Comments for Consideration by the CASAC Ozone Review Panel on the Reconsideration of the 2008 NAAQS for its teleconference deliberations on February 18, 2011

Estimating Policy-Relevant Background Ozone Concentrations

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*The views expressed herein are exclusively the author's and do not represent any official policy of NOAA

February 7, 2011

1. Introduction

The EPA's proposed range for the primary standard is based on a combination of (1) human laboratory experimental results and (2) risk assessments that incorporate the assumptions of the modeled estimates for policy-relevant background (PRB) O_3 daily afternoon concentrations. Based on modeling results, the EPA (2010) notes that PRB O_3 concentrations are generally predicted to be in the range of 15 to 35 ppb in the afternoon and are generally lower under conditions conducive to man-made O_3 episodes. Correctly estimating PRB is very important because characterizing PRB O_3 levels that are too low can result in 1) overestimated human health risk predictions (e.g., human laboratory experimental results compared to a control of 0 ppb) and 2) optimistic policy expectations of the levels to which hourly average O_3 concentrations can be lowered as a result of emission reduction requirements.

2. Estimating policy-relevant background ozone concentrations

2.1 The influence of PRB concentrations at Trinidad Head (CA)

EPA's Policy-Relevant Background (PRB) estimates for risk analysis used a maximum monthly diurnal concentration mostly in the 0.015 to 0.025 ppm range (US EPA, 2007). Unlike the predicted PRB concentrations, actual diurnal concentrations experienced during PRB conditions range from approximately 0.030 ppm to 0.050 ppm (Lefohn, 2007). Measured hourly average PRB O_3 concentrations ≥ 0.050 ppm frequently occurred with maximum hourly average concentrations up to 0.065 ppm (Lefohn, 2007). The predicted PRB concentrations using models are below observed PRB levels that influence the low-elevation monitoring site at Trinidad Head (CA) (Oltmans and Lefohn, 2005; Lefohn, 2007; Oltmans et al., 2008; Oltmans et al., 2010). Figure 1 shows the location of Trinidad Head, which is a small town of about 400 people located on the California's north coast. A location in southern California (Channel Islands National Park) demonstrates many of the characteristics during the spring as Trinidad Head in terms of air flow patterns and O_3 amounts suggesting that background levels of O_3 entering southern California from the Pacific Ocean are similar to those in northern California.

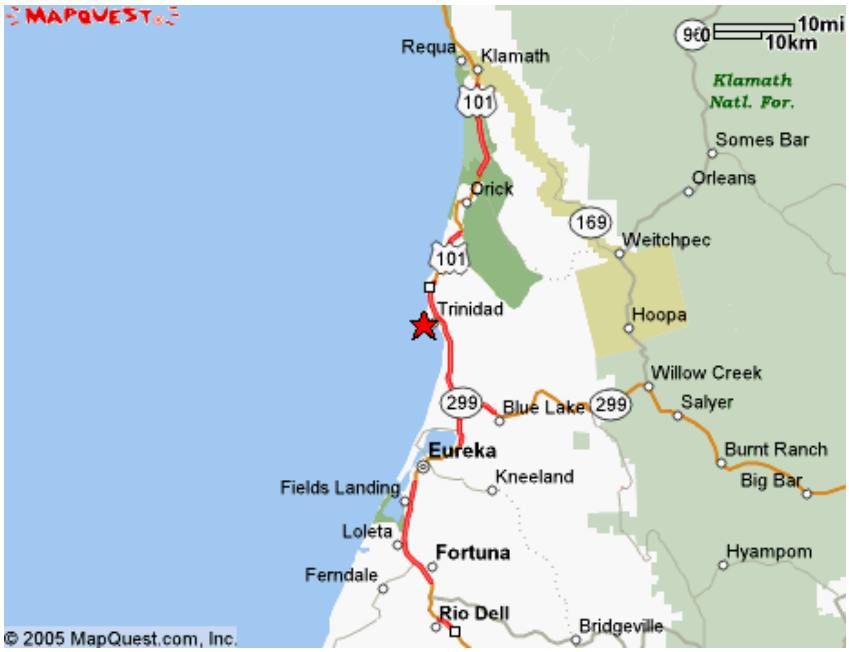

Figure 1. The location of Trinidad Head, California. Source: MapQuest.com, Inc.

