ATTACHMENT B

CONTRIBUTION OF TRANSBOUNDARY ANTHROPOGENIC BACKGROUND OZONE TO THE AUGUST 10, 2012 EXCEEDANCE AT THE FRESNO DRUMMOND AVE. MONITOR

1. INTRODUCTION

Under the federal Clean Air Act (CAA) Section 179B, a nonattainment area showing that it would have attained a federal air quality standard but for emissions emanating from outside of the United States are not subject to the sanctions and penalties associated with failing to attain the standard, including section 185 nonattainment penalties, since states and local air agencies lack regulatory authority over air pollutant emissions in other countries. The United States Environmental Protection Agency (EPA) has approved four 179B demonstrations for cases regarding emissions impacts from Mexico on bordering air districts in the U.S.[1] Despite the longer transport distances, there is significant evidence supporting a similar 179B determination for the impact of transpacific sources on the San Joaquin Valley.

Anthropogenic emissions are increasing in Asia and have been shown to influence ozone levels in the United States and Canada. The rapid increase in Asian energy production has resulted in a corresponding annual growth in transport of Asian emissions of ozone precursors (including peroxyacetylnitrate (PAN), CO, and methane) to North America, with the largest documented ozone impacts seen in the West.

Meanwhile, emissions control measures implemented in California (as well as other parts of the United States) have been achieving significant emissions reductions, with corresponding air quality improvements. As the fraction of ground level ozone caused by local emissions declines, air districts must come to grips with a proportional, per unit decline in the ability of subsequent local control measures to reduce ambient concentrations. Concurrently, EPA has been reviewing and periodically lowering its federal ozone standards (National Ambient Air Quality Standards, or NAAQS), now considering a standard between 60 and 70 parts per billion (ppb) to be finalized in 2015. With lower local emissions, lower EPA standards, and higher impacts of emissions transported from Asia, the role of international air pollutant emissions has become increasingly concerning for areas like the San Joaquin Valley.

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[1] See:

- 77 FR 58962 (9/25/12) for Nogales, Arizona for PM10 at http://www.gpo.gov/fdsys/pkg/FR-2012-09-25/pdf/2012-23118.pdf
- 69 FR 32450 (6/10/04) for El Paso, Texas for 1-hour ozone at http://www.gpo.gov/fdsys/pkg/FR-2004-06-10/pdf/04-13175.pdf
- 68 FR 39457 (7/2/03) for El Paso, Texas for CO at http://www.gpo.gov/fdsys/pkg/FR-2003-07-02/pdf/03-16579.pdf
- 66 FR 53106 (10/19/01) for Imperial, California for PM10 at http://www.gpo.gov/fdsys/pkg/FR-2001-10-19/pdf/01-26406.pdf

This document will review evidence of the impact of transboundary anthropogenic ozone (TAO) (defined here as the fraction of total transboundary ozone that has been generated by human activity from transpacific sources, Asia in particular)[2] on surface ozone levels in the United States. These TAO impacts will have even greater significance as regions like the San Joaquin Valley (Valley) address EPA's 2008 and 2015 8-hour ozone standards. However, these impacts are of more immediate significance for the Valley for the 1-hour ozone standard.

Utilizing peer-reviewed published research as well as recent research sponsored by the San Joaquin Valley Air Pollution Control District (District), this document shows that:

- Transboundary Ozone is influencing ozone concentrations at Chews Ridge and other California coastal areas.
- Chews Ridge is a legitimate window on air flows impacting the Valley.
- In the Valley, transboundary ozone is influencing ozone concentrations above the boundary layer, and there is exchange across the boundary layer.
- Therefore, the Valley is being impacted by TAO, resulting in the exceedance of the 1 hr. ozone standard by 3 ppbv over the standard at the Fresno Drummond Ave. monitor on August 10, 2012.

2. BASELINE GEOPHYSICAL EVIDENCE FOR THE HYPOTHESIS THAT THE AUG. 10, 2012 EXCEEDANCE WOULD NOT HAVE OCCURRED BUT FOR THE CONTRIBUTION OF TRANSBOUNDARY ANTHROPOGENIC OZONE (TAO)

Subsequent sections of the document will focus on evidence regarding (1) the general upward trend in TAO, (2) supportive transboundary ozone case studies from peer-reviewed scientific literature, (3) evidence of transboundary ozone gathered in the summer of 2012 by the District and ARB, and (4) an ozone budget analysis for August 10, 2012 that provides a quantitative estimate of the TAO contribution to Drummond Ave observations. However, for this body of evidence to support the District's larger weight of evidence case, a threshold case must be made that the geophysical conditions (meteorology in particular) in the period immediately prior to and including Aug. 10, 2012 must have been conducive for the entrainment of transboundary ozone containing a significant fraction of TAO into the SJV boundary layer. Based on the supporting evidence presented in this section and buttressed by a larger body of scientific evidence presented in subsequent sections, conditions were in fact conducive to enhanced ground level concentrations from TAO in Fresno on Aug. 10, 2012.

[2] In distinction with TAO, transboundary ozone is defined in this document as ozone produced from biogenic, geogenic, stratospheric, or anthropogenic sources that is transported to the US west coast of the United States from transpacific, offshore sources.

2.1 Meteorological Conditions and Air Mass Back Trajectories Were Conducive to Surface Impacts from Transboundary Ozone in Fresno on Aug. 10, 2012

A strong high pressure pattern developed over the region on August 6 and continued through the middle of August. This high pressure caused strong stability, hot surface temperatures, thermally driven wind flow, and subsidence of transboundary air masses from the free troposphere. These conditions facilitated entrainment of ozone and ozone precursors into the San Joaquin Valley boundary layer, resulting in increased 1-hour ozone concentrations at ground level. Table B-1 shows the increase in Fresno's maximum temperature during the days preceding the 1-hr. ozone exceedance. The daily maximum temperature at Fresno was above 105 degrees Fahrenheit before and after the event, indicating that the strong high pressure system was established and constant throughout this time period. The daily progression of ozone concentrations at Fresno area monitors from Aug. 5-14, 2012 are shown in Table B-2. While average temperatures were consistently high through much of this period, average maximum hourly ozone concentrations for Fresno area monitors were more variable in comparison, with peak average hourly concentrations registered on Aug. 10, 2012.

Table B-1: Fresno Daily Maximum Temperature (in Fahrenheit at the Fresno Air Terminal)

August, 2012	5	6	7	8	9	10	11	12	13	14
Fresno	99	101	102	103	107	109	111	105	110	109

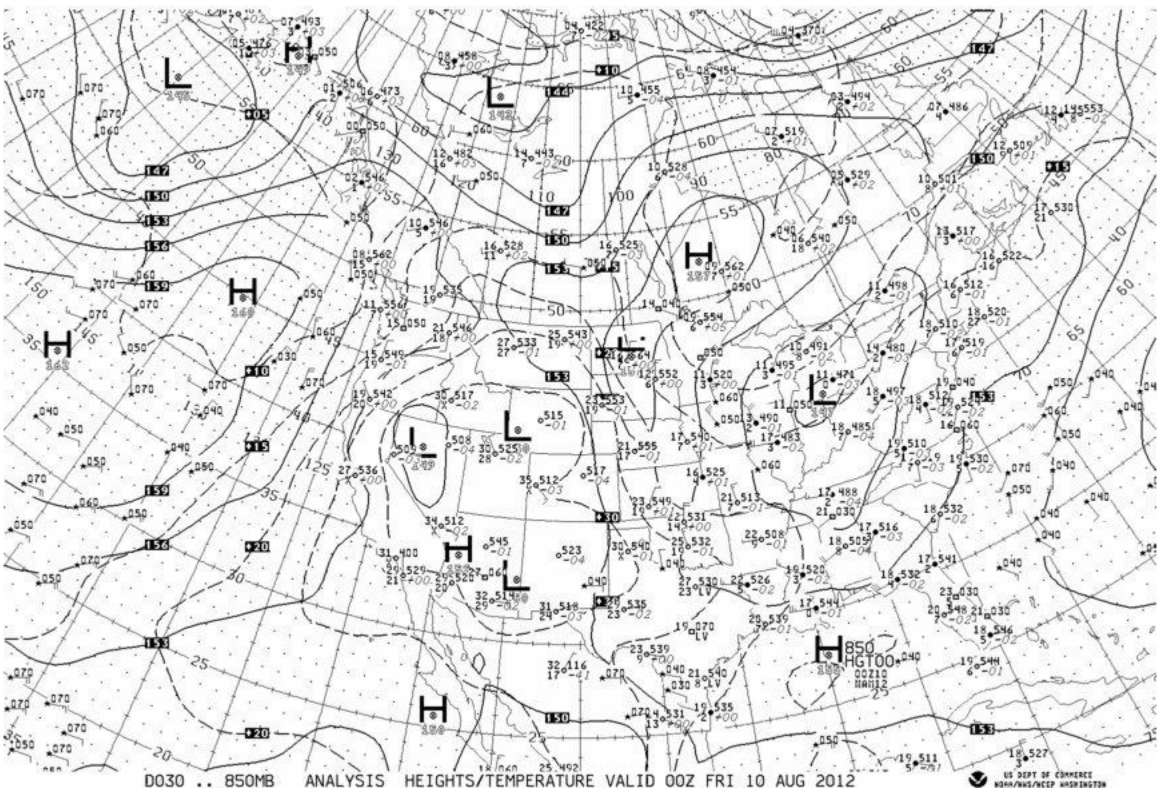
Table B-2: Maximum 1-Hour Ozone (ppb) by Site by Day in Fresno County

Date	Fresno-SSP*	Fresno-Garland	Clovis	Fresno-Drummond	Parlier	Avg.
8/5/2012	61	70.4	68	72	76.6	69.6
8/6/2012	62	75.1	87	72	90.6	77.3
8/7/2012	63	81.3	85	79	87.5	79.2
8/8/2012	77	98.6	98	96	99.7	93.7
8/9/2012	88	111.2	119	108	98	104.8
8/10/2012	100	117.9	115	127	117.7	115.5
8/11/2012	102	118.5	114	124	102	112.1
8/12/2012	92	93.7	104	89	77.6	91.3
8/13/2012	79	87.3	107	85	82	88.1
8/14/2012	72	79	85	83	87	81.2

* Sierra Sky Park

The upper level charts on Aug. 9 and 10 showed a strong high over the Four Corners Region, with a ridge extending westward into southern California. The 850 mb pressure chart for 5 pm Aug. 9 is shown in **Figure B-1**. The morning surface chart on August 10 indicated strong highs positioned over the Four Corners Region and 750 nautical miles west of Seattle. A thermal low near Las Vegas had an inverted trough curving northwestward to another thermal low near Modesto. This high pressure pattern caused thermally driven wind flow and a very strong surface based morning inversion in the Valley. The morning aircraft sounding from Fresno depicted a strong inversion of 15 degrees Fahrenheit from the surface up to 607 m (2,000 ft.). The lower air profiler from Visalia that afternoon showed light westerly wind flow up to 914 m (3,000 ft.) becoming northwesterly then northerly above.

Figure B-1. 850 mb pressure chart for 5 pm, Aug. 9, 2012.
Source: National Oceanic and Atmospheric Administration (NOAA)



The ozone rose and wind rose data from the Fresno Drummond monitor on Aug. 10 are depicted in **Figures B-2** and **B-3**, respectively. The pollution rose indicates that the 1-hr. ozone concentration of 127 parts per billion (ppb) came from the west-southwesterly quadrant (depicted in beige). The wind rose indicates that the predominant wind flow pattern during morning hours was from the east to southeast, then rotating to the southwest to northwest during the afternoon hours. This diurnally driven wind flow pattern is typical in the Valley during strong high pressure stagnation events. Equally significant, the very high surface temperatures on Aug. 10 have demonstrated in past events to generate very strong thermal lifting from the Valley floor and especially from adjoining slopes of the Sierra and Coast ranges. This thermal lifting is a key mechanism for driving boundary layer entrainment of ozone from the free troposphere (shown in **Figure B-16** below).

Figure B-2. Fresno-Drummond Ozone Rose for August 10, 2012.
Source: SJVAPCD

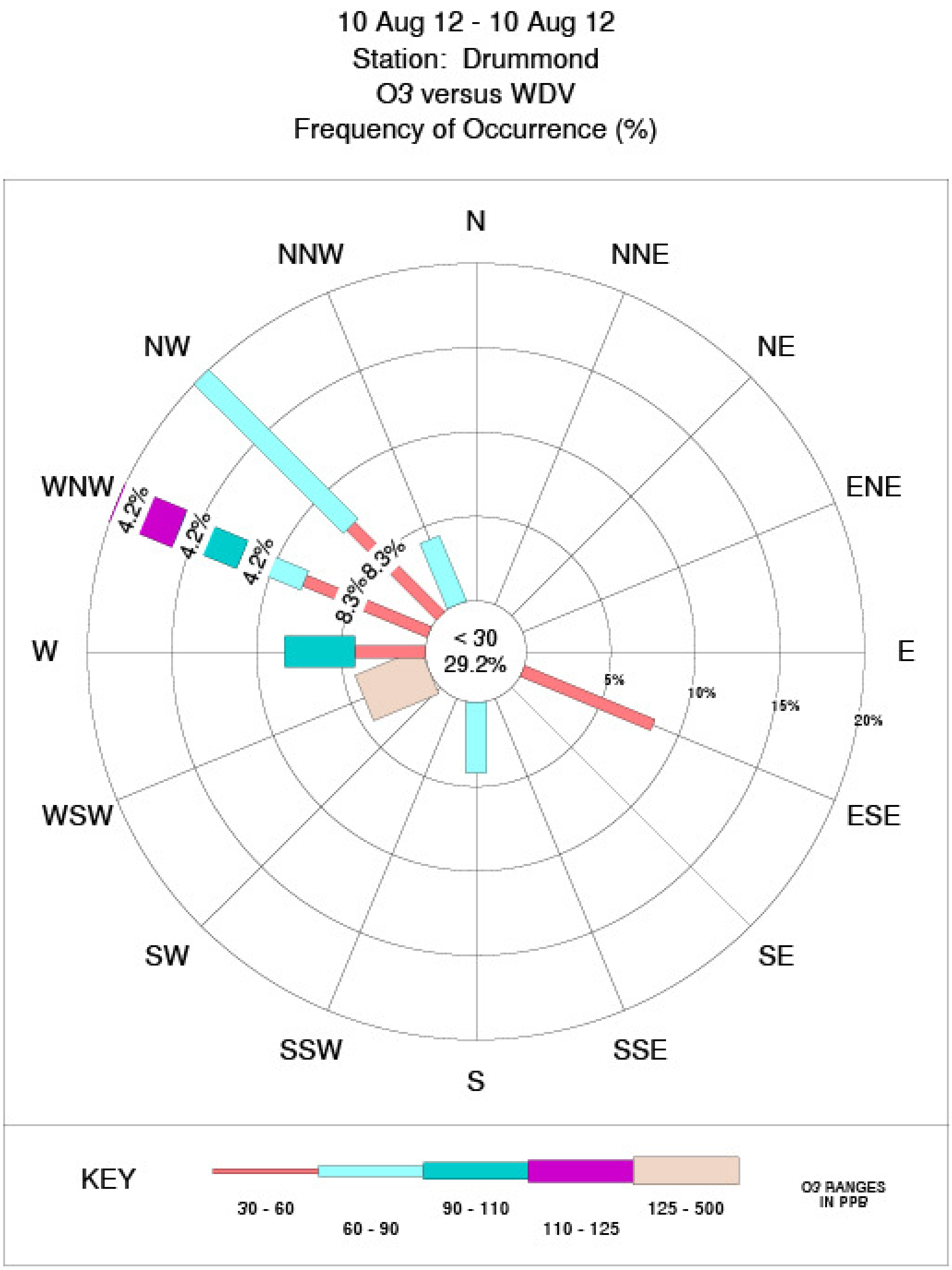
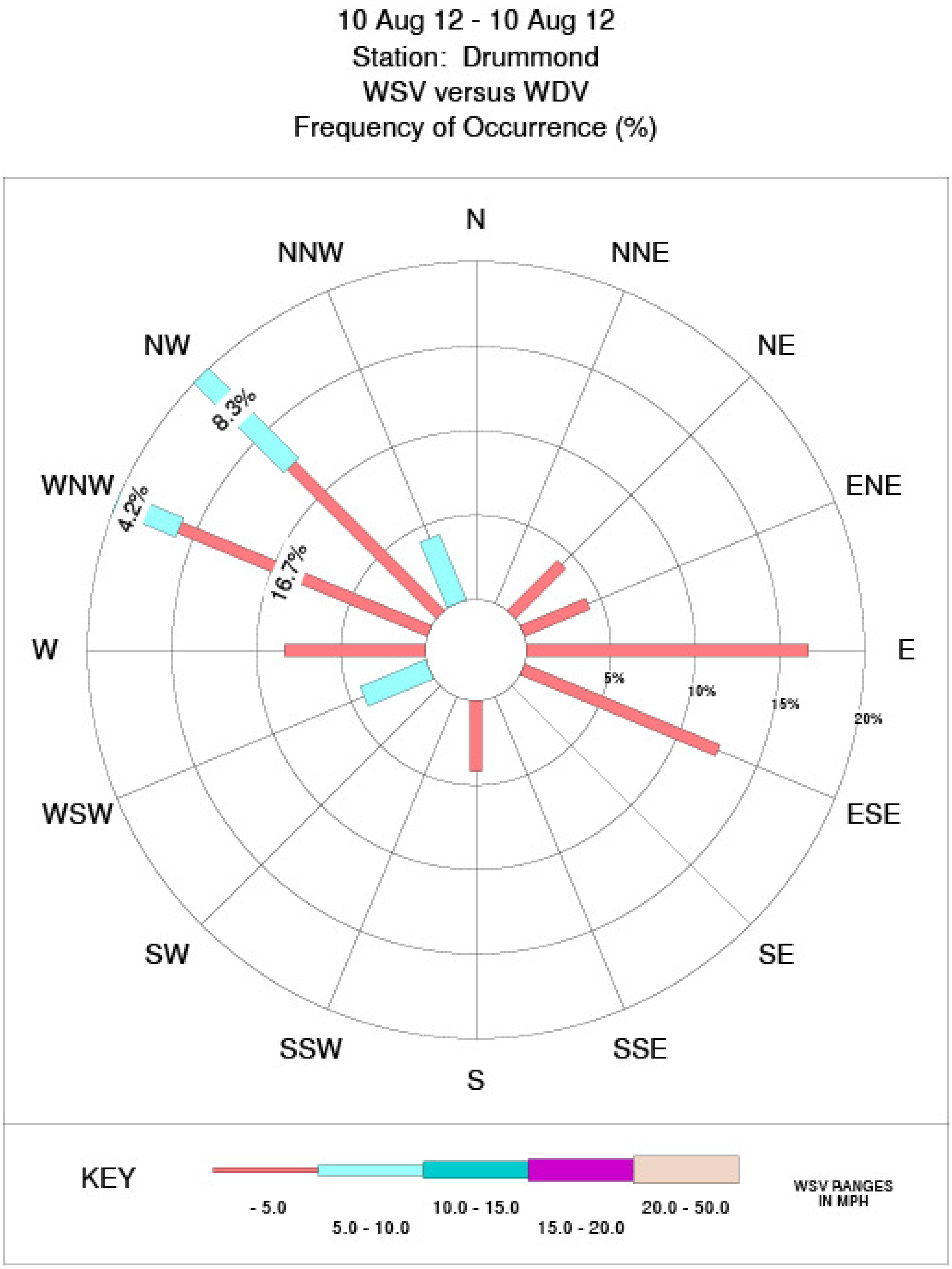
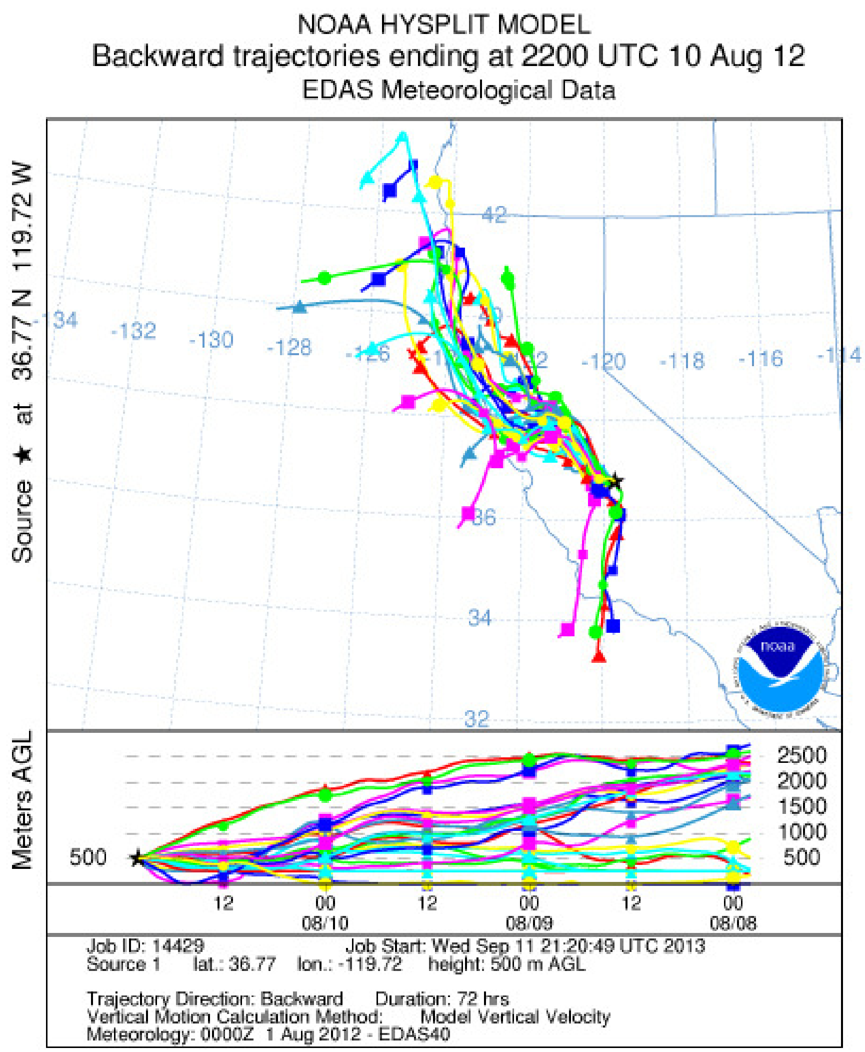


Figure B-3. Fresno-Drummond Wind Rose for August 10, 2012.
Source: SJVAPCD



Corroborative evidence for TAO entrainment in the SJV during the regional high pressure environment up to and including Aug. 10 is found in the 72 hr. back trajectories from Fresno as shown below in **Figure B-4**. The predominant pathways indicate northwesterly flows from offshore the northern California coast in combination with air mass subsidence from the 2500—1500 m layer of the free troposphere. The net effect of these meteorological conditions was to facilitate entrainment of ozone and ozone precursors such as PAN into the Valley boundary layer, with subsequent enhancement of 1 hr. ground level concentrations. The predominant spatial pattern of the back trajectories, combined with evidence of subsidence from the free troposphere into the boundary layer of the central SJV, is consistent with the findings of the Intercontinental Chemical Transport Experiment Ozonesonde Network Study (IONS-2010) campaign of May-June, 2010 that is discussed in more detail in Case Study #2 below.[3]

Figure B-4. 72 hr. back trajectories from Fresno for 5 pm, Aug. 10, 2012
Source: NOAA



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[3] Cooper, O. R., et al. (2011) Measurement of western U.S. baseline ozone from the surface to the tropopause and assessment of downwind impact regions. *J. Geophys. Res.*, 116, D00V03, doi:10.1029/2011JD016095.

