Ozone and Aerosol concentrations during March 2010 Controlled Burns Near Storm Peak Lab (SPL), CO

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ABSTRACT

On 30 March 2010, aerosols from controlled burns of diseased Aspen trees reached Storm Peak Lab (SPL) on Mt. Werner, CO. Aerosols from fires have been shown to be highly absorbing, and thus induce a warming of the atmosphere. The total concentration of large aerosols was compared to concentrations of ozone, temperatures, and wind direction during the period from 28 March – 1 April 2010. Aerosol concentrations were correlated with ozone increases, likely due to diurnal variations in sunlight availability and/or corresponding erosion of the boundary layer, allowing pollution transport up to high altitudes. Tropospheric ozone has many negative effects, including greenhouse warming, decreased ecosystem productivity, and deterioration of lungs. One period of increased ozone occurred during the night from 0200 to 0500 LT 1 April 2010, indicating influence from decreased temperatures or advection of pollutants. Aerosol and ozone concentrations were compared to diffuse irradiance of multiple wavelengths; all wavelengths had similar trends and the fire-produced aerosols limited irradiance at all wavelengths.

1. Motivation

1.1 March 2010 CO Fires and Fire-Produced Aerosols

There were multiple fires burned between 28 March and 1 April 2010, but aerosols from the fires only reached SPL between 13-14 UTC and1600-1630 UTC on 30 March 2010 (Personal Communication, Claus Moberg, 27 April 2010). Fires in Northern-Hemisphere forests have been found to significantly contribute light-absorbing aerosols (Stohl et al., 2006). These light-absorbing aerosols are often black-carbon soot particles and induce positive radiating forcing which enhances global warming (Jacobson, 2002; Ramanathan et al., 2005) Not only do these larger particles absorb and re-emit large amounts of sunlight, their large size often decreases forward scattering efficiency (Marley et al., 2009). Additional aerosols and other pollution may have arrived at SPL from the city of Steamboat Springs, 5.2 miles west of SPL, and from nearby power plants: Stage Coach Power House, 13.5 miles south of SPL, and Xcel Energy 21.6 miles west of SPL, during the time period studied.

1.2 Chemical Tropospheric Ozone Production and Decay

The major source of tropospheric ozone is the conversion of NO_2 to O_3 through peroxy radicals, produced by hydrocarbons. Important molecules that play a role in these reactions are emitted by decomposition of organic materials, live plant processes, (Allen, 2002), automobiles, gasoline vapors, fossil fuel power plants, refineries, and certain other industries ("Tropospheric ozone," 2010). Other sources of tropospheric ozone include small amounts of stratospheric ozone mixed down in relation with large synoptic features, and lightning, (Allen, 2002).

The production of O_3 through reaction of NO_2 and light (eqn. 1) is normally equilibrated by the consumption of O_3 to produce NO_2 again (eqn. 2).

$$NO_2 + h\nu \rightarrow NO + O_3 \text{ (eqn. 1)}$$
$$NO + O_3 \rightarrow NO_2 \text{ (eqn. 2)}$$

This balance is disturbed and O_3 is net-produced, however, with the introduction of peroxy radicals (HO_2 (eqn. 3), RO_2 (eqn. 4)), as depicted in Figure 1. First, the OH radical is produced by photolysis of O_3 by shorter-wavelength energy not absorbed in the upper atmosphere. The OH radical oxidizes hydrocarbons to produce peroxy radicals and carbonyl compounds (aldehydes and ketones) which undergo further oxidation and recycle the OH radical (Walcek and Yuan, 1995, Plummer, 2003)

$$NO + HO_2 \rightarrow NO_2 + OH\cdot \text{ (eqn. 3)}$$
$$NO + RO_2\cdot \rightarrow NO_2 + RO\cdot \text{ (eqn. 4)}$$

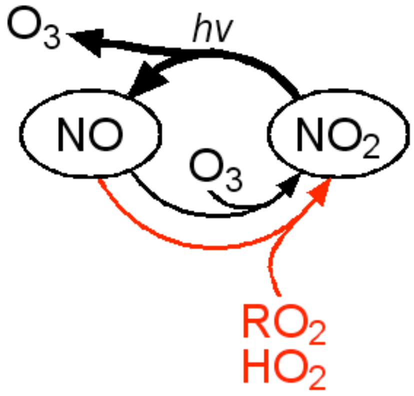

FIG. 1. The O_3-production-favored reaction through the addition of peroxy radicals. From Plummer, 2003.