Table 1 summarizes the number of hourly average concentrations ≥ 0.05 ppm for the nine-year period 2002- 2010 for the months of March – July. In 2003, the first complete year of data collection, the maximum hourly average concentration of 64 ppb was measured in April, which was the month that experienced the most frequent occurrences of hourly average concentrations ≥ 0.05 ppm (188). In 2008, the maximum hourly average concentration of 61 ppb occurred during the month of April with 120 occurrences of hourly average concentrations ≥ 0.05 ppm. In 2009, the maximum hourly average concentration of 65 ppb occurred during the month of April. April 2009 experienced the most frequent occurrences during the year of hourly average concentrations ≥ 0.05 ppm (73) for the year. In 2010, the latest period of record, the maximum hourly average concentration of 58 ppb was observed in March and April and the most frequent occurrences of hourly average concentrations ≥0.05 ppm (51) occurred in April. As shown in Table 1, numerous occurrences of hourly average concentrations ≥ 0.05 ppm are exhibited the springtime .

Table 1. Summary of the number of hourly average concentrations ≥ 0.05 ppm and maximum hourly average value (in parentheses) measured at Trinidad Head, California for the 9-year period, 2002 through 2010. Source: Modified from Oltmans and Lefohn (2005).

Year	March	April	May	June	July
2002	No Data	36 (54 ppb)	18 (53 ppb)	0 (41 ppb)	0 (45 ppb)
2003	23 (52 ppb)	188 (64 ppb)	95 (57 ppb)	13 (54 ppb)	0 (41 ppb)
2004	38 (62 ppb)	30 (54 ppb)	3 (50 ppb)	2 (50 ppb)	0 (38 ppb)
2005	58 (55 ppb)	72 (56 ppb)	6 (52 ppb)	0 (46 ppb)	0 (39 ppb)
2006	37 (55 ppb)	56 (60 ppb)	43 (64 ppb)	0 (47 ppb)	0 (35 ppb)
2007	21 (52 ppb)	46 (57 ppb)	30 (55 ppb)	0 (40 ppb)	0 (33 ppb)
2008	26 (53 ppb)	120 (61 ppb)	34 (56 ppb)	3 (52 ppb)	0 (42 ppb)
2009	18 (54 ppb)	73 (65 ppb)	11 (54 ppb)	0 (43 ppb)	0 (35 ppb)
2010	38 (58 ppb)	51 (58 ppb)	6 (52 ppb)	0 (42 ppb)	0 (32 ppb)

Figure 2 summarizes the vertical distribution of O_3 that was observed between August 1997 and July 2007 at Trinidad Head. The figure illustrates the variability of the O_3 concentrations as a function of elevation as well as period of the year. From the surface to 2 km, the mixing ratio nearly doubles with the steepest gradient between the surface and 1 km and during the summer months when surface values are lowest. At 2 km during all months, the average is ≥ 50 ppb. This suggests that there is a significant reservoir of O_3 just above the boundary layer at Trinidad Head that can be mixed down to the surface.