2.2 Data from Remote Monitoring at Chews Ridge, Ozonesonde Launches, and Satellite Retrievals Provide Further Evidence of Surface Impacts from Transboundary Ozone at Fresno on Aug. 10, 2012

As detailed further below, key sources of empirical data in support of transboundary ozone entrainment in the SJV on Aug. 10, 2012 include the hourly ozone concentrations and related met conditions as measured in 2012 and 2013 with instruments housed at the Oliver Observing Station on Chews Ridge, an astronomical observatory operated by the Monterey Institute for Research in Astronomy.[4] The Chews Ridge field station is operated by UC Davis with District funding (see **Figure B-22** below). Located 168 km west/southwest of Fresno at 1,525 m in the Santa Maria range, the Chews Ridge station is well-positioned to measure transboundary ozone in the lower free troposphere that is entering California airspace via transpacific air masses. Because the Chews Ridge station is located only 30 km due east of the Pt. Sur sonde launch location used in the IONS-2010 campaign discussed below, ozone concentrations in westerly flows measured at 1,500 m by the IONS-2010 ozonesondes launched from Pt. Sur are highly representative of concurrent concentrations found at Chews Ridge (see location of Pt. Sur in **Figure B-18** below).[5]

Furthermore, as shown in **Figure B-5**, the correlation coefficient between ozone concentrations measured by ozonesondes launched from Pt. Reyes on the California coast north of San Francisco and from Pt. Sur during the IONS-2010 campaign at the 1,500 m altitude is quite high, approximately 0.84. This high correlation between ozonesondes launched from Pt. Reyes, near the midpoint of the predominant northern coastal entry point for the lower tropospheric air masses depicted in **Figure B-4**, and Pt. Sur, located on the coast 30 km east of the Chews Ridge field station, provides the empirical basis for using Chews Ridge ozone concentrations at 1,525 m as a surrogate for northern California flows at the same lower tropospheric altitude in the vicinity of Pt. Reyes.

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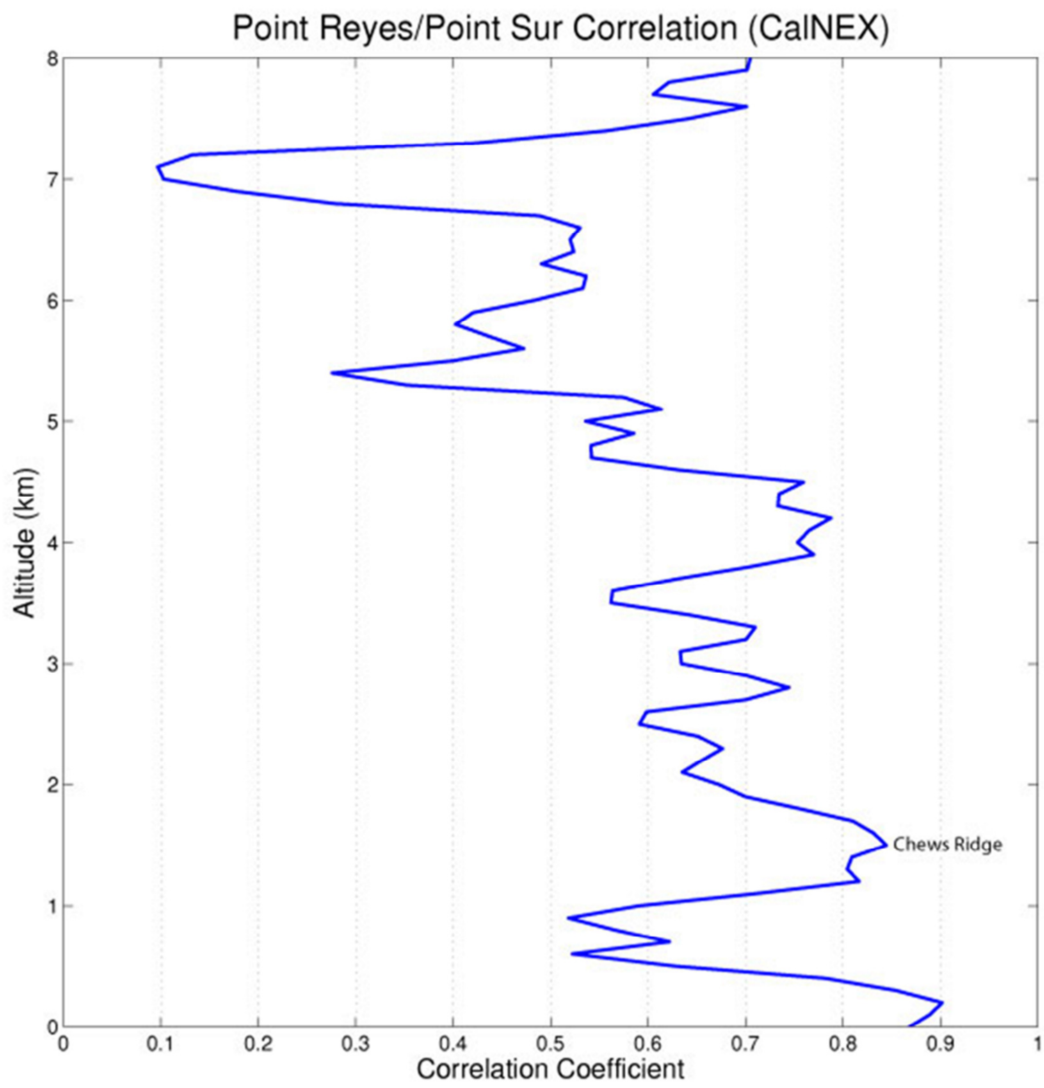
[4] See MIRA website at http://tycho.mira.org/oosweather/

[5] Ozonesondes are balloons with an ozone monitor attached. As the balloon rises it sends a radio signal at high time intervals, allowing researchers to record the vertical profile of ozone concentrations above the launch site.

Figure B-5. Altitude-specific correlation between daily ozonesonde profiles launched during IONS-2010 from Pt. Reyes and Pt. Sur in relation to Chews Ridge altitude.
Source: NOAA
(http://www.esrl.noaa.gov/csd/groups/csd7/Measurements/2010calnex/ionsOzone)



Finally, as shown in **Figures B-6** and **B-7**, satellite data retrievals from the week of Aug. 4-10 reveal transpacific flows of ozone and NO2. The concentration levels indicate consistent elevation across the west to east hemispheric transport corridor into California airspace. It should be noted that total column ozone partially reflects the natural background ozone found in the troposphere and stratosphere in addition to anthropogenic emissions. However, NO2 total column data is generated largely from anthropogenic sources. As such, the NO2 retrievals provide a solid basis for identifying TAO flow into California airspace that is being generated primarily by Asian emissions. The spatial scope and concentration levels depicted reveal the clear potential for TAO impacts on ground level monitors in the San Joaquin Valley under the conditions of high pressure subsidence that prevailed at the time of the exceedance.

In conclusion, the assembled evidence presented above provides substantial empirical support for the hypothesis that conditions were conducive for transport of TAO and related precursors to the Fresno area on Aug. 10, 2012. Meteorological conditions prevailing in the days up to and including Aug. 10 were quite favorable for the entrainment of free tropospheric ozone and its precursors (e.g. PAN) into the boundary layer of the central San Joaquin Valley with subsequent enhancement of surface ozone concentrations. Subsequent sections in this appendix will provide further layers of scientific support for this hypothesis, culminating with a quantification of the TAO contribution to the Drummond Ave. exceedance of Aug. 10, 2012.

Figure B-6. Total column ozone retrieval averaged for Aug. 4-10, 2012.
Source: NASA; http://disc.sci.gsfc.nasa.gov/giovanni

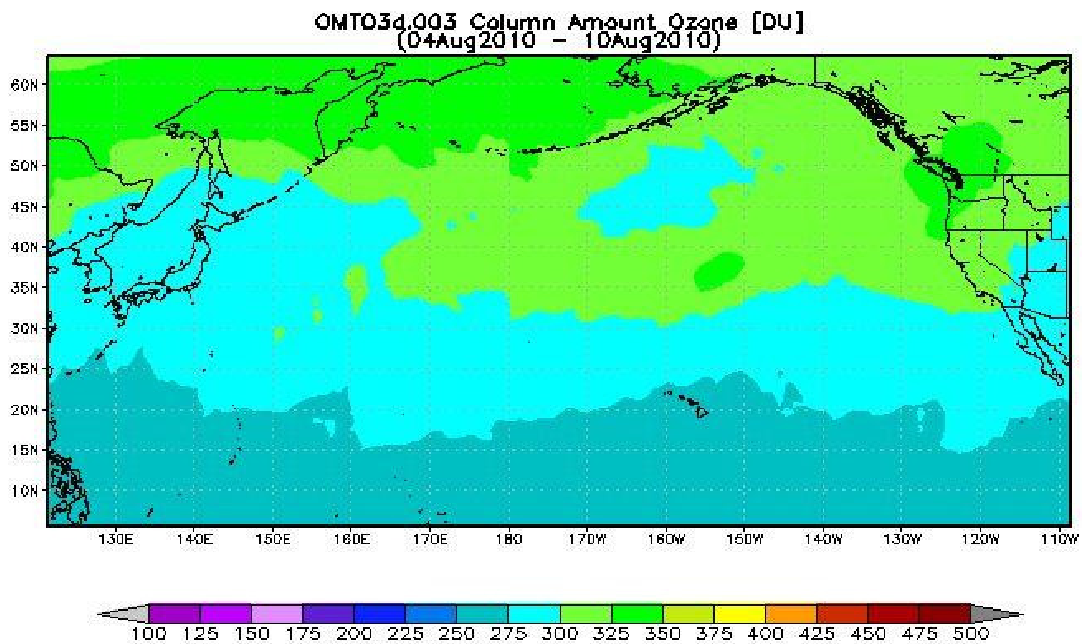
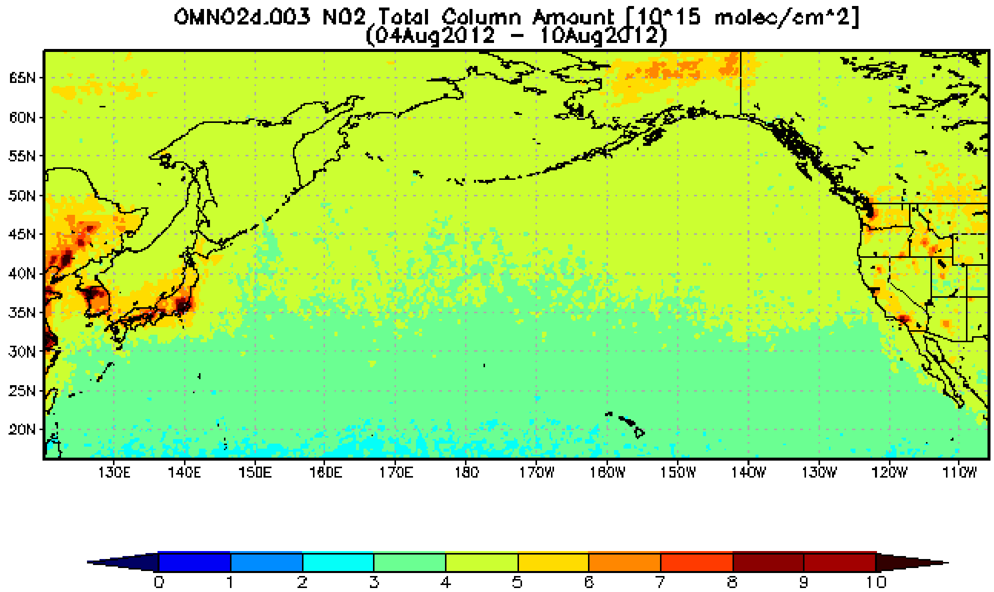


Figure B-7. Total column NO2 retrieval averaged for Aug. 4-10, 2012. Source: NASA; http://disc.sci.gsfc.nasa.gov/giovanni



3. PRIOR RESEARCH PROVIDES FURTHER EVIDENCE OF TRANSBOUNDARY ANTHROPOGENIC OZONE INFLOWS TO THE WESTERN US AND CALIFORNIA WITH SUBSEQUENT IMPACTS ON SURFACE CONCENTRATIONS

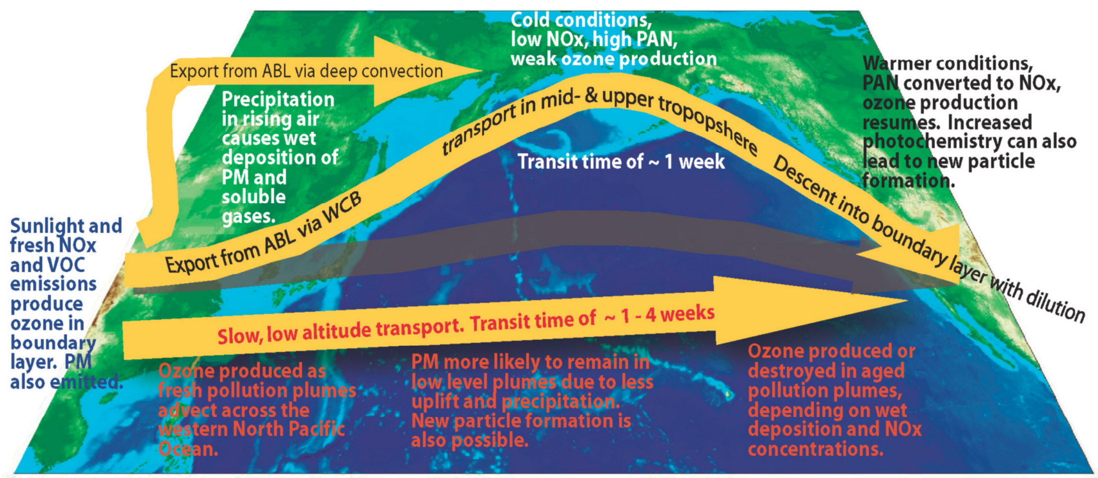
3.1 Ozone Precursor Emissions Have Been Rapidly Increasing in Asia Over the Past Four Decades

Sections presented below will focus on further background and empirical support for the hypothesis introduced above that the Aug. 10, 2012 exceedance would not have occurred but for entrainment of TAO into the SJV boundary layer. In distinction with TAO, transboundary ozone is defined in this document as ozone produced from biogenic, geogenic, stratospheric, or anthropogenic sources that is transported to the US west coast from transpacific, offshore sources, with TAO representing the anthropogenic fraction of total transboundary ozone. In particular, Asian anthropogenic emissions sources have been a predominant and growing component of total transboundary ozone impacts on ground level concentrations in California and the western United States (US). Given that transboundary ozone affecting the western US is predominantly from transport across the Pacific Ocean, transpacific ozone can be considered in this case as synonymous with transboundary ozone. In this document, however, the term transpacific will be generally used to connote the location of emission sources contributing to total transboundary ozone flows.

The clear evidence presented below of rapid TAO growth from Asian sources is a lynchpin element in the District's overall weight of evidence case. As shown in **Figure**

B-8, ozone transport within the marine boundary layer (MBL) from transpacific source regions is relatively inefficient due to high NOx concentrations, wet deposition, slow travel time, and resultant ozone destruction.[6] However, export of ozone and more stable precursors to the free tropospheric layer above the MBL is characterized by relatively rapid and stable transport of over long-distances to receptor regions such as the SJV. While short-lived precursors such as NOx are unlikely to be exported to receptor regions, stable precursors such as CO and PAN are much more likely to undergo long-distance transport in the free troposphere with subsequent conversion to ozone once they are subject to continental photochemistry.[7]

Figure B-8. Hemispheric transport processes with a focus on transboundary ozone transport to western North America.
Source: Cooper and Derwent, 2010, Part A, Chapt. 1, p. 7.



In the case of Asian TAO impacts on North America, the conditions for stable, long-distance transport in the free troposphere are ideal, as are the conditions for air mass subsidence from the free troposphere into the boundary layer of the western US. As shown in **Figure B-8**, deep convection of NOx, PAN, and ozone from Asian fossil fuel combustion is transported via the hemispheric warm conveyor belt (WCB) to the West Coast where subsidence leads to mixing into the boundary layer. The fraction of NOy (total nitrogen oxides) that is exported to the free troposphere via frontal lifting, deep convection, or boundary layer venting can lead to disproportionate production of ozone for long-distance transport. The PAN reservoir found in these same lower tropospheric air masses eventually decomposes upon subsidence into boundary layer environments, resulting in production of ozone with high efficiency. Aircraft

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[6] Jacob, D. J., et al. (1993) Factors regulating ozone over the United States and its export to the global atmosphere. *J. Geophys. Res.*, 98, 14 817–14 826.

[7] Carmichael, G. and Wild, O. (2010) Hemispheric Transport of Air Pollution, Part A, Chapt. 4., Global and Regional Modeling. Economic Commission for Europe, Air Pollution Studies No. 17.

research has found that PAN decomposition may represent a dominant element of ozone production in transpacific plumes from Asia.[8]

A number of processes, including dilution and ozone destruction in the boundary layer, complicate the empirical estimation of TAO enhancements of ground level concentrations in the San Joaquin Valley and elsewhere in the US West. However, in the face of this complexity there is little question that the steady, multi-decadal process of annual increases in ozone and its precursors from Asia are putting upward pressure on ambient concentrations and thus counteracting the effectiveness of local precursor reductions. Increases in Asian NOx emissions, from China in particular, have been the most important contributing factor. International trends in NOx emissions (and 1970-2005) are shown in **Figures B-9a (**1984-1998) **and B-9b** (1970-2005), revealing a striking divergence in trends between Asia, North America, and Europe.[9] Rapid growth in Chinese emissions, the predominant Asian NOx source, has continued since 2000. China's 2005--2010 estimated annual NOx growth rate was 4.01 ± 1.39%, following a period of very rapid annual growth from 2000-2006 of 5.8–10.8%.[10] For CO2, growth rates in 2012 were 5.9% for China and 7.7% for India. In contrast, US and European 2012 CO2 emissions declined by 3.7% and 1.8%, respectively.[11]

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[8] Hudman, R.C. et al. (2004) Ozone production in transpacific Asian pollution plumes and implications for ozone air quality in California. *J. Geophys. Res.*, 109, D23S10, doi:10.1029/2004JD00497.