Although the above reaction is the most prevalent, NOx has a fairly short life of 6 hours in lower troposphere (several days in upper troposphere), is variant spatially, and relies on a fairly equal NOx:VOC ratio. Other processes also contribute to ozone production in the troposphere; the oxidation of CO, alkanes (such as methane which has a photochemical life of 10 years and is uniform in atmos), other nitrogen species, and methyl chloroform (lifetime of 5-6 years), all contribute to ozone production (Plummer, 2003). Some have found that the lifetime of some of ozone's precursors in the troposphere are sufficiently long that they can produce ozone hundreds or even thousands of miles away before further chemical reactions transform ozone into oxygen and other chemicals (Allen, 2002).

1.3 Temperature and Background Effects on Tropospheric Ozone

Temperature plays a complicated role in the production of ozone. It decomposes some nitrogen species (Plummer, 2003), however, it also increases reaction rates in many of the chemical reactions. Some have found that elevated isoprene concentrations may be a large factor contributing to higher oxidant levels on hotter days (Walcek and Yuan, 1995) A ten-year study shows no statistically significant relation between ozone and temperature below 10 km, although differences here were small, and ozone and temperature were inversely related from 10-25 km, where differences were relatively large. (Hsu, 2007). The most important temperature effect is probably that it is an indicator of increased sunlight. Downward UVB has been shown to significantly exceed clear-sky values especially when snow cover and broken cloud allow multiple reflection (Wetzel and Borys, 2000). Fractional cloudiness may be the most important, yet uncertain, factor in tropospheric ozone production (Walcek and Yuan, 1995)

Another significant source of tropospheric ozone is background ozone, advected internationally. Asia has the fastest-growing ozone precursor emissions (van der et al., 2008) and for much of the springtime, East Asian pollution is exported eastwards towards western North America

(Stohl et al. 2002). The increase in springtime background ozone mixing ratio in the future may hinder the USA's compliance with its ozone air quality standard (Cooper et al., 2010) of 120 ppb in one hour or 75 ppb over eight hours ("National Ambient," 2010).

1.4 Tropospheric Ozone Effects on the Atmospheric and Health

Since 1900 the amount of ozone near the earth's surface has more than doubled ("Tropospheric ozone," 2010), thus it is important to understand its effects. Although ozone breaks down most pollutants and some greenhouse gases, high concentrations of tropospheric ozone are toxic, and have a detrimental effect on human health, ecosystem productivity, and global warming (IPCC, 2007)

Ozone has been linked to tissue decay, the promotion of scar tissue formation, and cell damage by oxidation. It can impair an athlete's performance, create more frequent attacks for individuals with asthma, cause eye irritation, chest pain, coughing, nausea, headaches and chest congestion and discomfort. It can worsen heart disease, bronchitis, and emphysema. It is a particular threat to people who exercise outdoors or who already have respiratory problems. High concentrations of ozone can additionally slow down photosynthesis and plant growth. It causes plants to close their stomata, the cells on the underside of the plant that allow carbon dioxide and water to diffuse into the plant tissue ("Tropospheric ozone," 2010). Finally, ozone absorbs both solar and infrared radiation, contributing to significant warming, however it has been found to be 10 % less effective at absorbing in the planetary boundary layer (PBL) than in the upper troposphere (Chalita, 1996).

Overall, aerosols and ozone have complicated roles in the atmosphere, and the purpose of this study is to investigate whether they relate to each other during forest fires in CO, and to attempt to identify some of the factors influencing their concentrations and the factors their concentrations influence.

2. Methods

Multiple atmospheric variables were measured from March 28 – April 1, 2010 at Storm Peak Laboratory (SPL) on Mount Werner near Steamboat Springs, CO. Ozone was measured with a Dasibi Ozone Monitor. Aerosols greater than 2.5 um in diameter were measured by a TSI 3010 Aerosol condensation nuclei monitor. Wind speed and direction were measured by a de-iced anemometer and de-iced wind vane, respectively. Temperatures were measured by a temperature sensor. ("Storm Peak", 2010).

