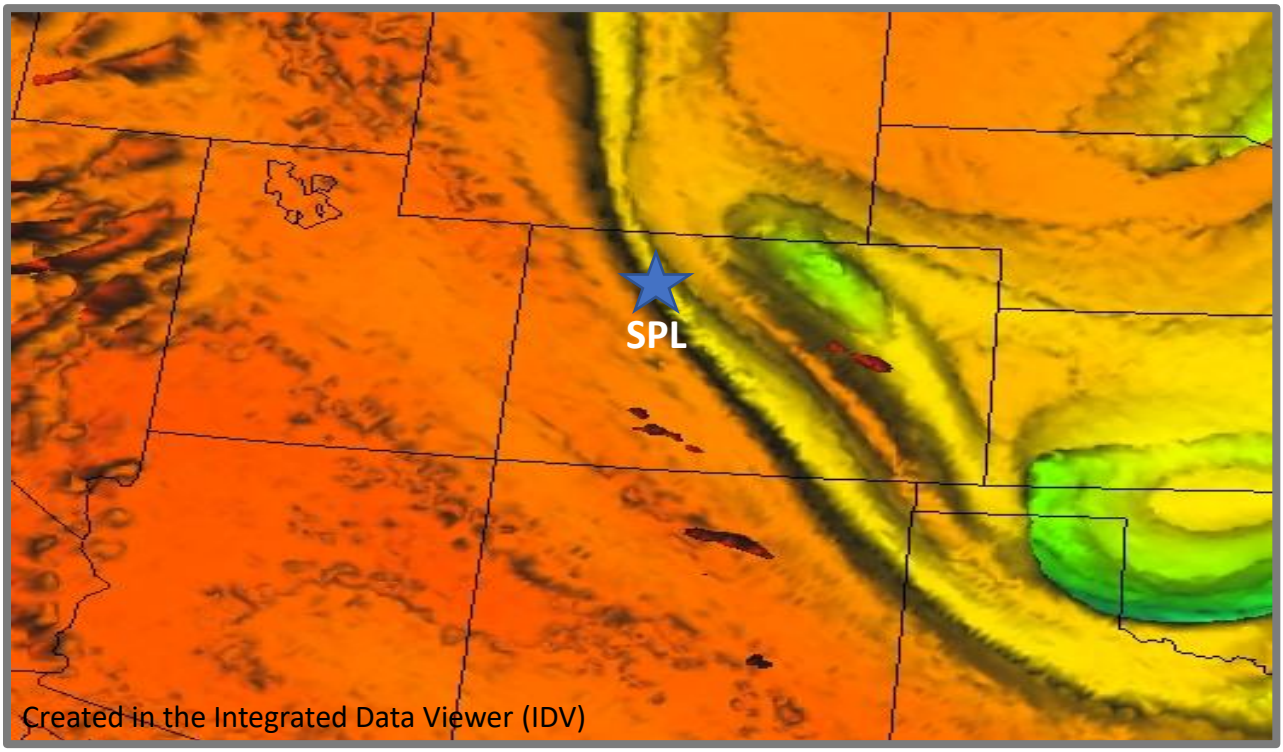

Figure 11: *This image depicts the height of the dynamic tropopause at 10:00 AM MST on April 21st 2016. Cooler colors represent lower heights. This event was not a tropospheric fold and yet ozone concentrations still increased by approximately 20 ppbv.*

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