[9] Akimoto, H. (2003) Global Air Quality and Pollution. *Science,* 5 December: 1716-1719. DOI:10.1126/science.109266.

[10] Gu, D, Y. Wang , C. Smeltzer , and Z. Liu (2013) Reduction in NOx Emission Trends over China: Regional and Seasonal Variations. *Environ. Sci. Technol.*, 47 (22), pp 12912–12919, DOI: 10.1021/es401727.

[11] Global Carbon Atlas (2013). Available at: http://www.globalcarbonatlas.org/

Figure B9a. Trends in International NOx Emissions: 1970-1998.
Source: Akimoto, 2003, p. 1718.

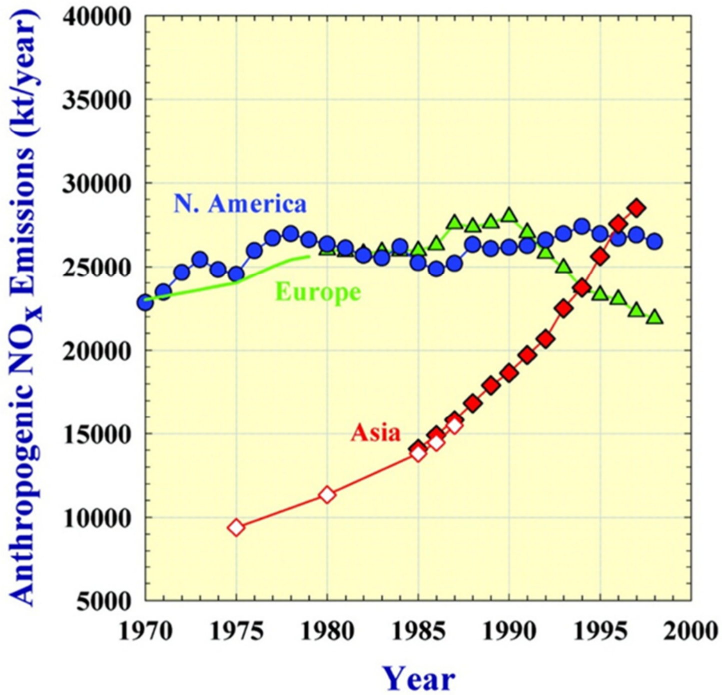
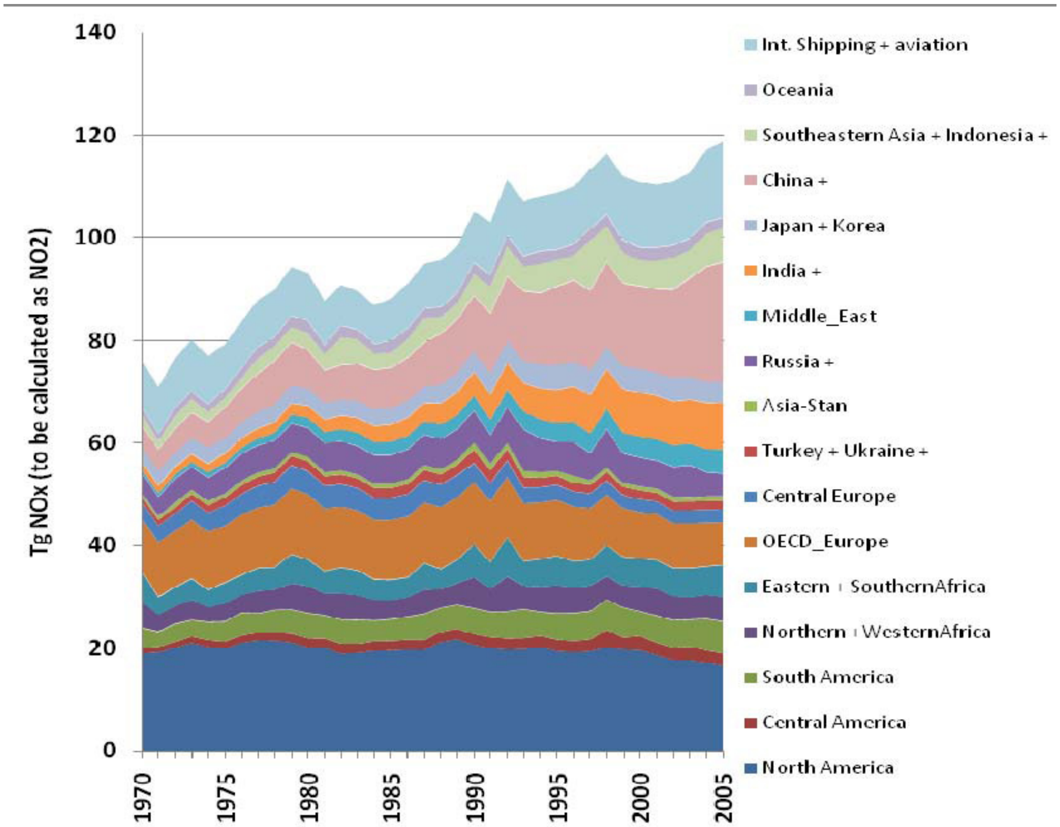


Figure B9b. Trends in International NOx Emissions: 1970-2005.
Source: Emission Database for Global Atmospheric Research (EDGAR) v4.1.
http://edgar.jrc.ec.europa.eu/results_v41.php



These rapid annual increases in Asian production of NOx, PAN, and ozone are accompanied by a corresponding increase in their hemispheric transport from Asia to North America. Jaffe et al. (2003) report that background ozone levels in western North America have increased approximately 10 ppbv from 1984 to 2002, with a mean annual increase of 0.26 ppbv.[12] With more recent data, the most comprehensive estimate for North American growth in free tropospheric ozone has been compiled by Cooper et al. (2010). Using data from extensive springtime observations in the US West, ranging from 1,663 samples in 1984 to 8,587 samples in 2006, the authors report a higher annual rate.[13] Between 1984 and 2008 their analysis indicates a median annual springtime increase in free tropospheric ozone of 0.66 ppbv, or approximately 15 ppbv over the entire period (see **Figure B-10**). The authors note that there is little likelihood that this increased increment is attributable to ozone with North American or European origins given that emissions from these regions have been declining since the mid-1980s as have extreme ozone events in urban centers across much of the US, including the San Joaquin Valley.

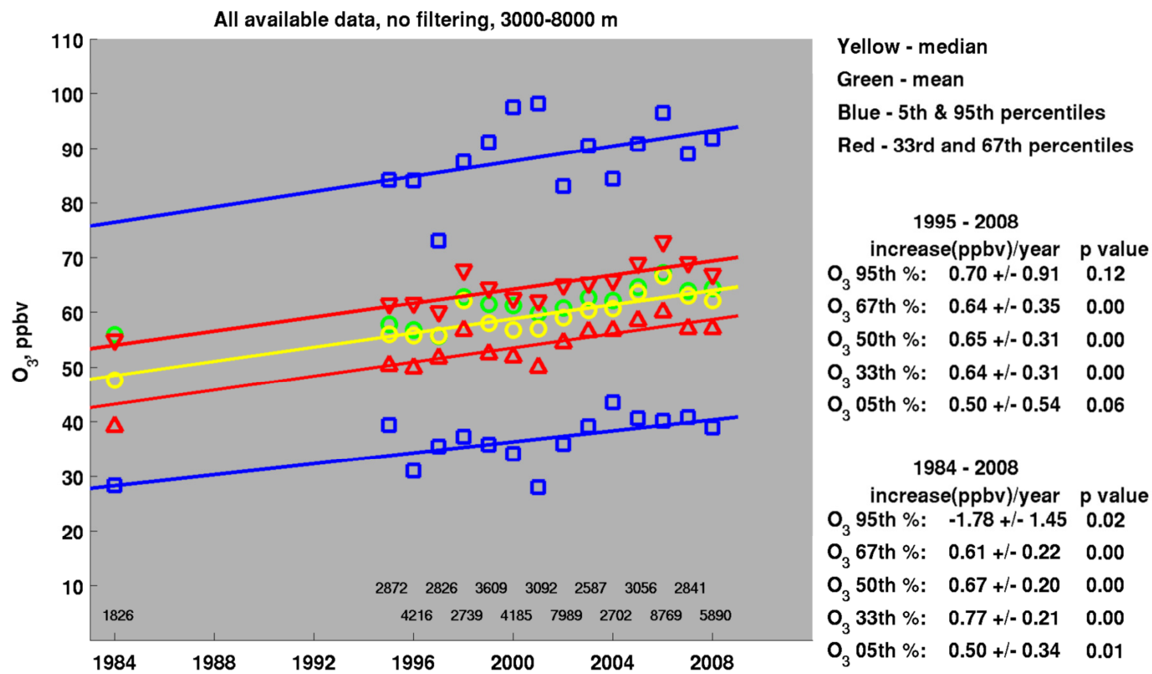
In conclusion, there is cumulative and compelling evidence that free tropospheric ozone concentrations as measured in the US West during springtime have increased by approximately 15 ppbv since 1984. Given the coincident rapid growth in fossil fuel combustion from Asian sources, the most likely source of this increase is transboundary anthropogenic ozone (TAO) and precursors generated in Asia, i.e. China, India, and Southeast Asia. High altitude sites in the US West are directly exposed to TAO via free tropospheric air masses. Other areas such as the San Joaquin Valley are chronically impacted by TAO in subsiding tropospheric air masses in spring and summer months.

Regarding seasonal differences in free tropospheric ozone flows to the West Coast, 2012-2013 transboundary flows measured at the Chews Ridge observatory (1.5 km at sea level) as well as NOAA's 2000-2008 ozonesonde measurements taken 2 km above Trinidad Head reveal little significant difference between summertime and springtime concentrations (see **Figures B-13 and B-27**). Based on the weight of evidence, 10 to 15 ppbv therefore represents a conservative estimate of the TAO fraction contained within total transboundary ozone entering the West Coast airspace in the lower free troposphere. This estimate is based only on the rapid increase in Asian emissions since 1984 and does not include the current European TAO contribution, the Japanese or South Korean TAO contributions, nor does it include the pre-1984 baseline TAO contribution from Asia.

[12] Jaffe, D., et al. (2003) Increasing background ozone during spring on the west coast of North America. *Geophys. Res. Lett.*, 30(12), 1613, doi:10.1029/2003GL017024.

[13] Cooper, O.R., et al. (2010) Increasing springtime ozone mixing ratios in the free troposphere over western North America. *Nature Letters*, Vol. 463, 21 January, doi:10.1038/nature08708.

Figure B-10. North American trends in springtime background ozone from 1984 to 2008.
Source: Cooper et al., 2010.



3.2. Case Investigations Provide Substantial Evidence that Transboundary Ozone is Impacting Surface Concentrations in California and the San Joaquin Valley

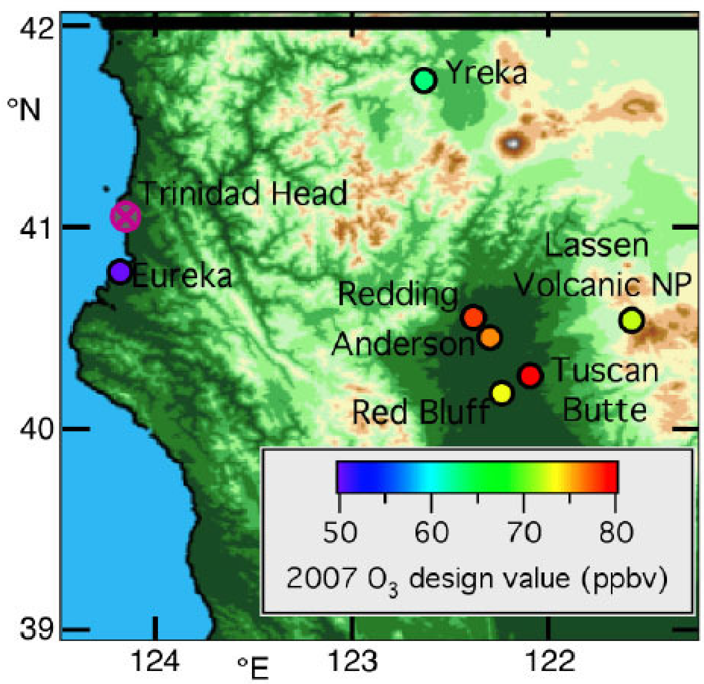
A successful invocation of §179B must base its weight of evidence analysis on scientifically valid methods for estimating the contribution of TAO to ground level concentrations in the San Joaquin Valley. Critical insights into the empirical techniques and data sources required to meet this objective can be found in a three peer-reviewed research analyses of transboundary ozone in the Sacramento and San Joaquin Valleys. These analyses and their relevance to the 1 hr. exceedance at the Fresno Drummond Ave. monitor on August 10, 2012 are reviewed in the next three sections. Equally important, these case studies provide a scientific context for assessing the validity of data collected at Chews Ridge and the San Joaquin Valley by UC Davis and CARB.

3.2.1 Case Study #1 (Parrish et al): Ozonesonde research at Trinidad Head in 2000-2008 demonstrates that transboundary ozone inflows are affecting surface concentrations the Northern Sacramento Valley

This case study is based on long-term ozonesonde research conducted by NOAA at the Trinidad Head California Baseline Observatory site on the northern California coast (see

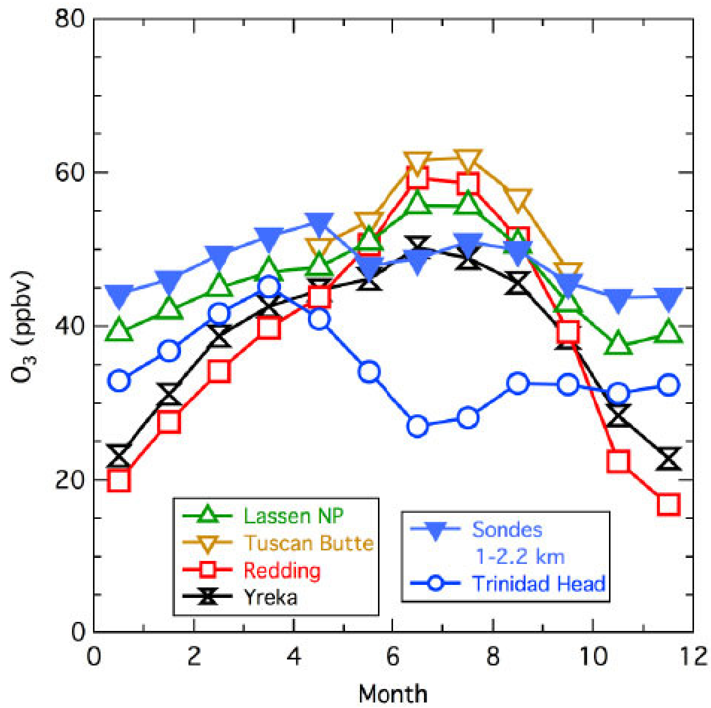
Figure B-11).[14] When released, ozonesondes provide a near continuous radio signal of ozone concentrations and weather data as they rise to an altitude of over 35 km before bursting. The net result is a vertical profile of ozone concentrations and concurrent weather conditions starting from ground level, rising through the boundary layer into the free troposphere, and eventually into the stratosphere. Nearly 700 sondes have been launched between 1997 and 2008 from Trinidad Head, a coastal location that is almost completely insulated from local ozone production due to its isolated location and absence of local emission sources. The study's primary objective was to assess the correlation between daily variations in ozone concentrations found in transpacific air masses in the free troposphere above the coastal sonde launch site at Trinidad Head and daily variations in ozone levels at six surface sites in northern California, including three in the northern Sacramento Valley (NSV) and a high-altitude site at Lassen National Park (see **Figure B-11**).

Figure B-11. Map of Northern California ozone measurement sites for Parrish et al, 2010. Symbol color indicates the ozone design value for the 75 ppbv 8 hr. ozone NAAQS (Redding and Tuscan Butte are in non-attainment).
Source: Parrish et al., 2010, p.10094.



[14] Parrish, D.D., et al., (2010) Impact of transported background ozone inflow on summertime air quality in a California ozone exceedance area. *Atmos. Chem. Phys.*, 10, 10093–10109, doi: 10.5194/acp-10-10093-2010.

Figure B-12. Average seasonal cycle of O3 from 12:00 to 16:00 (local standard time) from 2000 through 2008 at five surface sites compared with that measured by sondes averaged over the 1–2.2 km altitude range.
Source: Parrish et al., 2010, p. 10097.

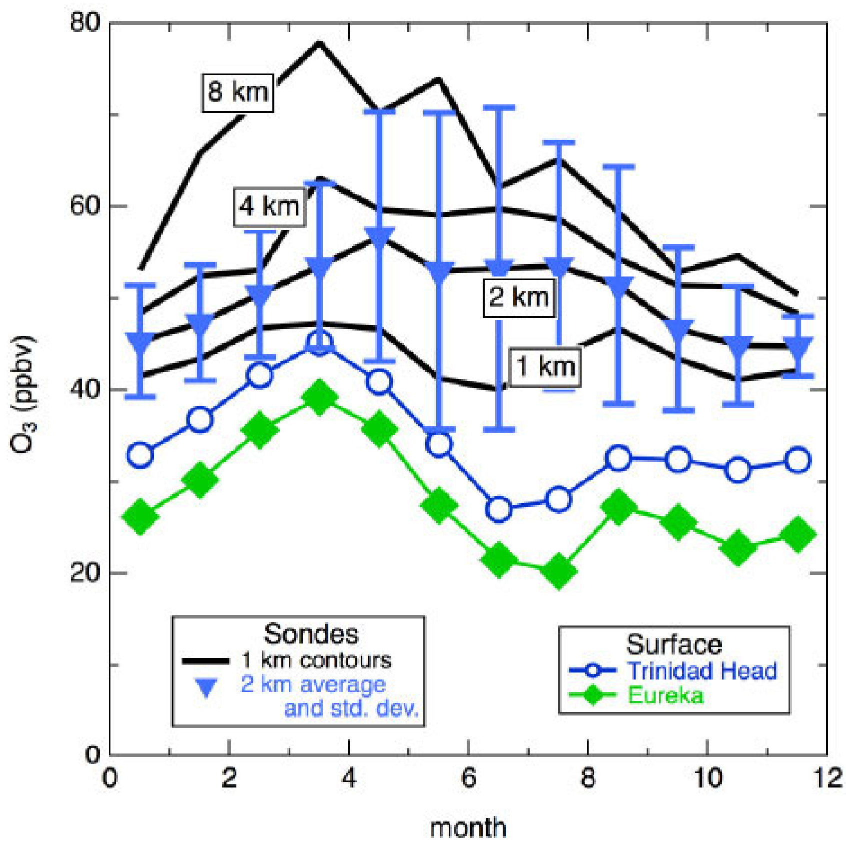


A central hypothesis motivated their correlational analysis: Transboundary air mass inflows 1 to 2.2 km above Trinidad Head are contributing consistently to ground level concentrations via subsidence and entrainment into the atmospheric boundary layer of the NSV. Preliminary evidence in support of the hypothesis is found in the average seasonal diurnal cycles of peak afternoon (12:00 to 16:00 local standard time) ozone at the five surface sites compared to the 1 to 2.2 km average ozone concentrations as measured by ozonesondes launched from Trinidad Head. Results are shown in **Figure B-12** for the years 2000 through 2008. Note that variations in the ozonesonde measurements across the ozone season of May through August are relatively small, ranging from approximately 54 to 48 ppbv, indicating relatively minimal seasonal differences in TAO flows between spring and summer. It is important to note that this concentration range is quite similar to the summer season averages of transboundary airmasses measured at the Chews Ridge observation station (see **Figure B-27**).

Figure B-13 depicts average profiles of ozone as measured by the sondes at different altitude levels relative to the baseline coastal sites of Trinidad Head and Eureka. These results also underscore the consistency of monthly averages of free tropospheric ozone on the northern California coast across the months of May, June, July, and August rather than a distinctly higher level of springtime concentrations. As further discussed in

Section 5, these monthly findings are comparable to those from the Chews Ridge monitor in the Santa Maria range at 1.5 km at sea level (a.s.l).

Figure B-13. Seasonal cycle of the vertical ozone gradient above Trinidad Head, California based on monthly averages of all sonde data collected within 200 m of indicated altitude. For the 2 km contour, the error bars indicate the standard deviations. The monthly average data collected from 12:00 to 16:00 local standard time (LST) for the years 2000 through 2008 are shown for two Northern California coastal sites. Source: Parrish et al., 2010, p.10099.