The above variables were compared in order to attempt to discern whether the fires that reached SPL on 30 March 2010 influenced ozone at the lab. Downward diffuse solar radiation was additionally measured in order to investigate aerosol influence on different solar radiation bands. Visible and UV irradiances were measured by a Yankee Multi-Filter Rotating Shadowband Radiometer and Yankee UV Multi-Filter Rotating Shadowband Radiometer, respectively ("Storm Peak", 2010). Although Langley calibrations are more accurate, Lamp calibrations were utilized as Langley calibrations were not available for all wavelengths or days involved in the study. Although not pictured, Langley-calibrated data was compared to Lamp-calibrated; magnitudes varied slightly for some wavelengths, but the overall trends were nearly identical.

Finally, HYSPLIT model trajectories were retrieved from the Air Resources Laboratory. All of the default values were used except the following: the latitude and longitude were set to that of SPL, at 40.46 and -106.74, respectively, trajectories were run backward, start time was set to 2 April

2010 00 UTC, duration was set to 48 hours, new trajectories were set to start every 12 hours, the maximum number of trajectories was set to 10, and the release height was set to 5m above ground level.

3. Results and Discussion

Aerosols greater than 2.5-um in diameter measured at SPL are shown in Figure 2. Observations showed that it was sunny 28 March 2010, mostly sunny 29 March 2010, partly sunny 30 March through 31 March early evening, and was cloudy and snowed 31 March evening through 1 April. Photochemical activation of aerosols and/or the erosion of the boundary layer is seen from 28-30 March as a diurnal spike in concentrations peaks near 13–14 Local Time (LT, MDT). Data was only taken every 11 hours and 57 minutes, thus three minutes of zero data is seen every 12 hours. Data from the evening of 30 March 2010 was not available. The suppressed concentrations from the evening of 31 March through 1 April 2010 show evidence that precipitation scavenged aerosol particles.

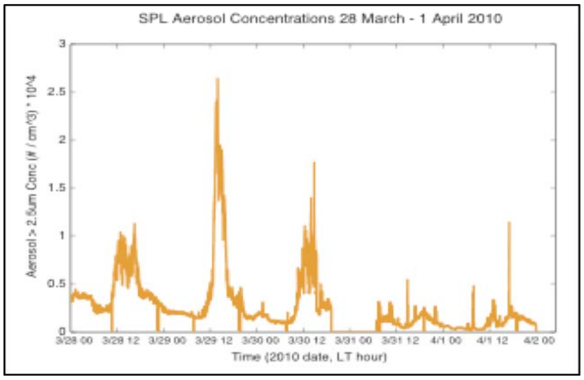

FIG. 2. Aerosol concentrations measured at SPL 28 March-1 April 2010.

Figure 3 displays the HYSPLIT trajectories. It is notable that particles released before the evening of 31 March 2010 remained at similar altitudes and relative humidities as SPL, indicating a dramatic shift in parcel origin and initial state for trajectories arriving after this time. Also, it is clear that parcels arriving between 12 UTC 28 March and 12 UTC 30 March had a particularly local origin, from the west to SSW of SPL, where the main power plants are located (googlemaps).

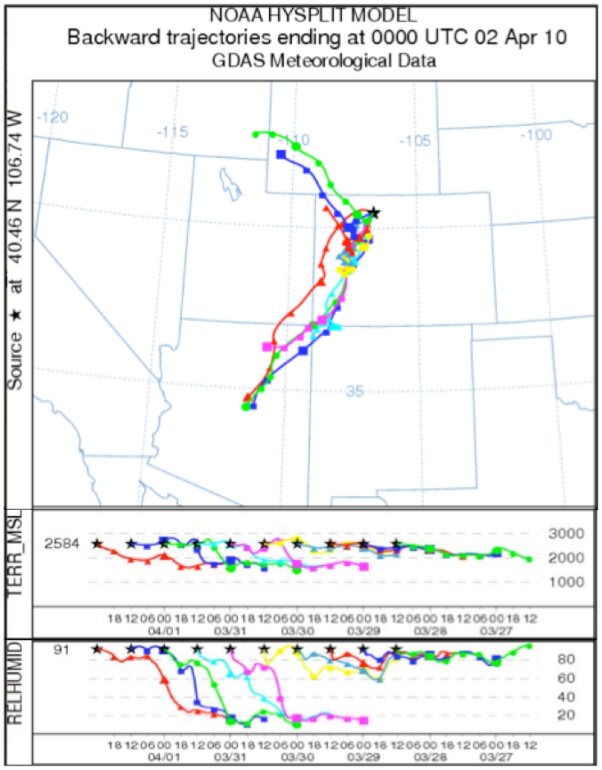

FIG. 3. HYSPLIT model particle released from SPL. The start time was 2 April 2010 00 UTC and trajectories were released backward in time from 5 m above ground level every 12 hours for 48 hours. Also pictured are the height above mean sea level pressure and the relative humidities of the trajectories.