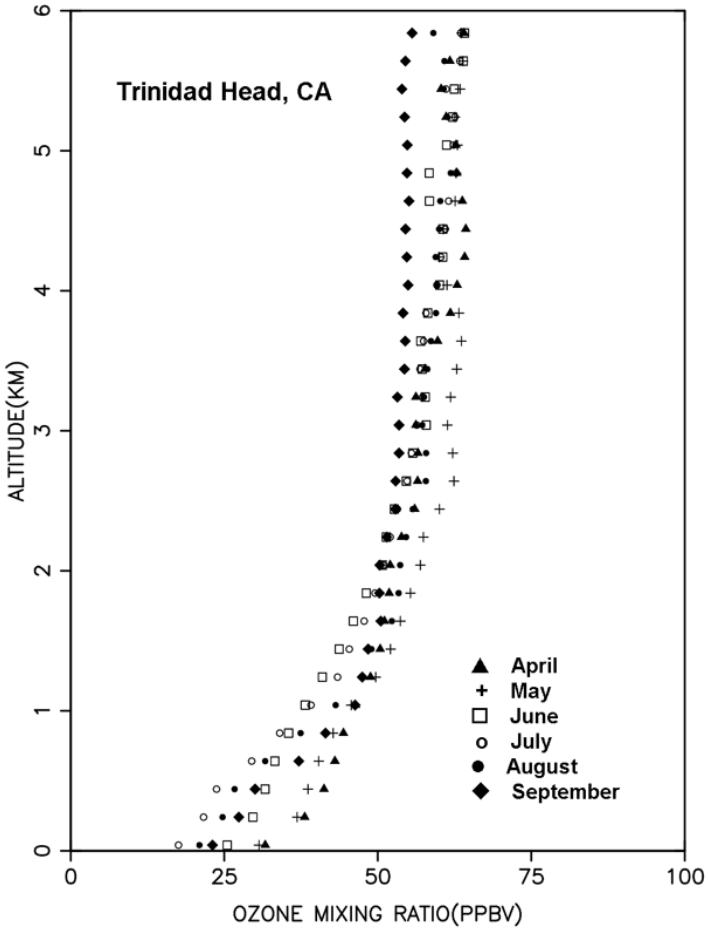

Figure 2. Average monthly ozonesonde profiles (1997-2007) of ozone mixing ratios (ppbv) at Trinidad Head, California in the lower troposphere for the 6 months of April to September. Source: Oltmans et al., 2008.

2.2 Long-range transport effects on PRB in the western US from Eurasian biomass burning

Eurasian emissions associated with biomass burning and their easterly transport contribute to O_3 concentrations at west coast O_3 monitoring sites under PRB conditions, as well as inland O_3 monitoring sites in Montana, Wyoming, and North Dakota (Oltmans et al., 2010). Published information indicates that biomass burning events in Eurasia are not infrequent. The effects of Eurasian biomass burning in producing O_3 enhancements in surface O_3 in the western US has been reported in the literature (Jaffe et al., 2004; Bertschi et al., 2004; Bertschi and Jaffe, 2005; Pfister et al., 2010; Oltmans et al., 2010). The year 2008 was one in which large Eurasian biomass burning occurred. Unusually high O_3 readings were recorded in April 2008 at surface O_3 monitoring sites from northern Alaska to northern California as well as inland monitoring sites in Montana, Wyoming, and North Dakota. At Denali National Park in central Alaska, an hourly average of 79 ppb was recorded during an 8-h period in which the 8-h average was over 75 ppb. At Trinidad Head, hourly O_3 readings were >50 ppb almost continuously for a 35-h period. At several sites in northern California, located to the east of Trinidad Head, numerous occurrences of O_3 readings exceeding 50 ppb were experienced during this period. As the biomass burning enhanced O_3 plume moved further into the interior of the US between 18-20 April through a northern tier of states (Montana, Wyoming, North Dakota), surface O_3 measurements at several monitoring sites appeared to have intercepted the plume (Oltmans et al., 2010). Trajectories from each site suggest that the enhancements observed during this period could have come from the burning region. The 8-h average O_3 enhancements were above the normal background concentrations observed at these monitoring sites (i.e., 45-55 ppb for Montana and North Dakota and 50-60 ppb for Wyoming). The 8-h daily maximum at Yellowstone on 19 April (69 ppb) suggests an enhancement during the period of suspected plume influence of 5-10 ppb above the

other relatively high values observed at this site. This is also about the amount of the perturbation seen at the other interior monitoring sites (Oltmans et al., 2010). At Trinidad Head in April 2008, the occurrences of hourly averaged O_3 concentrations ≥ 50 ppb were similar in magnitude to the number of events in April 2003, which over a 9-yr period experienced the highest occurrences of hourly average concentrations ≥ 50 ppb. Although a thorough study of 2003 was not undertaken, modeling of 2003 data found that biomass burning impacted the west coast of North America (Pfister et al., 2010) and may have been the cause of the elevated surface O_3 amounts at Trinidad Head in April 2003 as well (Oltmans et al., 2010).

Figure 3 illustrates the 3-year average of the fourth highest annual daily maximum 8-h average concentrations for four background O_3 monitoring sites for the 2008-2010 period that appear to have been influenced in April 2008 by a PRB component that was associated with the long-range transport of emissions from Eurasian biomass burning.