Correlation coefficients between daily ozonesonde values in the lower free troposphere (1 to 2.2 km) and regional surface sites ranged from 0.43 in Redding, 0.51 at Red Bluff and Tuscan Butte, 0.61 at Lassen NP, to 0.70 in Yreka. Maximum correlations occurred when the surface data were shifted 22.4 ± 0.6 h earlier. This time delay represents the average of total time required for the air mass sampled by the ozonesonde above Trinidad Head to be transported inland and mix to the surface. The authors conclude as follows (p. 10106):

> The correlation coefficients shown in Figs. 9 and 12 *(not shown here but cited above)* are not particularly large, but strong correlations cannot be expected for two reasons. First, the correlations of the MDA8 O3[15]

[15] MDA8 O3: Maximum daily 8 hour average ozone.

concentrations between sites in the NSV are themselves not perfect. For example, r =0.70 for Tuscan Butte and Redding. The square of the correlation coefficient, r^2, can be taken as an estimate of the fraction of the variance of a dependent variable that can be explained by its dependence on an independent variable. Thus, only about half of the variance of O3 at either site can be explained by influences common to both sites. These common influences are represented by the sum O3 (background) + O3 (regional) in Eq. (1) *(not shown).* The strongest correlations between the sondes and the surface MDA8 O3 are about r =0.50, which indicates that O3 (background), as measured by the sondes, accounts for approximately 25% of the total variance, which corresponds to about one-half of the variance due to O3 (background) + O3 (regional). The fact that the sonde data can capture approximately one-half of the variance caused by these two terms, and that they can capture approximately that fraction of the variance for all six inland surface sites is remarkable.

The authors acknowledge that a fraction of these daily air parcels represent recirculation back to sea from California via daily land-sea breezes. However, their back trajectory analysis supports the hypothesis that the Trinidad Head sondes generally sampled air flowing ashore from the Pacific followed by transport inland to the northern Sacramento Valley (see **Figure B-14**). In addition, the authors note that these recirculated air masses within the 1 to 2.2 km altitude are largely above the California boundary layer and as such are unlikely to contain ozone generated by anthropogenic activity from North America in the absence of strong thermal lofting from forest fire plumes.

Figure B-15 provides process insight into how transboundary ozone in the free troposphere is ultimately entrained into the Sacramento and San Joaquin Valley boundary layers. According to their empirical analysis, this transport mechanism is a predominant one, i.e. that on an average summer day, transboundary ozone contributes approximately 49 ppbv on average to the 8 hr. maximum daily average (MDA8), corresponding to 75 to 86% of the average MDA8 ozone of 57 to 65 ppbv observed at the four NSV sites. Based on the trend shown in **Figure B-10**, the contribution of TAO from transpacific sources to the 49 ppbv average is at minimum 15 ppbv and more if both the pre-1984 Asian and European TAO contribution is included. In light of this, an estimate of 10 to 15 ppbv represents a conservative estimate of the TAO that is impacting surface concentrations in the US West.

The authors conclude with the following observations: (1) the relatively high correlation between the five surface sites and the sonde observations taken approximately one day earlier provides firm correlational evidence that transboundary ozone is boosting observed ozone levels at the ground level sites; (2) similar correlations with sonde observations were found at Yreka and NSV ground sites even though Yreka is in a small valley that is topographically and meteorologically isolated from the NSV, suggesting a common source that is not influenced by California anthropocentric activity in the NSV; (3) there is no evidence that North American ozone is being transported to the 1 to 2.2 km altitude range sampled by the sondes; (4) the relatively high correlations with ground level sites are occurring within a narrow altitude range in the lower free troposphere; and (5) the correlations track well with peak seasonal ozone flows, are much poorer in fall and spring, and disappear in winter.

Figure B-14. Map of 5-day HYSPLIT back trajectories at 2.5 km a.s.l. above Trinidad Head beginning upon the launch of summertime ozone sondes. Black dots shown in inset correspond to site locations highlighted in Fig. C4. Source: Parrish et al., 2010, p.10107.

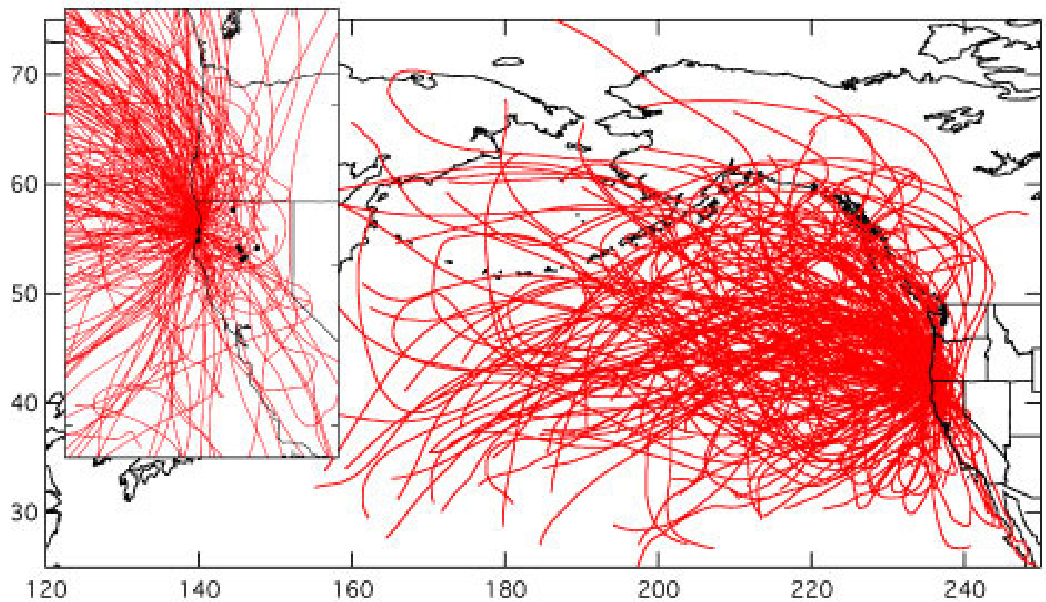
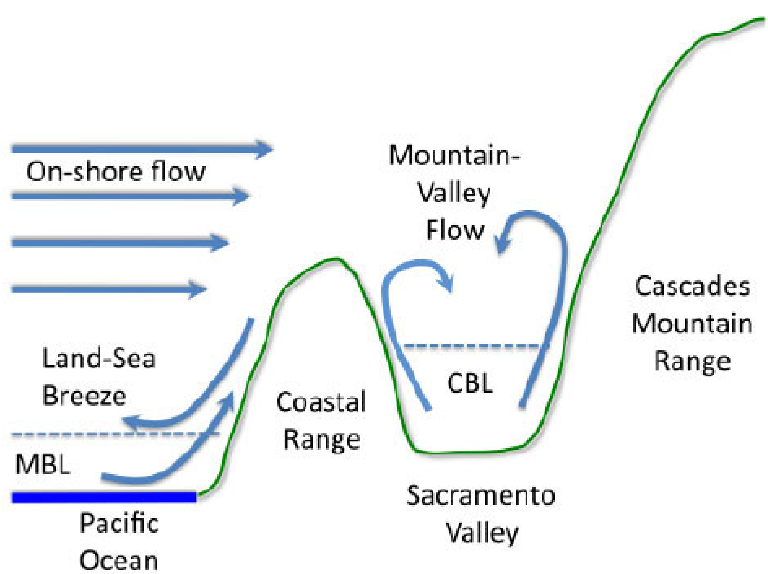


Figure B-15. Diagram of east-west cross-section of Northern California topography with transport mechanisms associated mid-afternoon air flow patterns. MBL and CBL represent marine boundary layer and convective boundary layer, respectively. Source: Parrish et al., 2010, p.10104.



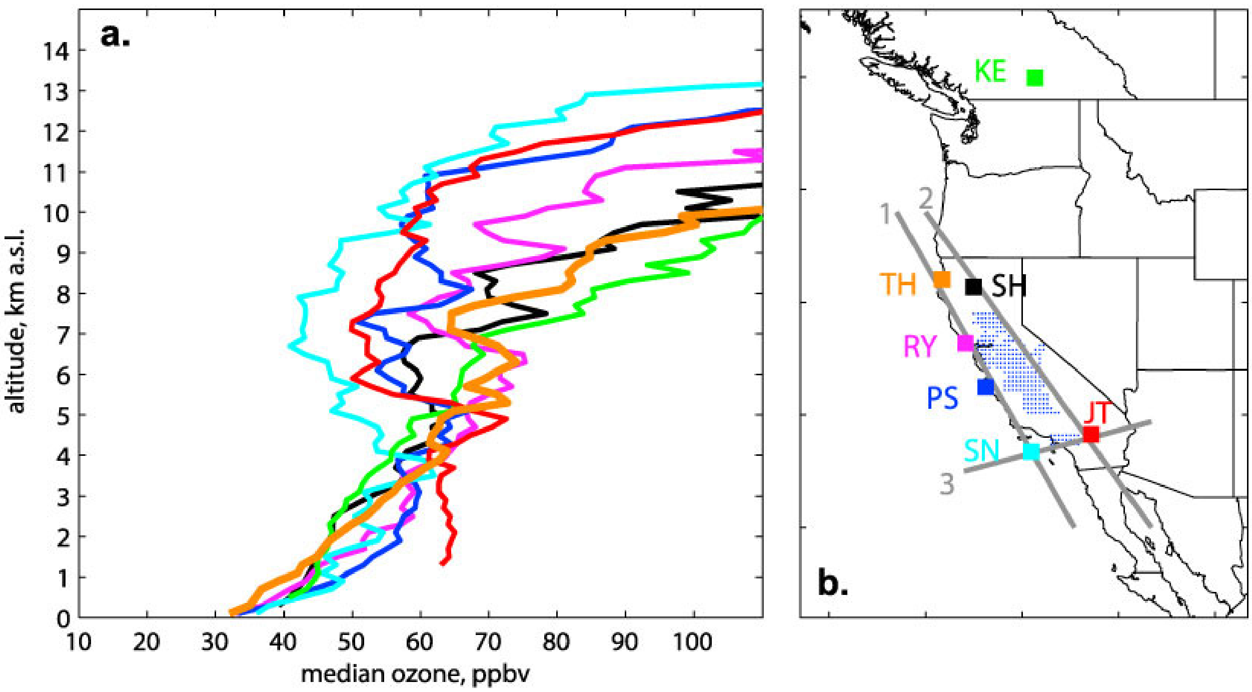
Relevance to Drummond exceedance case: While there are several structural environmental differences between the NSV and the central SJV, i.e. the level of locally produced anthropogenic ozone, Parrish et al. provide strong correlational evidence that most of the NSV's variability in ground level ozone is being caused by import of transboundary ozone from transpacific sources rather than local production or up-valley transport from the Sacramento and San Francisco Bay air basins. Instead, these correlations provide strong support for the hypothesis that the valley-mountain convective processes shown in **Figure B-15** play an important role in transporting transboundary ozone to the surface. Furthermore, evidence cited above indicates that TAO is contributing at minimum 10 to 15 ppbv to the total transboundary ozone inflow affecting the NSV. Given that rising Asian fossil fuel consumption is the most logical cause for the upward climb in transboundary ozone concentrations in the West, it follows that TAO is making a critical marginal contribution to Butte County's current non-attainment status for the 8 hr. ozone NAAQS.

3.2.2. Case Study #2 (Cooper et al): CalNEX/IONS-2010 ozonesonde research in 2010 show that Pt Reyes and Pt Sur are impacted by the same transboundary ozone flows with subsequent surface impacts in the SJV

The Intercontinental Chemical Transport Experiment Ozonesonde Network Study (IONS-2010) was conducted by NOAA and NASA from May 10 to June 19, 2010 as part of the larger 2010 CalNEX campaign. The study generated a rich body of empirical evidence regarding transboundary ozone impacts on surface ozone concentrations in the western U.S., the west coast of California, and the San Joaquin Valley.[16] For these reasons it has particular relevance to the Drummond Ave. exceedance. In particular, the study demonstrates that the same processes of transboundary ozone entrainment to ground level sites that were identified by Parish et al. (2010) in the northern Sacramento Valley are also occurring in the San Joaquin Valley. The study also builds on data drawn from over 10 years of data from ozonesonde releases at Trinidad Head that were discussed in the first case study. In addition to Trinidad Head, IONS-2010 incorporated seven new ozonesonde launch sites. As shown in **Figure B-16 (b)**, the four coastal ozonesonde sites included, from north to south, Trinidad Head (TH), Point Reyes (RY), Point Sur (PS), and San Nicholas Island (SN). These were supplemented by inland sites including Kelowna (British Columbia), Shasta (SH), and Joshua Tree (JT).

[16] Cooper, O. R., et al. (2011) Measurement of western U.S. baseline ozone from the surface to the tropopause and assessment of downwind impact regions. *J. Geophys. Res.*, 116, D00V03, doi:10.1029/2011JD016095.

Figure B-16. (a) Median ozone profiles above the IONS-2010 ozonesonde sites using all available profiles. Line colors correspond to the site label colors in (b). (b) Locations of the seven IONS-2010 ozonesonde sites. NOAA P3 aircraft sampling locations are shown in blue dots. Flight data was used to create ozone composite profiles in the Central Valley and LA Basin. Gray transects indicate locations of the three ozone vertical cross sections described in the text: coastal, inland, and southern California. Note the similarity between the Pt. Sur (PS) and Pt. Reyes (RY) profile concentrations.
Source: Cooper et al., 2011, p. 9.



Several objectives of IONS-2010 are of relevance to the Drummond exceedance case, including: (1) determining the latitudinal and altitudinal variability of transboundary ozone along the California coast from the surface to the lower troposphere, (3) assessing the influence of boundary layer processes on the transport of free tropospheric ozone to the surface, and (3) making an observation-based quantification of transboundary ozone's contribution to net ozone production within California's lower troposphere.

A focal point of their analysis was an assessment of transboundary ozone concentrations along three different transects shown in **Figure B-16 (b)**: a coastal transect (spanning TH, RY, PS, and SN), an inland transect in the south (SH to JT), and a southern California transect (SN to JT). Beginning with the coastal transect, **Figure B-16 (a)** depicts median ozone profiles for all the IONS-2010 sonde sites. Among the coastal sites in particular, concentrations across the sites are relatively similar at 1.5 to 3 km a.s.l., averaging approximately 50 to 60 ppbv. This concentration range is consistent with the 2012 summertime concentrations measured at the Chews Ridge monitoring site operated by UC Davis at 1.5 km a.s.l. and 30 km east of the Pt. Sur ozonesonde site (PS). As in the case of Trinidad Head discussed above, the authors conclude that the lack of local emissions and absence of statistical evidence of recirculation from inland ozone sources support the conclusion that the ozone measured above these coastal sites is predominantly transboundary ozone from transpacific sources.

A subsequent element of their analysis focused on the quantification of ozone transported to seven receptor regions within California, including the northern Central (Sacramento) Valley, the mid-Central Valley (Sacramento), the south Central Valley (south San Joaquin Valley), the LA Basin, Lassen Volcanic National Park, Yosemite-Sequoia-Kings National Parks, and Joshua Tree National Park. The quantity of ozone transported from each sonde site to the lowest 300 m layer of each receptor region is shown in **Figure B-17 (b-e).** The quantity of ozone delivered to the receptor regions is influenced significantly by air mass altitude. Air masses entering the coastal sonde sites above 3 km were found to have their largest impact on the high altitude receptor regions whereas the ozone coming ashore below 2 km has the strongest impact on the low altitude receptor regions such as the San Joaquin Valley.

The authors also report that airflow impedance by the coast range has the effect of channeling off shore air mass flows in the lower free troposphere through the gap in the range between Pt. Reyes and the Carquinez straight, with subsequent divergence into the Sacramento and San Joaquin Valleys (see **Figure B-18**). As a result, Cooper et al found the Pt. Reyes (RY) sonde site to be the best overall California site for monitoring transboundary ozone because of the lower elevation of the coast range in that area.[17] As depicted in **Figure B-17 (c)**, below 2 km the Pt. Reyes (RY) site is responsible for a relatively high level of delivery to the mid- and south Central Valley when compared to the other coastal sonde sites. This transport pathway is consistent with the results of the back trajectory analysis of the Drummond exceedance case shown in **Figure B-4**.

It is also noteworthy that the median ozone altitude profiles for the coastal sonde sites shown in **Figure B-17 (a)** indicate a high degree of consistency below 2 km between the Pt. Reyes (RY) and Pt. Sur (PS) sonde profiles during the IONS-2010 (CalNEX) campaign. The altitude-specific correlations between the two sites were shown above in **Figure B-5**, indicating a very high correlation for the stratum between 1.6 and 1.8 km a.s.l., consistent with the finding that transboundary ozone below 2 km is the primary source for ground level impacts at low-elevation sites such as the San Joaquin Valley. This real time correlation provides evidence that inflows from the same air masses are concurrently affecting both sites on a regular basis. This relative altitudinal and latitudinal continuity in offshore air masses provides support for using transboundary ozone concentrations measured at Chews Ridge as a surrogate measure for transboundary air masses affecting Fresno via the Pt. Reyes/Carquinez Strait gap. This issue will be revisited in the Drummond exceedance modeling analysis below and is consistent with previous ozonesonde research findings.[18]

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[17] See also: Cooper, O. (2012) Ozonesonde and aircraft measurements during CALNEX, 2010. Presentation made to the WESTAR Council and the University of Nevada Conference on Western Ozone Transport, October 10-12, Reno, NV.

[18] Liu, G., et al. (2009) Ozone correlation lengths and measurement uncertainties from analysis of historical ozonesonde data in North America and Europe. *J. Geophys. Res.*, 114, D04112, doi:10.1029/2008JD010576.

Figure B-17. (a) The seven receptor regions (gray circles indicate the locations of the IONS-2010 ozonesonde sites). (b–e) Estimates of ozone (in Dobson units, a measure of total ozone concentrations in a vertical column from the surface to the top of the atmosphere) from each of the four coastal sites that is transported to surface layer (0 – 300 m) of the atmosphere in the seven receptor regions. Line colors correspond to the region colors in (a). Note that the South Central Valley (in red) receives its highest surface delivery via the Pt. Reyes (RY) pathway (c).
Source: Cooper et al., 2011, p. 16.

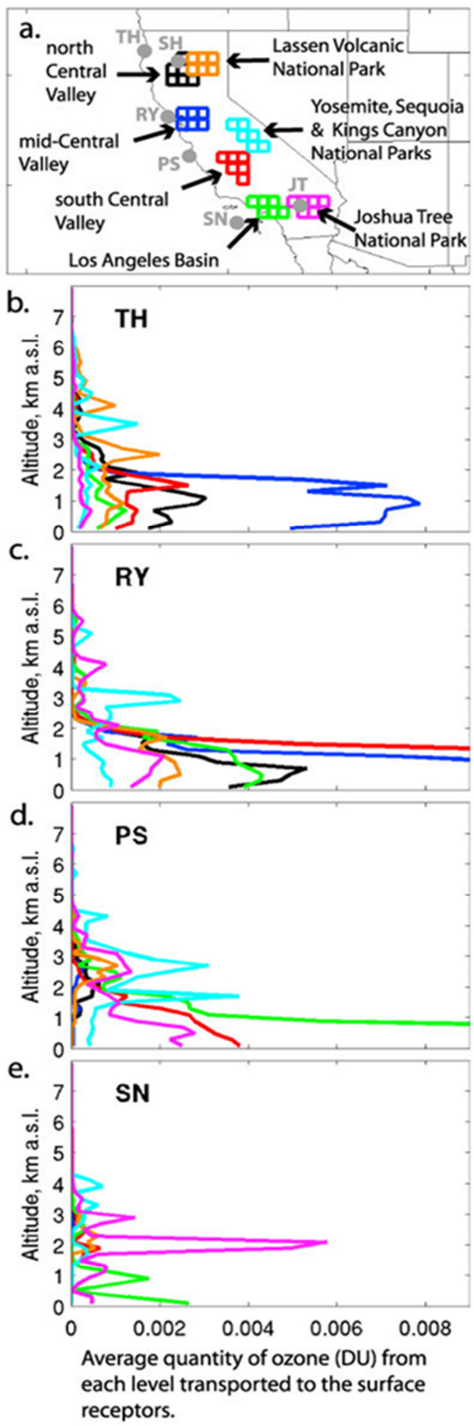
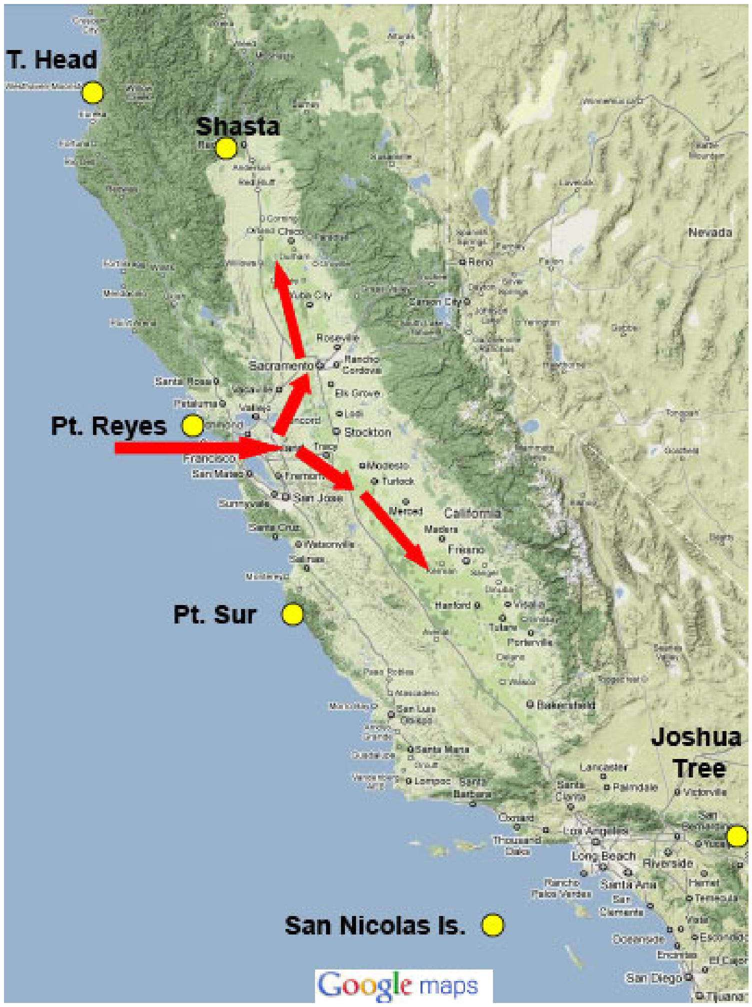


Figure B-18. Summertime predominant pathways of lower tropospheric transport into the Sacramento and San Joaquin Valleys in relation to CalNEX ozonesonde sites.
Source: Cooper et al, 2012.