Figure 4 depicts ozone concentrations, temperatures, and wind directions from 28 March to 1 April 2010. Although temperatures and ozone are related throughout the time period, it is difficult to say why; increased temperatures increase reaction rates for most reactions involving the creation and degradation of tropospheric ozone. Additionally, temperature trends are relative to downward solar energy and tropospheric ozone production is catalyzed by sunlight. Finally, ozone concentrations remain fairly steady throughout the period while temperatures increase and then decrease significantly.

Throughout the time period, ozone increases at the greatest rates approximately six times, from 0620 to 1330 LT 28 March, 1200 to 1330 and 1700 to 1800 LT 29 March, LT, 0530 to 0930 LT 31 March, 0200 to 0230, and 0730 to 0900 1 April 2010. Most of these increases are associated with increased sunlight, however, the increase from 0200 to 0230 LT (and corresponding ozone pulse from 0230 to 0500) on 1 April clearly occurred during night hours. This increase is associated with a large change in wind direction, from southeasterly to west-northwesterly, possibly indicating a transfer of pollutants from previously-mixed-up emissions from the nearby power plants. Another source of pollution at night could be international, as SPL is above the PBL at this time. Ozone maxima are correlated to the aerosol spikes from Figure 2, however, this is likely due to the availability of sunlight and/or erosion of the boundary layer causing pollution to mix upward.

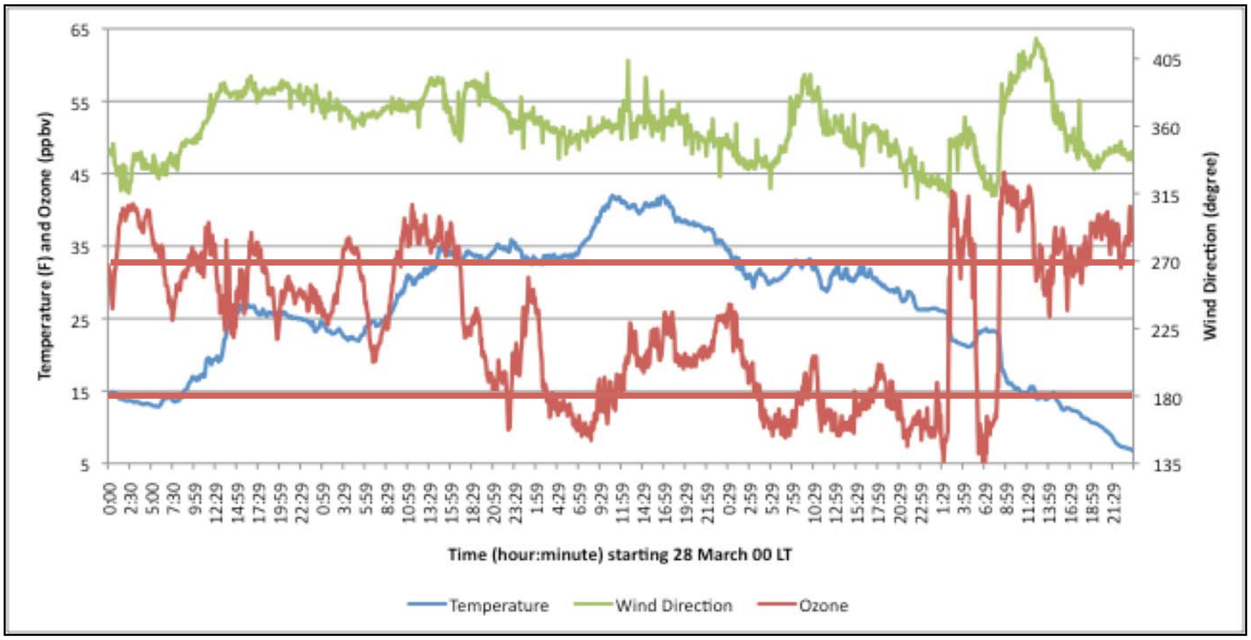

FIG. 4. Temperature, ozone, and wind direction at SPL from 28 March – 1 April 2010. The two bold red lines indicate 180-degree (southerly) and 270-degree (westerly) wind directions.