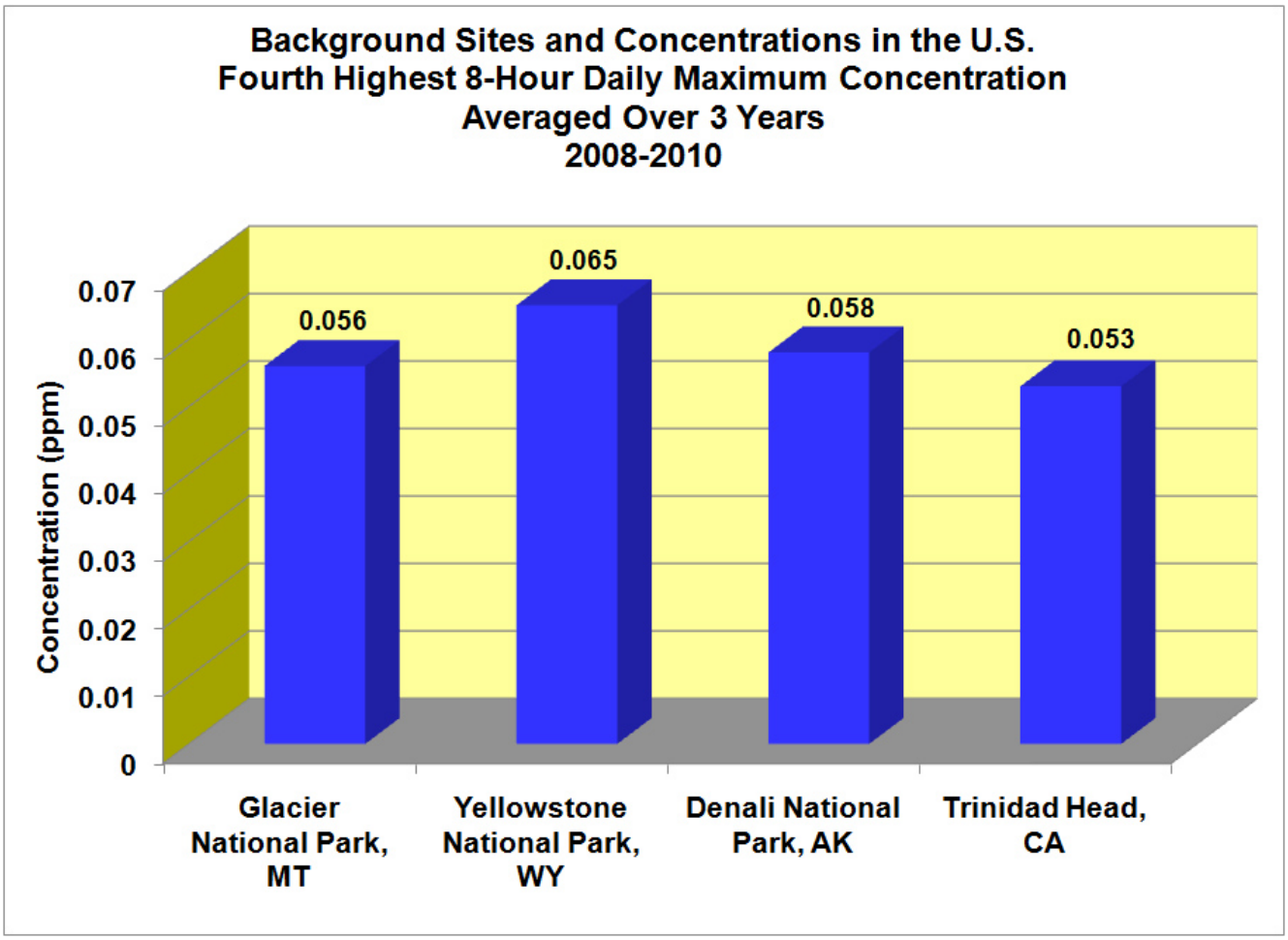

Figure 3. Four O_3 monitoring sites influenced by PRB long-range transport with their fourth highest 8-h daily maximum concentrations averaged over 3 years for 2008 to 2010. The concentrations are in units of ppm.