A final element of the Cooper et al. analysis entailed quantifying the relative share of transboundary ozone vs. locally-produced ozone found in the northern Sacramento Valley (NSV), the southern San Joaquin Valley (SSJV), and the Los Angeles basin. Specifically, this was done by comparing the quantity of ozone as measured by the coastal baseline sonde profiles with inland ozone measured either by sonde (NSV) or aircraft (SSJV and LA Basin). In the case of the SSJV, the baseline profiles were based on the coastal locations of Trinidad Head (TH), Pt. Reyes (RY), and Pt. Sur (PS). For the SSJV, it was estimated that below 3 km, the net locally-produced photochemical enhancement above the transboundary background measured at the coastal sonde sites was 12% for Pt Sur, 20% for Pt. Reyes, and 23% for Trinidad Head. In other words, approximately 80% of the ozone found up to 3 km above sea level (a.s.l.) in the southern San Joaquin Valley was estimated to be from transboundary anthropogenic and natural sources.

For the entire Central Valley, the average concentration of ozone below 6 km a.s.l. as estimated via aircraft was between 50 to 60 ppb (see **Figure B-19 (a)**). As discussed in more detail in a subsequent section, this concentration range is consistent with summer ozone levels measured at the Chews Ridge fixed ozone monitor located at 1.5 km a.s.l., 30 km east of Pt. Sur, and 168 km west/southwest of Fresno. The contribution to surface concentrations from transboundary flows below 2 km was greatest at low altitude sites such as Bakersfield and Fresno whereas flows above 2 km contribute primarily to high altitude sites.

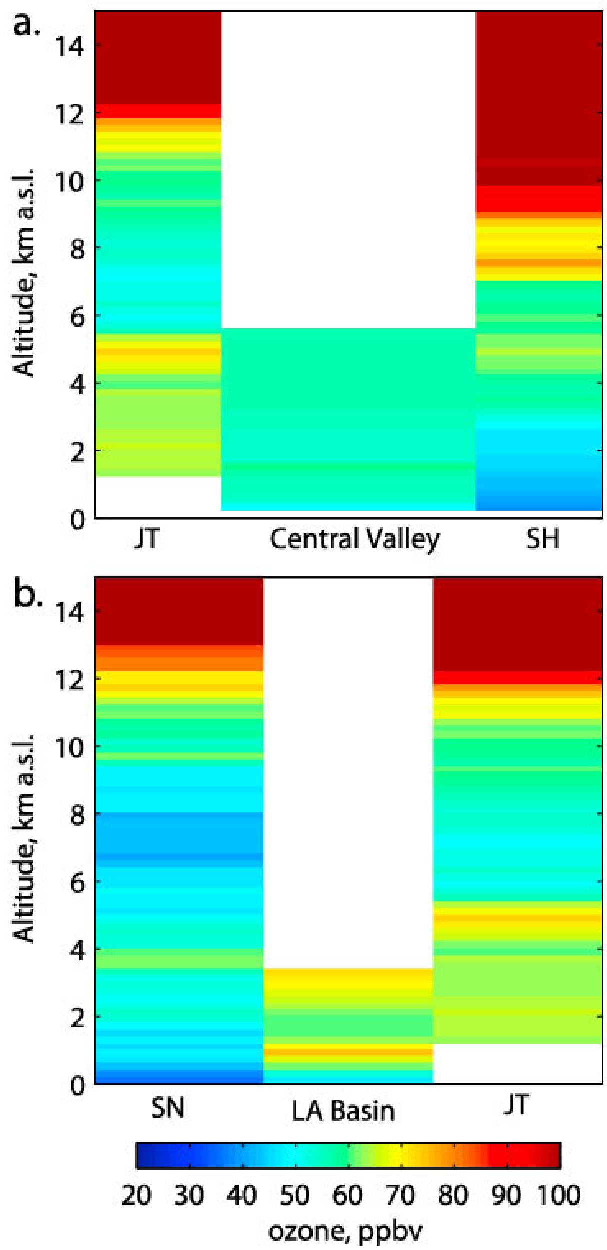
<u>Overall relevance to Drummond exceedance case</u>:

1. The research provides solid empirical evidence indicating that the Pt. Reyes/Carquinez Strait area is the primary entry point for transboundary ozone (and precursors such as PAN) that are subsequently resulting in elevation of surface concentrations in the San Joaquin Valley.

2. While the Santa Lucia range east of the Pt. Sur (PS) sonde site impedes delivery of transboundary ozone to the SJV, the vertical concentration profiles from the IONS-2010 sondes at Pt. Sur (PS) and Pt. Reyes (RY) are highly correlated in strata below 3 km a.s.l., indicating that they are measuring the same air masses. This correlation is particularly high (0.84) in the stratum located between 1.5 and 1.8 km. This corresponds with Cooper et al.'s finding that free tropospheric delivery of transboundary ozone to the lower elevation sites in the southern SJV occurs primarily below 2 km. As discussed in more detail in Section 4.1 below, this latitudinal and altitudinal commonality underscores the validity of using ozone data collected at the UC Davis Chews Ridge observation site east of Pt. Sur (1.5 km a.s.l.) as a surrogate estimate for ozone delivered to the SJV via the Pt. Reyes/Carquinez Strait gap in the coast range.

3. The ozone curtain analysis presented in **Figure B-19** indicates that about 80% of the total ozone found below 3 km in the southern SJV is transboundary ozone from transpacific sources, with the remainder attributed to local or regional sources. While this finding cannot be used to extrapolate the contribution of transboundary ozone to total surface concentrations, it does reveal the extent to which the San Joaquin Valley is enveloped by relatively high concentrations of transboundary ozone.

Figure B-19. (a) Median vertical ozone profiles (aka curtains) above three inland locations in California along the south-north transect shown in Figure B-16. (b) Median ozone profiles along the west-east transect shown in Figure B-16. Ozone measurements above the Central Valley and the LA Basin were made by the CalNEX aircraft flights as reflected by the smaller altitude range. Data from other sites were gathered by ozonesondes.
Source: Cooper et al, 2011, p. 18.



4. This envelopment by transboundary ozone (typically in the 45 to 60 ppb range above the boundary layer) contributes to higher ground level ozone concentrations via the downward convective mixing process discussed in Case Study #1.

5. The concentrations of transboundary ozone below 3km and above the Valley boundary layer as measured via CalNEX aircraft are very comparable to concentrations in the same altitude range gathered by CARB aircraft and the Chews Ridge site (discussed further in Section 4).

3.3.3 Case Study #3 (Huang et al): Sophisticated modeling based on model evaluation, sensitivity analysis, and data assimilation further demonstrates significant surface impacts from transboundary ozone in California and the SJV

Case study #3 provides model-based evidence that transboundary ozone is having significant impacts on ground level ozone in the San Joaquin Valley. The strength of observational studies is their ability to provide a strong empirical basis for accurate estimations of transboundary ozone in particular places at particular times. In contrast, global and regional chemical transport models (CTM) are capable of providing spatially and temporally resolved estimates of ground level enhancements from transboundary ozone over larger areas and timeframes albeit at a lower level of accuracy. Over the past several decades, however, the predictive performance of models that combine chemical transport and meteorological routines have improved considerably.[19] In particular, a number of techniques involving model refinement based on the assimilation of observational data have been developed to provide more robust estimates of ozone impacts from transported background. As such, well-developed CTMs now have the ability to estimate the surface contribution from transboundary ozone with a relatively high degree of accuracy.

A representative example of such a study is provided by Huang et al. (2013).[20] They examine the combined impact of transboundary ozone on surface maximum daily average 8 hr. ozone (MDA8) in the U.S. West, including California.[21] While broad-scale modeling research such as this cannot serve as the sole basis for estimating the quantity of TAO impacting the Drummond monitor on Aug. 10, 2012, they can and, in this case, do provide an important corroborative element in the District's overall weight of evidence case. The validity of Huang et al.'s modeling is enhanced by an extensive data assimilation effort using observational data from the ARCTAS field campaign conducted by NASA from mid-June to mid-July in 2008. In addition, they include a sensitivity analysis based on variations in model resolution, boundary conditions, and

[19] Carmichael, G. R., et al. (2008) Predicting air quality: Improvements through advanced methods to integrate models and measurements, *J. Comput. Phys.*, 227, 3540–3571, doi:10.1016/j.jcp.2007.02.024.

[20] Huang et al. (2013) Impacts of transported background pollutants on summertime western US air quality: model evaluation, sensitivity analysis and data assimilation. *Atmos. Chem. Phys.*, 13, 359–391. doi:10.5194/acp-13-359-2013.

[21] Huang et al. also examined transported background impacts on regional levels of the federal secondary standard related to crop and vegetative damage from ozone, known as W126. While these results are depicted in **Figures B-20 and B-21**, they are not relevant in the context of this document.

emissions. The importance of these techniques is summarized by the authors (p. 360-1):

> Reducing the uncertainties in modeling pollutant distributions and estimating the contributions of extra-regional sources to local air quality require a closer integration of observations and models. Sensitivity analysis and data assimilation (DA) (cf, Bouttier and Courtier, 1999[22]; Carmichael et al., 2008[23]; Sandu and Chai, 2011[24]) are important techniques to: (1) help understand the chemical and physical processes associated with the transport/subsidence processes; (2) assess the degree to which the current observations can detect/represent long range transport (LRT) airmasses and help reduce model uncertainties; . . .

Observational data used for model inputs in the study were derived from (1) surface ozone measurements from existing monitoring stations, (2) 20 ozone sondes released from Trinidad Head during the ARCTAS campaign, (3) CO, ozone, NOy, and PAN from an offshore air flight for modeling of boundary conditions, and (4) satellite retrievals from the Tropospheric Emission Spectrometer (TES) and the Ozone Monitoring Instrument (OMI) on board the NASA Aura satellite.

The model employed was the full-chemistry version of the Sulfur Transport dEposition Modeling system (STEM) that has been used and validated in a number of field campaigns in the past decade. Gas-phase chemistry reactions were based on the SAPRC 99 gaseous chemical mechanism (Carter, 2000).[25] Simulations designed to characterize pollutant distributions over the Pacific and continental US were performed using a continental scale 60 × 60 km polar stereographic grid with 18 vertical layers in the troposphere. Processes linking airmasses aloft to the surface were simulated via a 12 km × 12 km Lambert conformal conic grid over the western US, with 32 vertical layers in the troposphere. For simulations over California, daily anthropogenic and biogenic emissions for California from CARB's 4 km x 4km emissions inventory were re-gridded to the 12 km grid. As a result, the model output displayed below effectively reflects the complex topographic environment of California and the San Joaquin Valley.

<u>Observed vs. modeled baseline MDA8</u>: STEM modeling results for the MDA8 (max. daily avg. 8 hr.) monthly index (MI, defined as the monthly mean MDA8) during the June 16 to July 14, 2008 period are compared with actual observations in **Figure B-20** (see a, c, and e). Two aspects are noteworthy: First, the STEM MDA8 MI results for the 12

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[22] Bouttier, F. and Courtier, P. (1999) Data assimilation concepts and methods. http://www.ecmwf.int/newsevents/training/rcourse notes/DATA ASSIMILATION/ASSIM CONCEPTS/Assim concepts.html

[23] Carmichael, G. R., et al. (2008) Predicting air quality: Improvements through advanced methods to integrate models and measurements, *J. Comput. Phys*., 227, 3540–3571, doi:10.1016/j.jcp.2007.02.024.

[24] Sandu, A. and Chai, T.F. (2011) Chemical Data Assimilation an Overview, *Atmosphere*, 2, 426–463, doi:10.3390/atmos2030426.

[25] Carter, W. P. L. (2000) Documentation of the SAPRC-99 chemical mechanism for VOC Reactivity Assessment, final report to California Air Resources Board. Contract No. 92–329 and 95–308.

km grid (e) are in very good agreement with the observed values, including the San Joaquin Valley. The exception is found in the coastal sites comparison, where the model was less capable of capturing the influence of marine boundary layer flows, resulting in over-predictions. The model mean bias (modeled – observed) across all sites was 11.54 ppb, reflecting the coastal over-prediction. Second, the model output from this high resolution grid effectively reflects California's complex mixture of emissions, topography, and meteorology.

<u>Contribution from transpacific ozone</u>: Of particular relevance here is the authors' estimate of transboundary ozone and precursors in California and the San Joaquin Valley. Details of the empirical methods used to estimate the transboundary ozone are provided on pps. 370-2. Results are depicted in **Figure B-21 (a)**, revealing a substantial impact on surface MDA8 ozone concentrations in the Central Valley of California and the US West in general. Results are described as follows (p. 370):

> The maximum TBG (*transported background ozone, aka transboundary ozone*) contributions over the western US occur over northwestern US (e.g., ID and OR) and the Central Valley, respectively (**Fig. 21 a, d**). After exploring the relationships between the model biases in the base simulation and the estimated TBG contributions at surface sites, we concluded that the bias-corrected estimates of TBG contributions to MDA8 are ~ 30–35 ppb for Regions 9 and 10.

<u>Overall relevance to the Drummond exceedance case</u>: Huang et al.'s estimate of surface impacts from transboundary ozone reflects empirical evidence of strong offshore transport of ozone and precursors during the ARCTAS study period based on the model boundary conditions as measured by aircraft as well as the data assimilation from satellite retrievals and the sonde profiles. As such, their estimate serves as a well-validated estimate of summertime transboundary ozone impacts in the Fresno area. These findings underscore the pervasive nature of transboundary ozone in the West.

As seen in **Figure B-21 (a)**, there are broadly distributed impacts on surface concentrations in summertime, including the San Joaquin Valley. Most importantly in this context, the results provide evidence that the hourly contribution of TAO to the estimated 28-36 ppbv total transboundary contribution to ground level 8 hr. averages for the San Joaquin Valley is significantly larger than 3 ppb, the exceedance level registered at the Drummond Ave. monitor on Aug. 10, 2012. As emphasized above, this assertion derives its most fundamental validation from the body of evidence presented above and in **Figure B-10** that the current level of TAO found in transpacific ozone averages at minimum 10 to 15 ppbv.

Figure B-20. Comparison of observed vs. modeled MDA8 monthly index (MI) (W126 in lower plots b, d, and f are not relevant here). (a) Observed MDA8 MI at EPA surface monitoring sites; Modeled surface MDA8 MI are shown in (c) for the 60 km/18 layer grid and (e) for the 12 km/32 layer grids.
Source: Huang et al., 2013, p. 368.

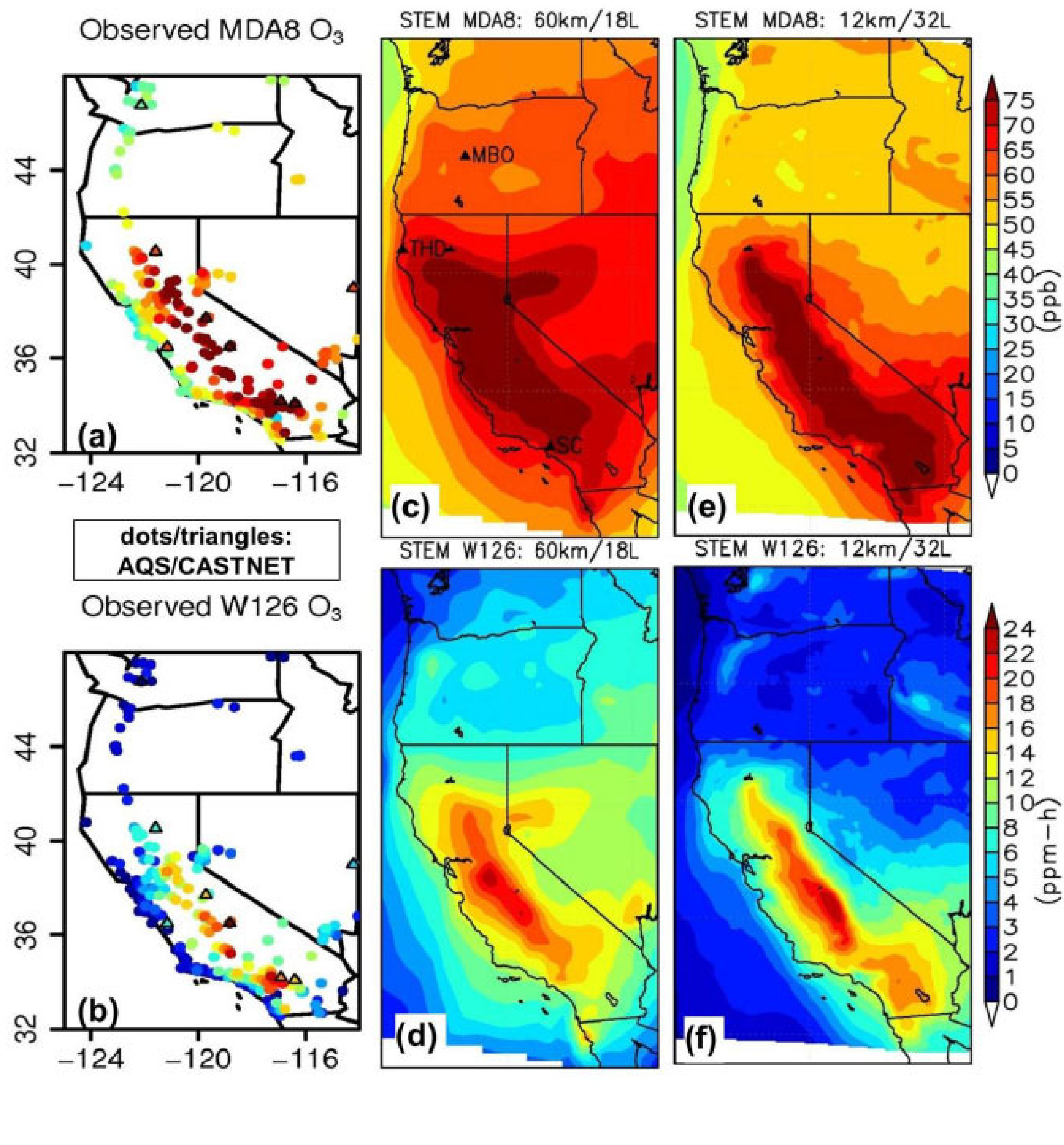
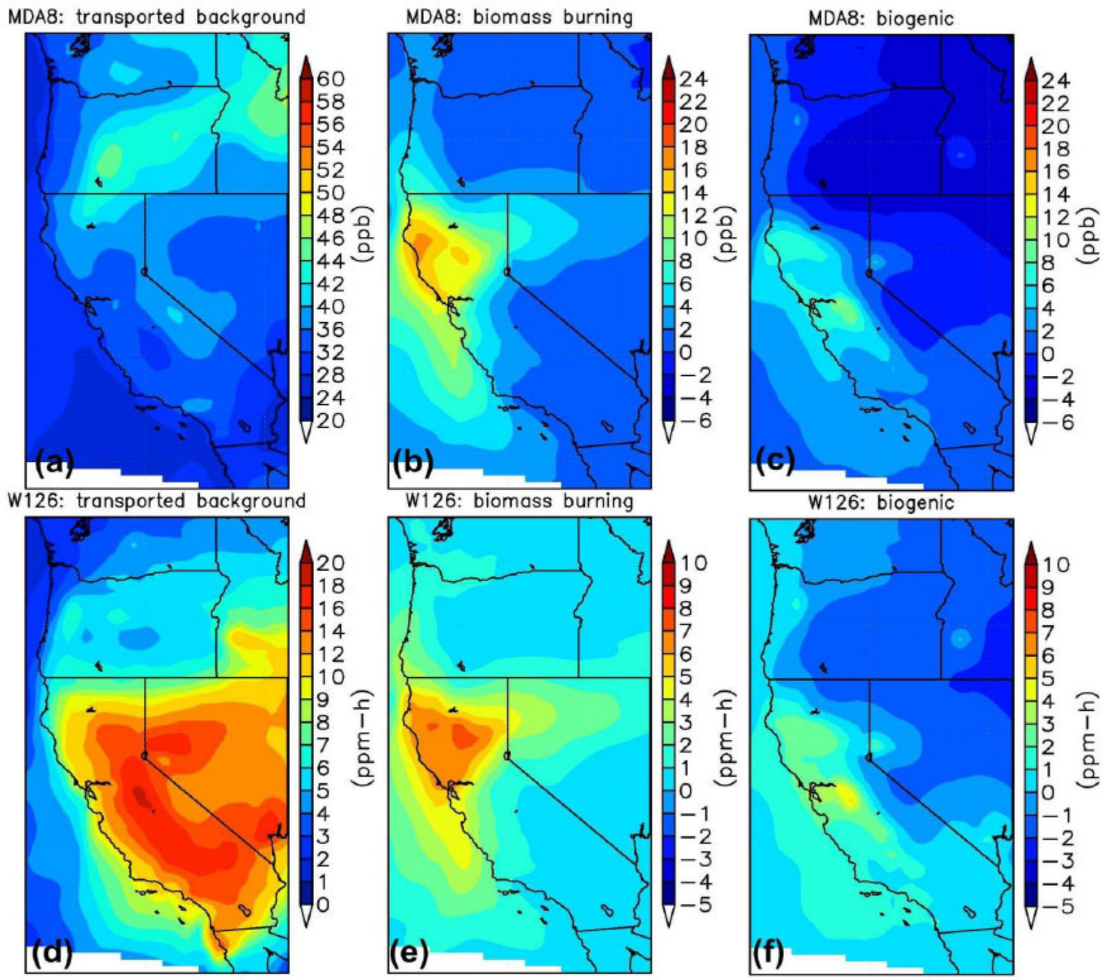


Figure B-21. Surface MDA8 contributed from (a) transpacific ozone and precursors (transported background), (b) North American biomass burning and (c) biogenic emissions. (W126 (d, e, f) is not relevant to this report)
Source: Huang et al., 2013, p. 371.