Figure 5 displays the diffuse UV radiation for all wavelengths measured by the shadowband radiometer from 28 March to 1 April 2010. It is clear that diffuse UV irradiance is slightly larger during mostly sunny and partly cloudy days, as patchy sunlight increases multiple reflectance when land albedo is high. Another noticeable trend is the large decrease in downward UV radiation at about 1300 LT 30 March. The decrease is highly correlated with the detection of fire-related aerosols at SPL. This indicates that those aerosols were mostly absorbing, and thus composed mainly of carbonaceous soot. Additionally, variations in ozone do not seem to have a large impact on irradiance, except maybe for 1 April. This is inconclusive as cloud cover was also much stronger on this day. Finally, although diffuse irradiance increases with wavelength, there are no noticeable variations in trend between the different bands measured.

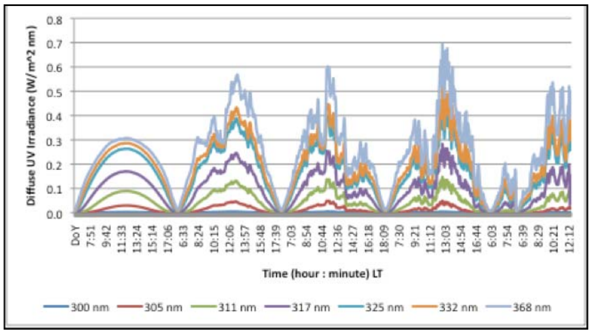

FIG. 5. Diffuse UV irradiance for all wavelengths measured by the shadowband radiometer at SPL from 28 March to 1 April, 2010.

Figure 6 depicts a similar picture to Figure 5, except it displays the visible wavelengths measured at SPL. All of the findings from the UV trends apply, except that the peak radiance is measured from the 665-nm channel, consistent with the peak in the solar spectrum. The influence of the fire-related aerosols, however, is more difficult to discern from regular sunlight variations. The increase from partly-sunny and partly-cloudy days is much more distinct, likely indicating that visible wavelengths are more influenced by multiple reflectance.

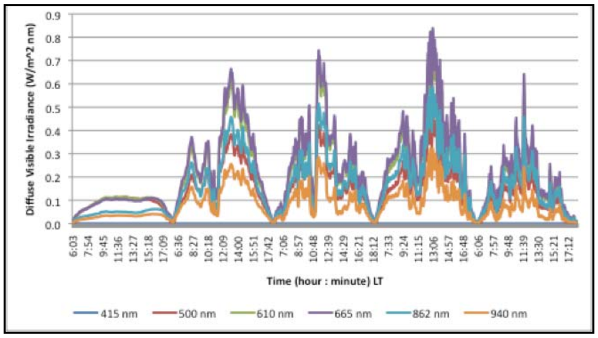

FIG. 6. As for Figure 5, except for visible irradiance.

4. Conclusions

Large spikes in aerosol concentrations at SPL occur during the sunny-to-partly-cloudy days, likely associated with photolytic activation and/or erosion of the boundary layer. Particle trajectories indicate that particles arriving at SPL between 12 UTC 28 March and 12 UTC 30 March 2010 are of mainly local south-to-southwesterly origin, indicating the aerosol spikes may be associated with local polluting power plants.

It is evident that ozone concentrations have a corresponding diurnal maximum, however some increases in ozone cannot be simply explained by the solar zenith angle. Variations in ozone may be due to varying temperatures that affect reaction rates, varying amounts of irradiance due to cloudiness, and variations in pollution advection. The pulse of ozone from 0200 to 0500 LT on 1 April 2010, however, is not induced by sunlight (it is the middle of the night). There is a slight decrease in temperatures and a large variation in wind direction; the pulse may have been created by an increase of southerly and westerly winds associated with advection of pollution from either previously-mixed-up emissions from nearby power plants or from far-away, possibly international sources.

The 30 March 2010 fires that reached the lab from 1300-1400 LT and 1600-1640 LT do not appear to have a significant influence on ozone concentrations, but do decrease incoming diffuse UV radiation. This implies that the fire-related aerosols had the greatest optical properties of any aerosols throughout the period, and that they were largely absorbing, likely soot particles. Different wavelengths of downward diffuse solar radiation all have similar trends, thus aerosol fluxes could not be differentiated through specific wavelengths.

The results of this study could be complemented by future work. As the data becomes available, columnar ozone and aerosol optical depth measured at SPL could be compared in order to resolve the levels or depth of each factor. This information might also be retrieved from satellite products.

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