2.3 The importance of the stratosphere in influencing surface ozone concentrations

Natural processes, such as stratospheric-tropospheric exchange (STE) and biogenic emissions, contribute to the replenishment of PRB O_3 concentrations across the entire United States (U.S. EPA, 2006). Naturally occurring STE processes contribute to background O_3 concentrations at the surface at both high and low-elevation monitoring sites (e.g., Ludwig et al., 1977; Haagenson et al., 1981; Schuepbach et al., 1999; Stohl et al., 2000; Lefohn et al., 2001; Cooper et al., 2005; Hocking et al., 2007; Ordóńez et al., 2007; Langford et al., 2009). Hourly

average concentration ≥ 0.05 ppm in the springtime can be attributed at times to these natural processes (Lefohn et al., 2001; Cooper et al., 2005; Langford et al., 2009). Key to the importance of STE processes in replenishing PRB is the frequency of STE events. Indications of the importance of the frequency of STE events affecting lower tropospheric O_3 concentrations have been reported (Ordóńez et al., 2007). Reed (1955) and Danielsen (1968) used instrumented high-altitude aircraft measurements of radioactivity and O_3 to document the exchange of air and trace constituents from the stratosphere into the troposphere. Building upon this research methodology, Ludwig et al. (1977) also examined the behavior of a surrogate for stratospheric O_3 by characterizing the behavior of radioactive debris injected into the stratosphere during nuclear weapons testing in the 1960s. Using ^{90}Sr, Ludwig et al. (1977) concluded that a significant stratospheric contribution to ground level O_3 concentrations in the middle latitudes of the Northern Hemisphere, with a maximum occurring in the springtime, was evident at both high- and low-elevation surface-monitoring sites.

At some monitoring sites, the stratospheric contribution to surface O_3 can be significant and can lead to exceedances of the 0.075 ppm 2008 NAAQS O_3 standard. During 1999, STE contributed to one of the 4 highest daily 8-h maxima at one or more surface sites in the metropolitan Denver area on at least 4 occasions during the March–October O_3 season (Langford et al., 2009). In addition to the Denver area, STE makes an important contribution in the springtime to the replenishment of O_3 concentrations at Yellowstone National Park in Wyoming. The range of the 3-year average of the 4th highest 8-h daily maximum values at Yellowstone National Park is from 63 to 67 ppb. For the period 1997-2008, 75% of the top four daily maximum 8-h average concentrations occurred during the springtime. The EPA has indicated that Yellowstone National Park would violate the primary O_3 standard for the 3-year 2006-2008

period if the level were set at 0.065 ppm. Natural processes, such as stratospheric-tropospheric exchange (STE) events and long-range transport from Eurasian biomass burning events contribute to the enhanced concentrations observed at Yellowstone National Park (Oltmans et al., 2010).

2.4 Background contribution at the surface in the western US is larger than current models indicate

Jaffe (2010) have examined O_3 data from 11 rural CASTNET sites in the western US for the period 1995-2009. The 11 surface sites show a similar seasonal cycle and generally a good correlation in the deseasonalized monthly means, indicating that there are large scale influences on O_3 that operate across the entire western US. These sites also show a good correlation between site elevation and annual mean O_3, indicating a significant contribution from the free troposphere. Jaffe (2010) examined the number of exceedance days for each site, defined as a day when the Maximum Daily 8-h Average (MDA8) exceeded a threshold value (i.e., 65 ppb, 70 ppb, or 75 ppb). Over this time period, more than half of these sites exceeded an MDA8 threshold of 70 ppb at least 4 times per year, and all sites exceeded a threshold value of 65 ppb at least 4 times per year. The transition to lower threshold values increased substantially the number of exceedance days, especially during spring, reflecting the fact that background O_3 peaks during spring. The author next examined the correlation between surface O_3 and free tropospheric O_3 in the same region, as measured by routine balloon launches from Boulder, CO. Using O_3 measured by the balloon sensor in the range of 3-6 km above sea level, Jaffe (2010) reported statistically significant correlations between surface and free tropospheric O_3 in spring and summer months using both monthly means, daily MDA8 values, and the number of surface exceedance days. The author suggested that during spring this correlation reflects variations in

the flux of O_3 transport from the free troposphere to the surface. In summer, free tropospheric and surface concentrations of O_3 and the number of exceedance days were all significantly correlated with emissions from biomass burning in the western US. Jaffe (2010) noted that the correlation between surface and free tropospheric O_3 was strongest at lower exceedance thresholds, which suggested according to the author that a greater importance of background O_3 at the lower thresholds. Jaffe (2010) concluded that the large interannual variations and the correlation between surface and free tropospheric O_3 observed in his study during both spring and summer indicate that background O_3 varies strongly from year-to-year and that the background contribution at the surface in the western US is larger than current models indicate.