4. UC DAVIS OBSERVATIONAL RESEARCH BASED ON FIXED SITE AND AIRCRAFT MONITORING IN 2012 AND 2013 PROVIDE FURTHER EVIDENCE OF TRANSBOUNDARY OZONE IMPACTS ON SURFACE CONCENTRATIONS IN FRESNO ON AUG. 10, 2012

As summarized above, peer-reviewed studies based on observational data and related modeling provide clear evidence that transboundary ozone is pervasive in the lower free troposphere above the Sacramento and San Joaquin Valleys. This section focuses on further evidence of transboundary ozone impacts on the Fresno area based on measurements at the Chews Ridge field station over the summer seasons of 2012 and 2013. As detailed more closely below, the Chews Ridge field station recorded concentrations of transboundary ozone typically in the 45 to 60 ppb range. These field observations are consistent with the correlational analyses conducted by Parrish et al. (2010) and Cooper et al. (2011) as well as observation-driven modeling conducted by Huang et al. (2013).

In total, this body of work provides substantive weight of evidence that transboundary ozone in the free troposphere above California is being entrained into the boundary layer of the SJV, resulting in subsequent increases in ground level concentrations. Given this background, the spatial and topical focus of this section narrows to a synoptic characterization of summertime flows of transboundary ozone in the free troposphere above central California as measured at Chews Ridge as well as correlations of transboundary ozone with concentrations at SJV surface sites during June, July, August, and September (JJAS) in 2012 and 2013. Locations of relevant observation sites are shown in **Figure B-22**.

As discussed above, the District has provided funding to UC Davis to gather transboundary ozone data at a fixed observation site in the highlands of the Santa Maria range 30 km east of the Pt. Sur (PS) ozonesonde launch site. Instruments are housed in the MIRA observatory at 1,530 m a.s.l. A 2B Technology ozone UV-photometric analyzer, a TSI Scanning Mobility Particle Sizer (SMPS) coupled to a condensation particle sizer (CPC), and a Rotating Drum Impactor (RDI) were installed and have operated successfully in the face of the extreme conditions present seasonally at Chews Ridge.[26] Remote access to the on-site computer and instruments ensures proper instrument function and facilitates access to data, with site visits occurring every 5-6 weeks or as needed for maintenance and RDI impactor film replacement.[27]

Data used in this analysis was gathered during the months of June, July, August, and September (JJAS) of 2012 and 2013. Additional related data was collected by UC Davis via episodic air flights during peak ozone days in the summer of 2012 designed to characterize ozone flows and concentrations both within and above the SJV boundary layer. Specific data elements include the following:

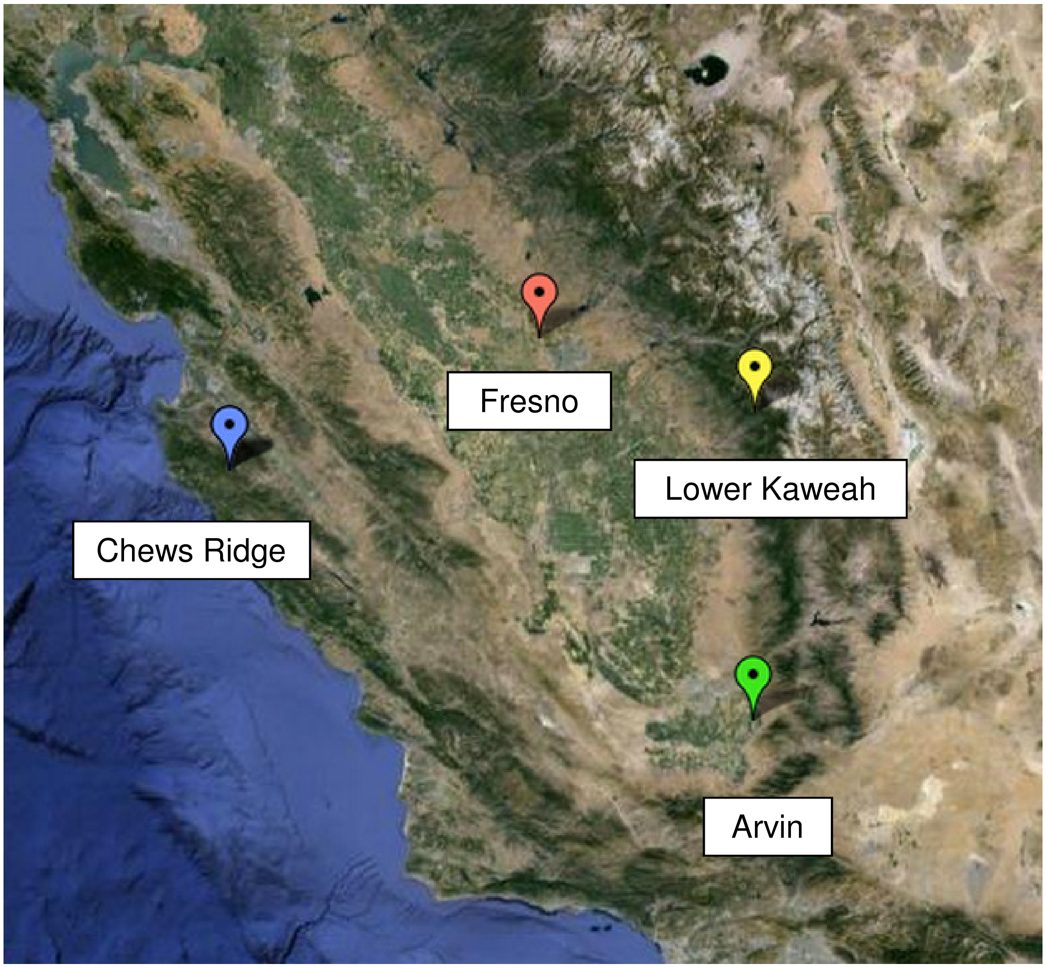
1. Hourly profiles of ozone, temperature, wind direction, wind speed, and specific humidity collected at the Chews Ridge observatory;

2. Hourly ozone data for the same time period from three surface monitoring sites in the SJV airshed, including Arvin (DiGiorgio located southeast of Bakersfield), Fresno (Sierra Skypark located in northwest Fresno), and Lower Kaweah (located at 1.9 km a.s.l. in Sequoia National Park);

[26] The extreme environmental conditions and remote location of Chews Ridge required the construction of a utility structure to house sensitive instruments and equipment. In addition to an on-site wind turbine and photovoltaic panel generation provided by MIRA, a 10-battery bank provides supplemental power required for continuous equipment operation.

[27] The RDI ceased operation in October of 2013 but the ozone analyzer has remained in continuous operation.

Figure B-22. Locations of ozone surface monitors.
Source: Post et al., 2013.

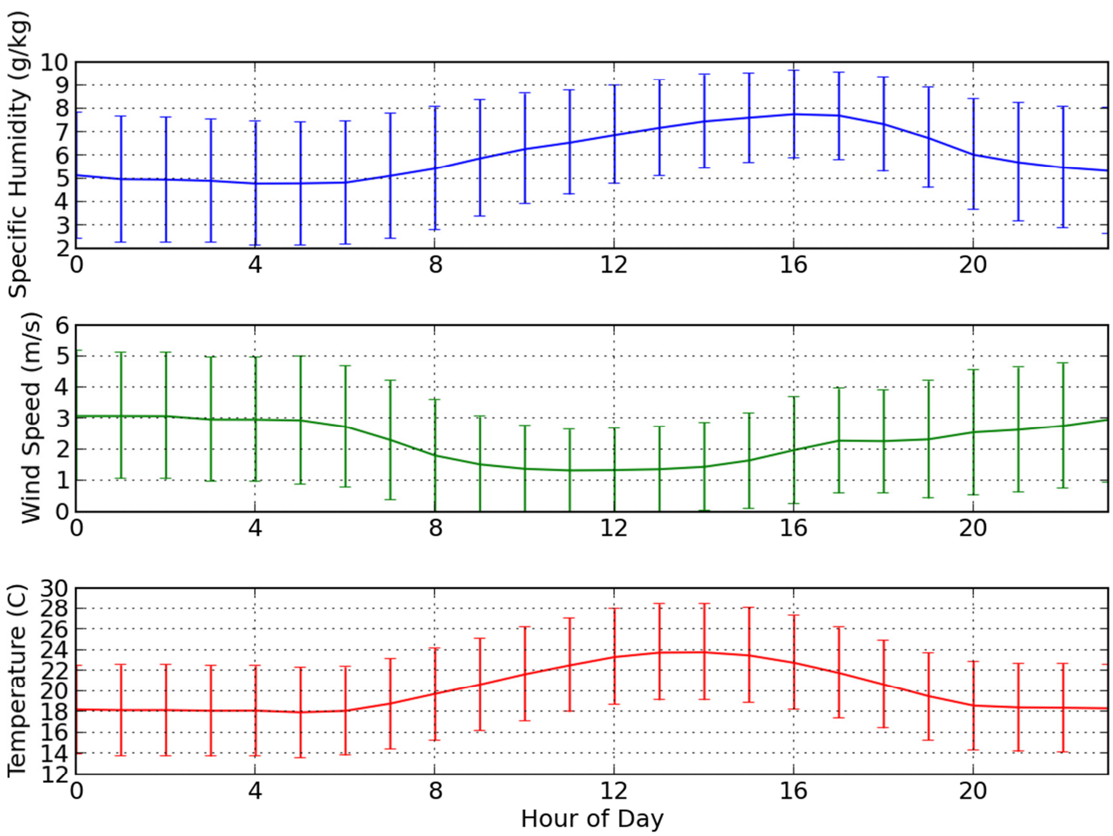


4.1 <u>Chews Ridge Observations Reveal Significant Transboundary Ozone Flows</u>

Chews Ridge mean diurnal profiles of wind speed, specific humidity, and ozone through June, July, August, and September (JJAS) for 2012-13 are shown in **Figure B-23**. In brief, during the daytime there is a rise in specific humidity with a 4 pm peak, a slackening of wind speed in mid-day, as well as a temperature peak in mid-afternoon. This diurnal pattern indicates the development of a convective boundary layer on the mountainous terrain in the daytime with subsequent effects on observed ozone concentrations. The convective coupling in general increases surface drag and reduces windspeed, while increased solar radiation promotes stomatal conductance from vegetation and thus evapotranspiration leading to a rise in specific humidity and a fall in ozone concentrations due to dry deposition.

UC Davis researchers have concluded that this is the most plausible interpretation of these daily patterns, because there is no sign of a regular land-sea breeze or valley-mountain circulation driven by diurnal heating patterns.[28] **Figure B-24** shows the average diurnal ozone profiles for Chews Ridge, Arvin, and Fresno for the ozone seasons of 2012-13, defined here as June 1 through September 30. The three SJV sites display diurnal ozone profiles that are typical of sites found either in urban environments (Fresno), areas downwind from urban environments (Arvin), or elevated sites in the Sierra Range (Lower Kaweah). Photochemical production during the day and reaction of ozone (titration with fresh NO emissions and dry deposition) under a shallow nocturnal boundary layer at night dominates the profile of the two Valley floor sites.

Figure B-23. Chews Ridge mean diurnal profiles through June, July, August, and September (JJAS) for 2012 and 2013.
Source: Post et al., 2013.

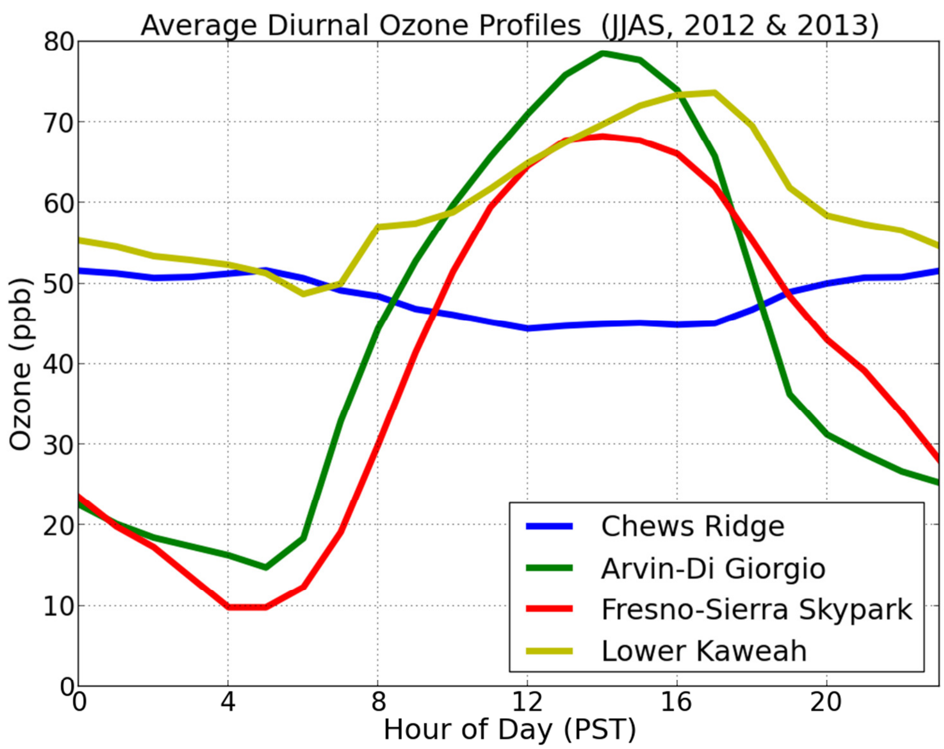


In contrast, the Chews Ridge diurnal profile sees a 6-8 ppb decrease in concentration during the day. The lack of any significant sources of NOx at Chews Ridge prevents any major photochemical production of ozone during the day. The small amplitude of the diurnal ozone profile further validates the use of concentrations measured at Chews Ridge as being representative of free tropospheric, or background, conditions. The

[28] Faloona, F., et al. (2013) A Study of Long Range Transport of Ozone and Aerosols to the San Joaquin Valley Air Quality Research Center. Annual Report to the San Joaquin Valley Air Pollution Control District. UC Davis, June. http://www.valleyair.org/General_info/pubdocs/pubdocs.htm

slight decrease in ozone during the day is quite likely due to stomatal uptake by vegetation and possibly weak photochemical destruction occurring in the convective boundary layer that is present during the day.[29] Regarding the possibility that easterly flows measured at Chews Ridge contain recirculated ozone from California-based anthropogenic sources, research by Parrish et al. (2010)[30] indicates that air sampled in the 1-2.5 km altitude range is representative of background mid-latitude air with respect to ozone and CO.

Figure B-24. Mean diurnal O3 profile at Chews Ridge and CARB/SJVAPCD monitoring sites for JJAS, 2012 and 2013.
Source: Post et al., 2013.



The distribution of ozone concentrations at Chews Ridge during the night (defined as 20:00 – 06:00 PST) and day, respectively, is shown in **Figures B-25 and B-26**. Two major wind modes are present during both day and night; a northeast (NE) offshore flow and a west/southwest onshore flow. During both periods the very highest concentrations of ozone tend to occur under west-southwesterly (WSW) flow

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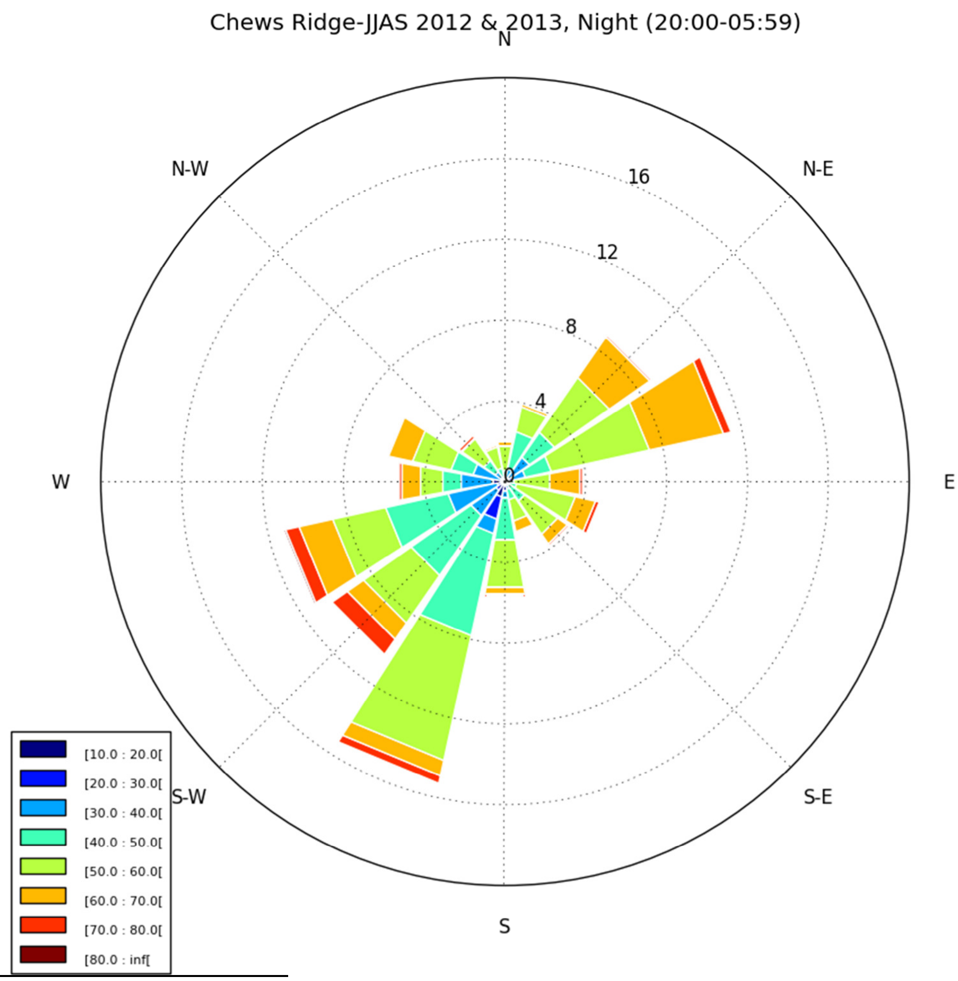
[29] Post et al. (2013) Lower tropospheric ozone and aerosol measurements at a coastal mountain site in Central California. Poster presentation at the AGU Fall Meeting (A53C-0199). Session: Constituent Source Characterization, Transport, and Chemistry II. Dec. 13.