2.5 The importance of stratospheric-tropospheric exchange processes in replenishing ozone in the free troposphere and its influence on surface ozone concentrations ≥ 50 ppb across the US

In our most current research, our team has used the Lagrangian Analysis Tool (LAGRANTO) trajectory model to identify specific days when stratosphere-to-troposphere transport was optimal to elevate surface O_3 levels (Manuscript in Preparation). The statistically significant coincidences between the number of days with a daily maximum hourly average O_3 concentration ≥ 50 ppb and stratosphere-to-troposphere transport to surface (STT-S) were quantified. In evaluating several monitoring sites across the US, we found that the high-elevation site at Yellowstone National Park in Wyoming exhibited the most statistically significant coincidences (i.e., more than 19 days a month) during the spring and summer for hourly average O_3 concentrations ≥ 50 ppb for the 3 years studied. At this site, the maximum hourly springtime average O_3 concentrations were usually in the 60-70 ppb range. The maximum daily 8-h average concentrations mostly ranged from 50 to 65 ppb. Figure 4 illustrates the frequency of the

stratosphere-to-troposphere transport events to the surface at Yellowstone NP for the 2006-2008 period.

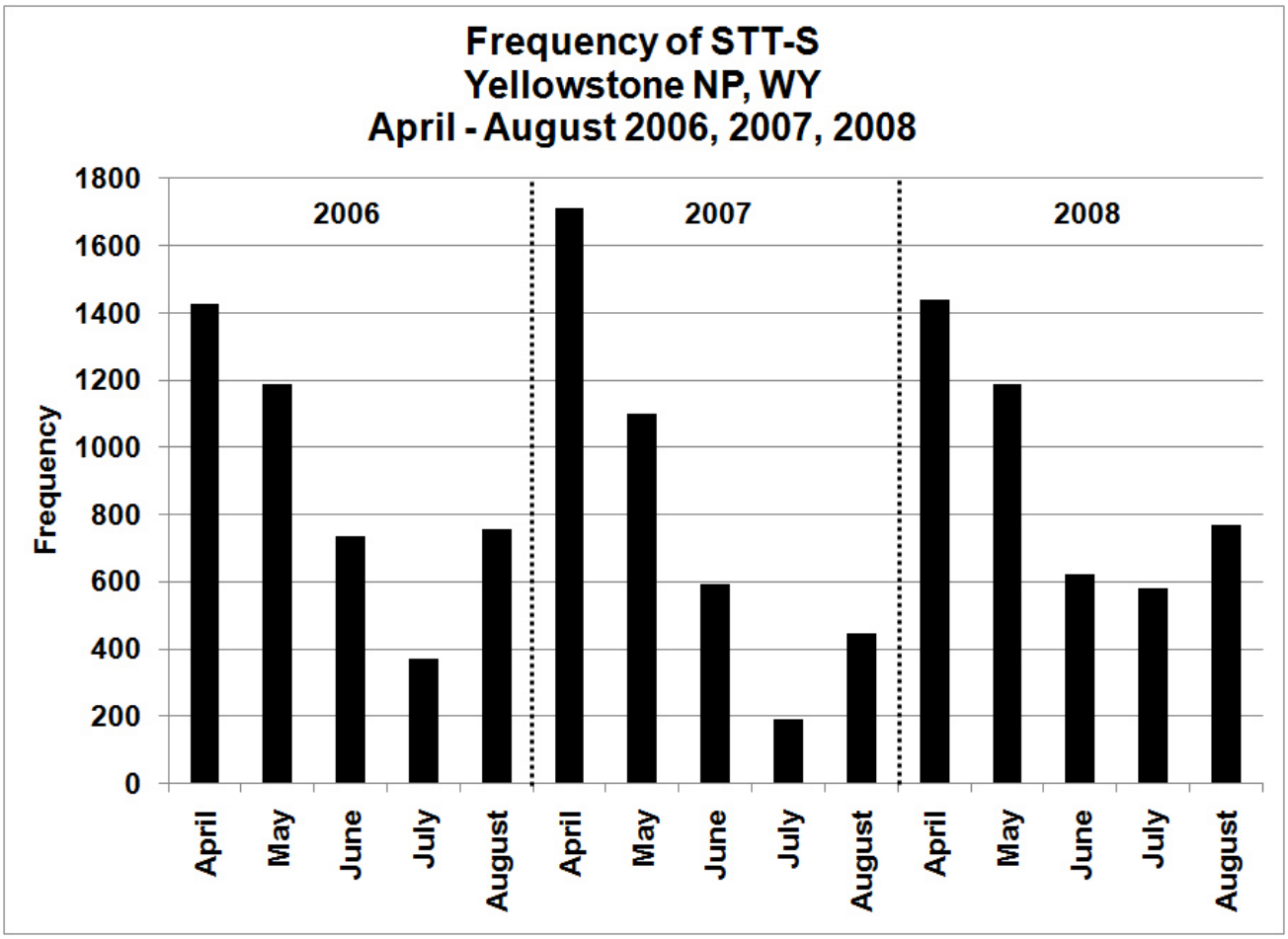

Figure 4. Frequency of stratosphere-to-troposphere transport to surface (STT-S) at Yellowstone National Park in Wyoming for April – August 2006, 2007, and 2008. Source: Manuscript in Preparation.

In addition to our applying the LAGRANTO trajectory model to the high-elevation Yellowstone National Park site in Wyoming, we investigated statistically significant coincidences at low-elevation monitoring sites across the US. At many of these monitoring sites, there was a preference for O_3 enhancements to be coincident with stratosphere-to-troposphere transport to the surface during the springtime, although summertime occurrences were sometimes observed. When enhancements occurred, the daily maximum hourly average

concentrations were mostly in the 50-65 ppb range and the daily maximum 8-h average concentrations were usually in the 50-62 ppb range.

3. Conclusion

Correctly estimating PRB is very important because inadequate characterization can lead to levels that are too low, resulting in 1) overestimated human health risk predictions and 2) optimistic policy expectations of the levels to which hourly average O_3 concentrations can be lowered as a result of emission reduction requirements. Observations indicate that O_3 concentrations measured under conditions representative of PRB are significantly higher than the EPA's modeled range of concentrations.