[30] Parrish, D.D., et al. (2010) Impact of transported background ozone inflow on summertime air quality in a California ozone exceedance area. *Atmos. Chem. Phys.*, 10, 10093–10109, doi: 10.5194/acp-10-10093-2010.

conditions.[31] This finding supports the hypothesis that the WSW ozone inflow at this altitude is transboundary ozone comparable to what the Pt Sur ozonesondes measured during the IONS-2010 field study at 1,500 m. And, as shown above in **Figure B-5**, the Pt. Sur and Pt. Reyes ozonesonde concentrations at 1,500 m were highly correlated due to the tendency for ozone transport to occur in broad laminae or stratified layers.[32]

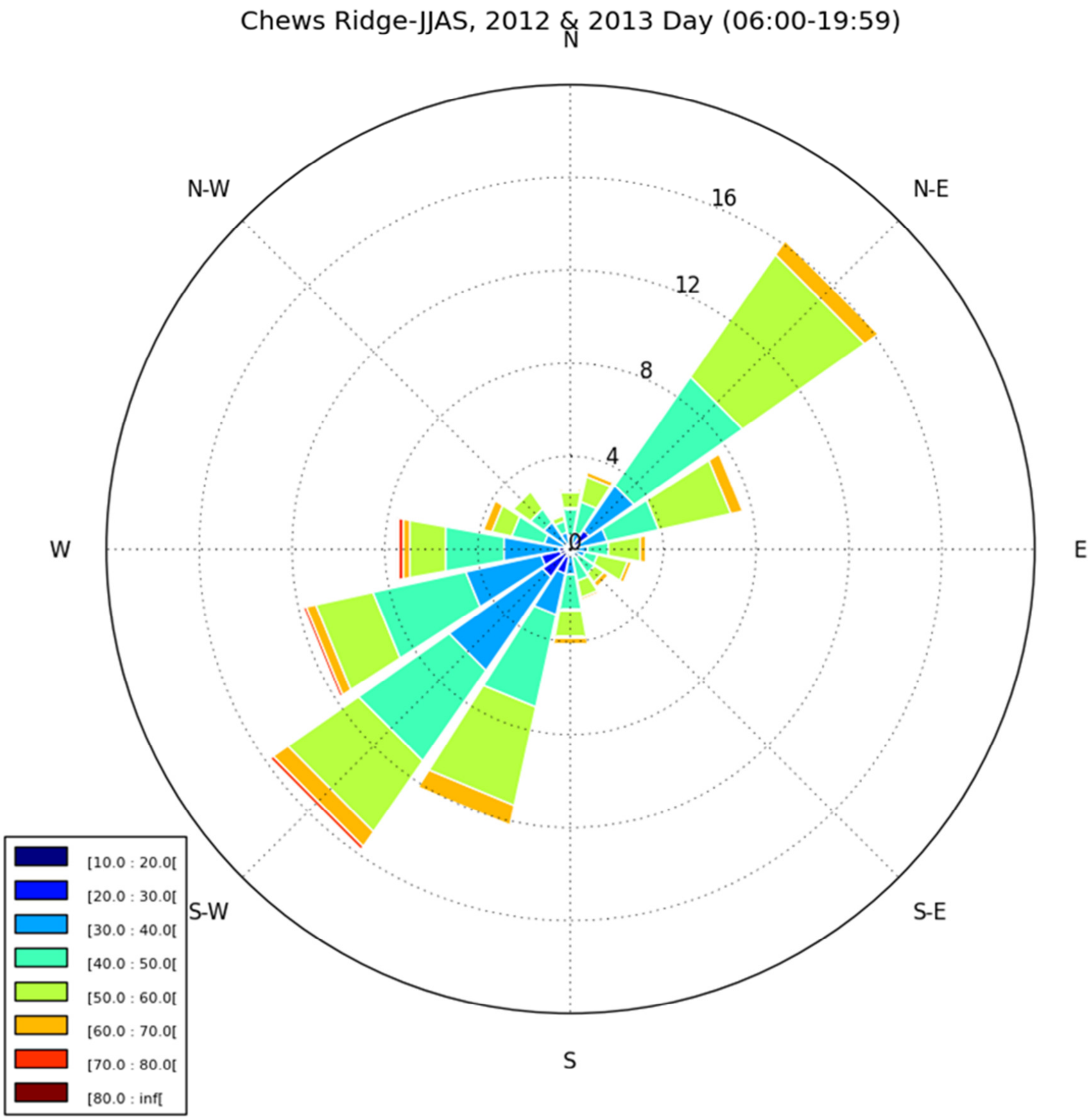
Figure B-25. Distribution of nocturnal ozone, wind speed, and wind direction at Chews Ridge.
Source: Post, et al., 2013.



[31] NCAR/NCEP reanalysis data of the region conducted by UC Davis indicates that while the prevailing geostrophic wind at the 700 mb level is southwesterly, the 850 mb surface is much less well defined with weak northerly or possibly northeasterly flow at that level (approximately the altitude of Chews Ridge), most likely strongly influenced by the local topography. See: Faloona, I., et al. (2013) A Study of Long Range Transport of Ozone and Aerosols to the San Joaquin Valley Air Quality Research Center. Annual Report to the San Joaquin Valley Air Pollution Control District. UC Davis, June. http://www.valleyair.org/General_info/pubdocs/pubdocs.htm

[32] Liu, G., et al. (2009) Ozone correlation lengths and measurement uncertainties from analysis of historical ozonesonde data in North America and Europe. *J. Geophys. Res.*, 114, D04112, doi:10.1029/2008JD010576.

Figure B-26. Distribution of daytime ozone, wind speed, and wind direction at Chews Ridge.
Source: Post, et al., 2013.



Again, these points are raised here to emphasize empirical support for the inference that (1) ozone concentrations measured in transboundary, onshore airmasses at 1,500 m by the Pt. Sur and Pt. Reyes ozonesondes in 2010 are also highly correlated with those measured at the same altitude by the Chews Ridge field station, and (2) Chews Ridge concentration levels measured in August 2012 can thereby serve as a surrogate for the level of transboundary ozone found in the offshore airmasses at 1,500 to 2,500 m shown in **Figure B-4** that were transported to Fresno on Aug. 10, 2012.

5. QUANTITATIVE MODELING BASED ON OBSERVATIONAL RESEARCH IN THE SJV PROVIDES CLEAR EVIDENCE THAT THE EXCEEDANCE IN FRESNO ON AUGUST 10, 2012 WOULD NOT HAVE OCCURRED BUT FOR THE CONTRIBUTION OF TAO TO SURFACE CONCENTRATIONS

As noted above, under the leadership of Dr. Ian Faloona's atmospheric science group at UC Davis, the District has supported the collection of two years of ozone data (2012-13) at an observation site located approximately 30 km east of Pt. Sur in the Santa Lucia mountain range of Monterey County at an altitude of 1,544 m a.s.l. The scientific motivation for establishing this high altitude, seaboard monitoring station is that unlike past studies that have relied on airborne or ozonesonde data. This experiment has made it possible to continuously monitor the composition of transboundary airmasses in the free troposphere, well above recent marine influence, as it flows onshore and influences the photochemical boundary conditions above the convective boundary layer of the San Joaquin Valley.

Meteorological observations indicate that the Chews Ridge site experiences two main flow regimes during the June-September ozone season: southwest-westerly winds occur (approximately 60% of the time), and northeasterly winds. The wind direction does not exhibit a diurnal oscillation, and thus these two flow patterns are not believed to result from a mountain-valley or land-sea breeze circulation. Above the site, at 700 hPa, the climatological trough that typically resides offshore during ozone season drives a southwesterly geostrophic wind, but when the inland thermal low grows deep enough and migrates southward, it can yield north-northeasterly flow at 850 hPa, approximately the altitude of Chews Ridge. It is the interplay of these two forcing features, the former from above and the latter from the surface, that predominantly determine the character of surface wind at the observation site. To account for this polarity, the data has been filtered for hours when the wind is onshore in all the ensuing analysis. Monthly mean concentrations for 2012-13 of onshore airmasses are shown in **Figure B-27**, indicating an approximate average in Aug. 2012 of 52 ppbv.

The nocturnal ozone pollution rose of **Figure B-26** illustrates this dual wind flow and some interesting characteristics of the background onshore flow. The radial measure is the frequency of the wind from that direction, and the colors denote the frequency of each binned ozone concentration in each wind sector. A very similar bimodal distribution of winds is seen for the daytime data, characterized by lower average ozone concentrations due to uptake by vegetation when the surface is strongly coupled to the flow in the lower free troposphere and photosynthesis is active. **Figure B-26** shows that while the median ozone is higher during northeasterly wind (~55 ppbv), the range of concentrations experienced is much greater during the onshore winds where, in fact, the highest ozone levels are found. This then represents the variability in the background ozone that is transported from distant sources to Central California.

Figure B-28 illustrates the wind direction and ozone on Chews Ridge during August 10, 2012 and the two days preceding the event, indicating the fairly typical, non-diurnal shift in the wind directions described above. Because observations made during the northeasterly flow could conceivably be contaminated by continental sources, this vector is not included here as a measure of the free tropospheric background. Instead the analysis focused on those ozone concentrations observed in the 24 hours prior to the exceedance that were found in onshore winds. The average concentration under these conditions, which all occurred at night when the ozone levels at Chews Ridge are relatively unmodified by uptake by vegetation, is 54.8 ppbv. Thus, we consider this to be representative of the air mass flowing over the San Joaquin Valley at the altitude just above the daytime atmospheric boundary layer (approximately 1.5 km).

Evidence that the ozone concentrations observed at Chews Ridge are representative of the lower free troposphere over the San Joaquin Valley is found in the correlation between the mountaintop ozone observations and those measured by daily aircraft profiles under the auspices of the California Air Resources Board. A total of 206 flights made during the ozone seasons of 2012 and 2013 above Fresno were compared against the ozone observed on Chews Ridge simultaneously and at multiple day intervals prior, with the results presented in **Figure B-29**. The peak correlation of the ozone concentrations at Chews Ridge occurs above Fresno at 1100 m, which is typically directly above the daytime convective boundary layer. Using NOAA's network of radar wind profiles equipped with radio acoustic sounding systems, a 2008 year-long study of atmospheric boundary layer (ABL) depths, found that midday maxima averaged between 700-1000 m from June to September at Chowchilla, a site about 60 km northwest of Fresno.[33]

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[33] Bianco, L., et al. (2011) Diurnal evolution and annual variability of boundary-layer height and its correlation to other meteorological variables in California's Central Valley. *Boundary-Layer Meteorology*. June 10, doi: 10.1007/s10546-011-9622-4.

Figure B-27. Monthly ozone concentrations (ppbv, with +/- 1 standard deviation) measured at Chews Ridge during hours of onshore flow at night. These conditions should be least likely to be contaminated by North American precursor emissions.
Source: Faloona, I., personal communication, Feb. 10, 2014.

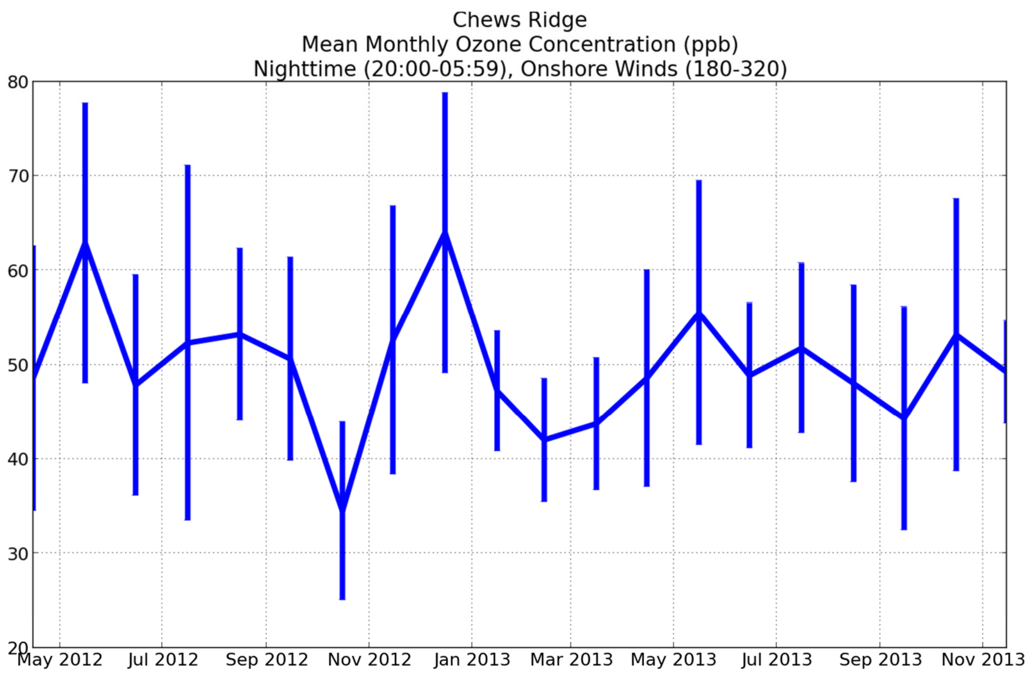


Figure B-28. Hourly ozone and wind direction at Chews Ridge observatory from Aug. 8-10, 2012 along with the corresponding surface ozone at the Arvin-DiGiorgio surface site in the southern San Joaquin Valley.
Source: Faloona, I., personal communication, Feb. 10, 2014.

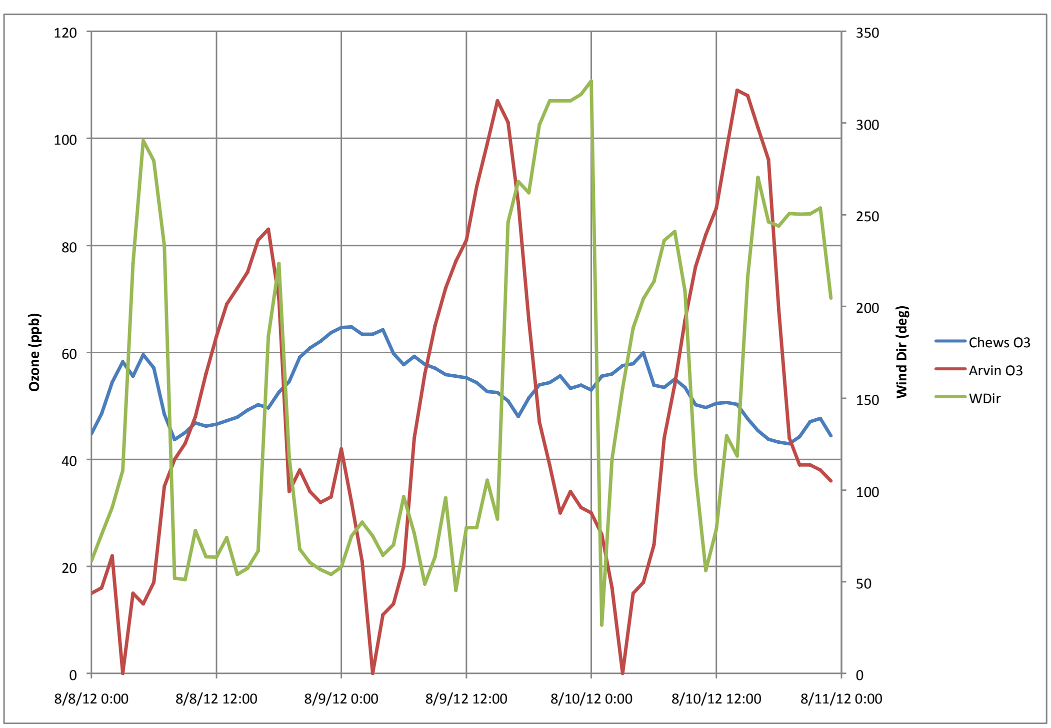
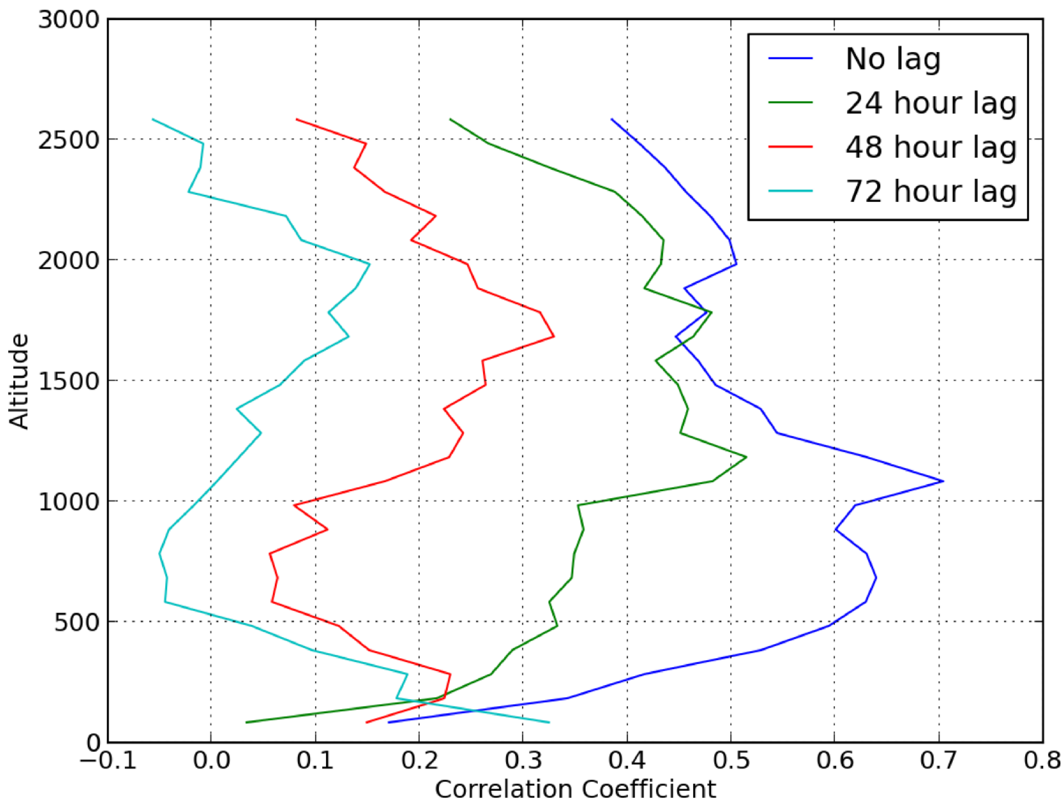


Figure B-29. Correlation coefficients between ozone measured by aircraft vertical profiles above Fresno and ozone at Chews Ridge for 0-3 days lag.
Source: Faloona, I., personal communication, Feb. 10, 2014.



The fact that the strongest correlation between ozone measured above the daytime valley boundary layer top and ozone at Chews Ridge is observed to be simultaneous is likely a consequence of the fact that ozone in the free troposphere generally exists in geographically broad laminae that decorrelate over 100's of km (Liu et al., 2009).[34] So rather than suggesting that the flow pattern between the two sites is via a direct trajectory from Chews to Fresno, evidence from the CalNEX/IONS-2010 campaign and the back trajectory results shown in **Figure B-4** provide reinforcing evidence that the primary flows to Fresno are via airmasses that enter the free troposphere of California through the coast range gap between Pt. Reyes and the Carquinez Straight. In total, these findings provide further evidence that transboundary ozone concentrations measured in onshore winds at Chews Ridge are representative of concentrations found in the Fresno Aug. 10., 2012 back trajectories to the Pt. Reyes/Carquinez gap at 1,500 to 2.500 m.

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[34] Liu, G., et al. (2009) Ozone correlation lengths and measurement uncertainties from analysis of historical ozonesonde data in North America and Europe. *J. Geophys. Res.*, 114, D04112, doi:10.1029/2008JD010576.