The frequent number of hourly average O_3 concentrations ≥ 50 ppb at sites influenced by PRB conditions indicates that the human health risk results may have been overestimated. Measured hourly average PRB O_3 concentrations ≥ 0.050 ppm frequently occurred with maximum hourly average concentrations up to 0.065 ppm at a low-elevation monitoring site at Trinidad Head (CA). A location in southern California (Channel Islands National Park) demonstrates many of the characteristics during the spring as Trinidad Head in terms of air flow patterns and O_3 amounts suggesting that background levels of O_3 entering southern California from the Pacific Ocean are similar to those in northern California. Eurasian emissions associated with biomass burning and their easterly transport enhance O_3 concentrations at west coast O_3 monitoring sites under PRB conditions, as well as inland O_3 monitoring sites in Montana, Wyoming, and North Dakota.

Natural processes, such as stratospheric-tropospheric exchange (STE) and biogenic emissions, contribute to the replenishment of PRB O_3 concentrations across the entire United

States. Naturally occurring STE processes contribute to background O_3 concentrations at the surface at both high and low-elevation monitoring sites. Large interannual variations and the correlation between surface and free tropospheric O_3 observed during both spring and summer indicate that background O_3 varies strongly from year-to-year and that the background contribution at the surface in the western US is larger than current models indicate. Statistically significant coincidences between the number of days with a daily maximum hourly average O_3 concentration ≥ 50 ppb and stratosphere-to-troposphere transport to surface indicates that high-elevation and low-elevation monitoring sites exhibit the most statistically significant coincidences during the springtime and in some cases during the summertime. At the high-elevation monitoring site at Yellowstone National Park in Wyoming, where the greatest frequency of stratosphere-to-troposphere transport to the surface (STT-S) events occurred, the maximum hourly springtime average O_3 concentrations were usually in the 60-70 ppb range; the maximum daily 8-h average concentrations mostly ranged from 50 to 65 ppb. Statistically significant coincidences at low-elevation monitoring sites across the US showed a preference for O_3 enhancements to be coincident with stratosphere-to-troposphere transport to the surface mostly during the springtime. When enhancements occurred, the daily maximum hourly average concentrations were mostly in the 50-65 ppb range and the daily maximum 8-h average concentrations were usually in the 50-62 ppb range. The replenishment of PRB O_3 concentrations across the US by stratospheric-tropospheric exchange is an important process. Stratosphere-to-troposphere transport to the surface events are frequent during the springtime and sometimes during the summertime and influence hourly average concentrations ≥ 50 ppb.

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