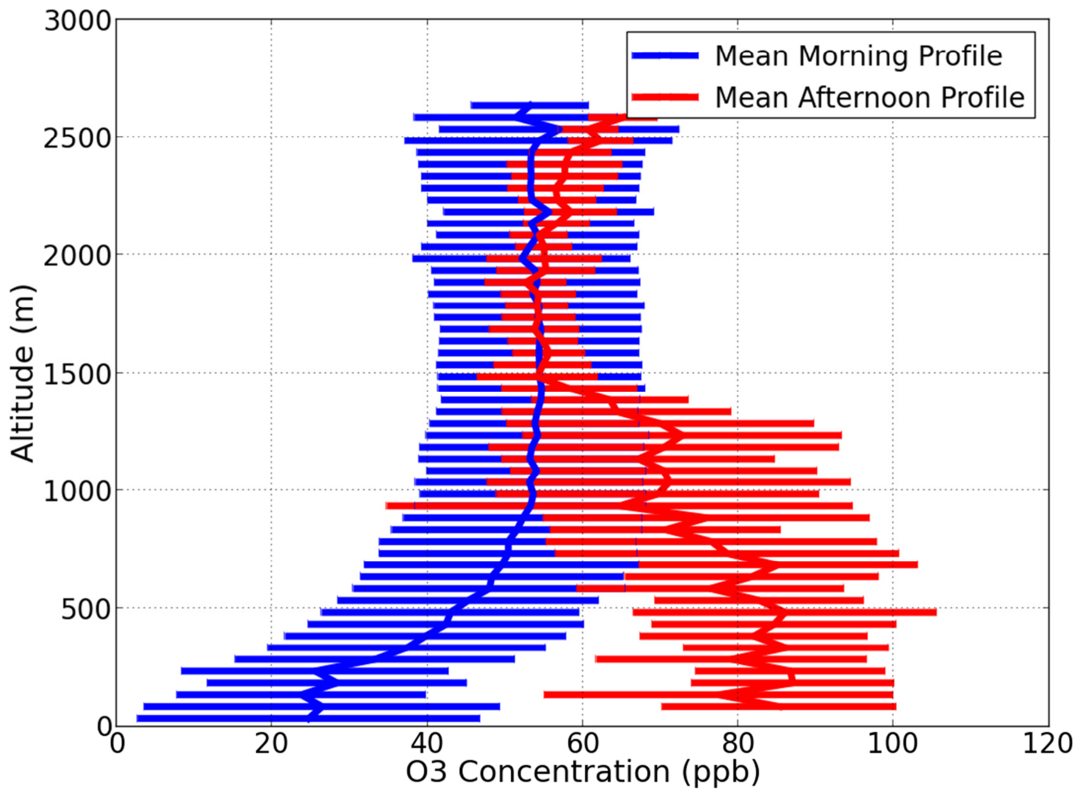
During the daytime, when ozone reaches its peak, convective thermals generated at the surface rise and penetrate into the stable layer that demarcates the interface between the turbulent boundary layer and the laminar (non-turbulent) free troposphere above it. The continuous action of these thermals penetrating into the laminar overlying air and falling back into the boundary layer gives rise to an irreversible mixing process that causes the layer to grow up through the mid-morning to afternoon, diluting the boundary layer air with that of the free troposphere. The overall process is referred to as entrainment, and when the two layers contain different amounts of ozone, such entrainment mixing contributes to surface ozone concentrations.

In other words, ozone concentrations in free tropospheric airmasses that are entrained into the Valley daytime boundary layer are lower than daytime ground level concentrations. As a result, this entrainment process does have the effect of diluting daytime ground level concentrations. <u>However, the dilution effect from entrainment is considerably less than would be the case if free tropospheric flows did not contain transboundary ozone</u>. So in effect, transboundary ozone, and the TAO fraction contained within it, does indeed have the net effect of enhancing ground level concentrations due to boundary layer entrainment.

Figure B-30 shows the average vertical profiles measured from the ARB flights performed above Fresno during the 2012/2013 ozone seasons separated into predawn and dusk flights. The averages and standard deviations (horizontal error bars) of the 50 m altitude bins nicely demonstrate the diurnal boundary layer behavior. It is clear that, day or night, above 1,500 m altitude, there are no systematic vertical ozone gradients and the average concentration is very similar to that observed at Chews Ridge (~55 +/-8 ppbv). For the early morning soundings this pattern continues to just below 1,000 m and then rapidly decreases towards the surface. There does appear to be a nearly well-mixed layer below 250 m at night which arguably corresponds to the approximate depth of the average nocturnal boundary layer. **Figure B-30** directly illustrates how the boundary layer ozone concentrations increase throughout the day due to photochemical production.

The key point here is that with a constant value in the lower free troposphere the entrainment mixing switches from a source of ozone to the surface in the morning hours to a dilution influence in the afternoon. Also, the ozone profiles appear to be well-mixed during the day to about 750 m, where we expect the climatological boundary layer height to be. Because there were only three afternoon flights, it is not clear what the exact origins of the fall off between 750 m and 1500 m are, but it is likely the result of convective lofting and horizontal advection from nearby regions of the San Joaquin Valley.

Figure B-30. Average ozone profiles measured on 206 flight profiles operated out of Fresno by CARB during the summers of 2012 and 2013. The horizontal bars represent +/- 1 standard deviation of each 50 m binned data. Only 3 of the flights were conducted in the late afternoon (~17:00 PST), and the rest were flown between 4:00-5:00 PST.
Source: Faloona, I., personal communication, Feb. 10, 2014.



To quantify its impact on the evolution of surface ozone concentrations in the San Joaquin Valley, the District supported an airborne campaign led by Dr. Faloona's group in the vicinity of Arvin, CA during the summer of 2013. Three flight intensives of three days duration each were conducted around and upwind of Arvin for 3-7 hours per day, for three successive days. Each of three flight intensives included 72 hr. observations of wind, temperature, water vapor, and ozone which were used to measure the principal dynamical components of the total ozone budget, i.e. advective up-valley transport within the ABL (boundary layer) and entrainment mixing from above. By comparing these measured dynamical terms with the observed ozone rise throughout the region during the afternoon, and using a reasonable parameterization of dry deposition, the net photochemical production rate can be inferred. Consequently, the relative contributions of these processes to the resulting surface ozone concentration can be estimated.

Table B-3 summarizes the preliminary results from this experiment, indicating that the entrainment velocity (an exchange coefficient that parameterizes the entrainment mixing rate) is between 4.9-10.7 cm/s during the summertime over the southern San Joaquin

Valley. Comparable values ranging from 1.4 to 9.6 cm/s were observed in a different aircraft study over the Central Valley using flux measurements of isoprene during June of 2011.[35]

Briefly, the ozone budget of the ABL can be mathematically represented as:

$$\frac{\partial O_3}{\partial t} = -U\frac{\partial O_3}{\partial x} - \frac{1}{z_i}\left(v_{dep}O_3 + F_{ent}\right) + P \qquad (1)$$

Where the first term on the left represents the observed temporal trend in a fixed region, the second term represents the advection (the influence of the mean wind, U, acting on the large scale gradient in the ozone field), z_i is the ABL depth, v_{dep} is the deposition velocity representing foliar uptake of ozone by plants at the surface, F_{ent} is the entrainment flux due to mixing at the top of the ABL, and P represents the net photochemical production.[36]

In these types of ABL budget studies, a common parameterization for the entrainment flux is employed that estimates it to be proportional to the difference in concentration between the ABL and the free troposphere, across the inversion interface. In the Arvin study, the budget for water vapor, a conserved quantity in the absence of precipitation, is used to infer the entrainment flux (similar to ozone this is a dilution or drying effect). Based on the observed difference in water vapor between the ABL and the free troposphere, the entrainment velocity is derived. In principle this entrainment velocity is applicable to any scalar quantity (e.g., potential temperature, water, ozone, or methane) and represents a net consequence of the turbulent action in the ABL. In strongly convective situations such as commonly experienced in the summertime San Joaquin Valley, the vigor of entrainment is a balance between the surface heating, which generates thermals that overshoot the ABL top, in opposition to the strength of the temperature inversion, which resists their vertical penetration (see also **Figure B-15**). The mathematical relationship between entrainment flux, F_{ent}, and entrainment velocity, w_e, and the jump in concentration between the ABL and free troposphere can be expressed as:

$$F_e = w_e \bullet \Delta[O_3]_{(FT\text{-}ABL)} \qquad (2)$$

[35] Karl, T., et al. (2013) Airborne Flux Measurements of BVOCs above Californian Oak Forests: Experimental Investigation of Surface and Entrainment Fluxes, OH Densities, and Damköhler Numbers. Vol 70: 3277-87. doi: 10.1175/JAS-D-13-054.1

[36] Conley, S., et al. (2011) A complete dynamical ozone budget measured in the tropical marine boundary layer during PASE. *J. of Atmos. Chem.* Aug. 19. doi: 10.1007/s10874-011-9195-0

Table B-3. A compilation of preliminary data from the airborne Arvin ozone study conducted by UC Davis. The four principal terms of the ozone budget, equation (1), are reported (in ppbv per hour, averaged over 5 midday hours) which sum to the overall time rate of change of ozone (second column) observed across the ~30 km region upwind of Arvin, CA. W_e is the entrainment velocity.

Date	dO_3/dt (ppb/hr)	O_3 Advection (ppb/hr)	O_3 Deposition (ppb/hr)	O_3 Entrainment Flux (ppb/hr)	Photochemical Production (ppb/hr)	w_e (cm/s)	O_3 8-hr max (ppb)
06/27/13	4.5	-3.4	-1.1	-4.8	13.8	4.9	59.0
06/28/13	5.2	-0.6	-1.5	-1.7	9.0	6.4	73.8
08/13/13	2.5	-5.8	-1.4	-1.8	11.5	8.6	74.4
08/14/13	5.4	-4.2	-1.6	-2.5	13.7	5.7	**81.1**
08/15/13	3.3	-5.9	-1.5	-0.7	11.5	5	**81.9**
09/28/13	5.0	-0.6	-1.2	-3.4	10.1	6.2	60.8
09/29/13	1.1	0.5	-1.3	-2.7	4.6	10.7	63.1
09/30/13	3.9	-0.3	-0.7	0.1	4.9	6.5	46.9
AVERAGES	**3.9**	**-2.5**	**-1.3**	**-2.2**	**9.9**	**6.8**	**67.6**
STD	**1.5**	**2.6**	**0.3**	**1.5**	**3.6**	**2.0**	**12.2**

The data from the airborne Arvin study indicate that, although it varies substantially from day to day, the entrainment mixing of ozone is on average more than 20% as large as that due to in-situ photochemical production. Notice, however, that in the summertime afternoon when ABL ozone is growing due to regional precursor emissions, the entrainment mixing represents a diluting influence tending to weaken the growth rate on the ABL ozone concentration. Thus the difference between no ozone flux and the average value of -2.2 ppb/hr, integrated over the course of the afternoon, results in a difference of approximately 12.5 ppbv by the time of the afternoon ozone peak.

Turning to the seasonal ozone patterns on Chews Ridge, there is a springtime peak that is consistent with the ozone sonde climatology at 2 km altitude reported for Trinidad Head in northern California (Parrish et al., 2010). **Figure B-27** shows the monthly mean ozone at Chews Ridge for nocturnal conditions of onshore flow, which are most characteristic of transboundary ozone concentrations in the free troposphere and least likely to be influenced by North American pollution sources. Note that the Aug. 2012 mean concentration of nocturnal offshore flow was elevated above the two year mean of 48.2 ppbv.

Given this combination of empirical factors based on flight intensives conducted in the San Joaquin Valley coupled with hourly ozone concentrations and related met parameters gathered at Chews Ridge, it is possible to calculate the net contribution of TAO to the peak hourly observation at the Drummond Ave. monitor on Aug. 10, 2012. Included here are two estimates, both representing conservative assumptions about the fraction of TAO contained within the total transboundary ozone that was being entrained on the day of the exceedance.

The monthly mean concentration of nocturnal onshore airmasses measured at Chews Ridge for Aug. 2012 was 52 ppbv (see **Figure B-25**). Ozone concentrations in nocturnal onshore winds at Chew Ridge during the 24 hours prior to the exceedance averaged 55 ppbv.[37] Therefore, the most conservative estimate possible would be to assume that the 3 ppbv elevation of transboundary flows in Aug. 2012 were representative of transboundary flows that were elevated above the mean due to TAO production by transpacific sources. This 3 ppbv increment could thereby represent the total fraction of TAO available for entrainment in the Valley boundary layer with subsequent impact on ground level monitors. This 3 ppbv increase equates to a difference in ozone entrainment flux of (3 x 0.068) = 0.20 ppb m/s, based on the average entrainment velocity observed during the Arvin aircraft experiment. Because the flux is then disbursed throughout the mixed boundary layer with a typical dimension of 800 m, this difference in entrainment dilution amounts to a rate of 0.9 ppb/hr. Over the course of 5 midday hours when the entrainment is strongest and the exceedance event takes place at the Fresno Drummond site, this amounts to an additional 4.5 ppbv of ozone at the peak hour of 1300 PST due to entrainment of TAO resulting from transpacific anthropogenic sources, i.e. Asian, shipping, and European emissions.

However, as noted above, the large assemblage of ozone observations in North America since 1984 by Cooper et al. (2010) provides the best empirical source for inferring the current fraction of TAO found in transboundary ozone entering California airspace (see **Figure B-10**).[38] They estimate an increase of approximately 15 ppbv since 1984. Given corresponding Asian emission trends, this increase in Northern Hemispheric background is a predictable result of increased TAO from transpacific emissions by Asia and South Asia. These data provide the firmest empirical foundation for estimating the fraction of TAO that was contained in the flows of transported background ozone that are measured at Chews Ridge and in the back trajectories shown in **Figure B-4**. This TAO increment was estimated at approximately 15 ppbv. Therefore a conservatively estimated range of the TAO fraction found in the airmasses shown in **Figure B-4** would be 10 to 15 ppbv. Employing the same linear formula used above, the hourly entrainment dilution per hour cumulative over 5 hours results in a net contribution from TAO to the peak hourly observed ozone at the Drummond Ave monitor of 15 to 22.5 ppbv respectively. The District has concluded that this range represents the most well-supported estimate of the TAO contribution to peak hourly observations at the Drummond monitor on Aug. 10, 2102.

6. SUMMARY OF EVIDENCE AND CONCLUSIONS

Based on the full measure of scientific evidence presented above, the District has concluded that transboundary anthropogenic ozone from transpacific sources made a critical contribution to ground level ozone concentrations on Aug. 10, 2012, resulting in the exceedance of the 1 hr. ozone standard by 3 ppbv over the standard at the Fresno Drummond Ave. monitor. This evidence is summarized below in the sequence presented above.

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[37] Faloona, F., et al. (2013) A Study of Long Range Transport of Ozone and Aerosols to the San Joaquin Valley Air Quality Research Center. Annual Report to the San Joaquin Valley Air Pollution Control District. UC Davis, June. http://www.valleyair.org/General_info/pubdocs/pubdocs.htm

[38] Cooper, O.R., et al. (2010) Increasing springtime ozone mixing ratios in the free troposphere over western North America. *Nature Letters*, Vol. 463, 21 January, doi:10.1038/nature08708.

I. There is Substantial Baseline Evidence in Support of the Hypothesis that the Aug. 10, 2012 Exceedance at the Drummond Ave. Monitor Would Not Have Occurred But For the Influence of Transboundary Anthropogenic Ozone.

A. A confluence of the following geophysical conditions prior to and on Aug. 10, 2012 were conducive for TAO transport to Fresno area surface monitors:

1. The strong high pressure system that had begun development on Aug. 6, 2012 set in place a meteorological environment that would facilitate entrainment of ozone and ozone precursors into the San Joaquin Valley boundary layer.

2. The very high surface temperatures on Aug. 10 generated very strong thermal lifting from the Valley floor and especially from adjoining slopes of the Sierra and Coast ranges. The effect of this thermal lifting was to promote downward entrainment of ozone from the free troposphere to the Valley surface.

3. The 72 hr. back trajectories from Fresno shown in **Figure B-4** provide compelling evidence that the predominant pathways for air masses arriving in Fresno on Aug. 10, 2012 were northwesterly flows from offshore the northern California coast. These pathways were identified by Cooper et al. (2011)[39] as the predominant pathway for transboundary ozone flows affecting surface concentrations in the southern SJV. In addition, the back trajectories also show a process of subsidence to the surface from the 2500—1500 m layer of the free troposphere where transboundary ozone from transpacific sources is most predominant.

4. The high correlation between data from ozonesondes launched from Pt. Reyes, near the midpoint of the predominant northern coastal entry point for the lower tropospheric airmasses depicted in **Figure B-4**, and Pt. Sur, located on the coast 30 km east of the Chews Ridge field station, provides substantial empirical support for using Chews Ridge ozone concentrations at 1,500 m as a surrogate for northern California flows at the same lower tropospheric altitude in the vicinity of Pt. Reyes.

5. As shown in **Figures B-6** and **B-7**, satellite data retrievals from the week of Aug. 4-10 reveal transpacific flows of ozone and NO2. The concentration levels indicate consistent elevation across the west to east hemispheric transport corridor into California airspace. The spatial scope and concentration levels depicted reveal the clear potential for TAO impacts on ground level monitors in the San Joaquin Valley under the conditions of high pressure subsidence that prevailed at the time of the exceedance.

[39] Cooper, O. R., et al. (2011) Measurement of western U.S. baseline ozone from the surface to the tropopause and assessment of downwind impact regions. *J. Geophys. Res.*, 116, D00V03, doi: 10.1029/2011JD016095.

II. Transboundary anthropogenic ozone inflows to the western US and California have grown rapidly in recent decades and have been shown to comprise a significant fraction of overall transboundary ozone.

A. The conditions for stable, long-distance transport of TAO in the free troposphere to the western US are ideal, as are the conditions for air mass subsidence from the free troposphere into the boundary layer of the western US. As shown in **Figure B-8**, deep convection of NOx, PAN, and ozone from Asian fossil fuel combustion is transported via the prevailing tropospheric air mass flows to the West Coast where subsidence leads to mixing into the boundary layer.

B. As shown in **Figure B-9a and B-9b**, Asian NOx emissions, from China in particular, have grown rapidly in recent decades while US and European emissions have declined.

1. China's 2005--2010 estimated annual NOx growth rate was 4.01 ± 1.39%, following a period of very rapid annual growth from 2000-2006 of 5.8–10.8%. For CO2, growth rates in 2012 were 5.9 % for China and 7.7 % for India whereas US and European 2012 emissions declined by 3.7 % and 1.8 % respectively.

2. These increases in Asian production of NOx, PAN, and ozone are accompanied by a corresponding increase in their hemispheric transport from Asia to North America. As measured at high altitude sites in western North America, Cooper et al. (2010) report a median annual increase in background ozone of 0.66 ppbv between 1984 and 2008, or approximately 15 ppbv over the entire period (see **Figure B-10**).[40] As authors note, there is little likelihood that this increase is attributable to ozone with North American or European origins given that emissions from these regions have been declining since the mid-1980s as have extreme ozone events in urban centers across much of the US, including the San Joaquin Valley.

3. This 15 ppbv increase since 1984 closely tracks the growth in Asian emissions. This estimate is conservative in that it does not include the pre-1984 contribution from Asia which, if known, would logically be added to the post-1984 level. It further does not include the contribution from European sources, which under §179B, is also not the responsibility of US air districts. As such, 15 ppbv represents a conservative lower bound estimate of the total fraction of transboundary anthropogenic ozone found in transboundary ozone that is entrained into the boundary layer of California and the San Joaquin Valley.

III. Three case studies of transboundary ozone impacts in California provide additional evidence of the link between transboundary ozone flows and ground level ozone concentrations in the Sacramento and San Joaquin Valleys.

[40] Cooper, O.R., et al. (2010) Increasing springtime ozone mixing ratios in the free troposphere over western North America. *Nature Letters*, Vol. 463, 21 January, doi:10.1038/nature08708.

A. Parrish et al. (2010)[41] found a high correlation between daily variations in ozone concentrations discovered in transboundary air masses in the free troposphere above the coastal sonde launch site at Trinidad Head and daily variations in ozone levels at six surface sites in northern California (see **Figure B-12**).

1. Correlation coefficients between daily sonde values in the lower free troposphere (1 to 2.2 km) and regional surface sites ranged from 0.43 in Redding, 0.51 at Red Bluff and Tuscan Butte, 0.61 at Lassen NP, to 0.70 in Yreka.

2. As shown in **Figure B-12**, May through August transpacific ozone inflows 1 to 2.2 km above Trinidad Head ranged from 54 to 48 ppbv, a concentration range that is quite similar to the summer season averages of transboundary airmasses measured at the Chews Ridge observation station.

3. Based on the weight of evidence, the authors conclude that transboundary ozone inflows 1 to 2.2 km above Trinidad Head are contributing consistently to ground level concentrations via subsidence and entrainment into the boundary layer of the northern Sacramento Valley.

B. The IONS-2010 ozonesonde study conducted by NOAA and NASA found evidence of transboundary ozone entrainment to ground level sites in the San Joaquin Valley comparable to findings identified by Parish et al. (2010) in the northern Sacramento Valley.

1. Transboundary ozone concentrations measured by coastal ozonesondes launched at 3 coastal California sites are relatively similar at 1.5 to 3 km a.s.l., averaging approximately 50 to 60 ppbv. This concentration range is consistent with the 2012-13 summertime concentrations measured at the Chews Ridge monitoring site.

2. Below 2 km, the Pt. Reyes (RY) site was found to be responsible for a relatively high level of delivery to the mid- and south Central Valley when compared to the other coastal sonde sites. This transport pathway is consistent with the results of the back trajectory analysis of the Drummond exceedance case shown in **Figure B-4**.

3. As shown in **Figure B-17**, the vertical concentration profiles from the IONS-2010 sondes at Pt. Sur (PS) and Pt. Reyes (RY) are highly correlated in strata below 2 km a.s.l., indicating that they are measuring the same air masses at the same time. This provides further support for conclusion I.A.4. made above that concentrations of transboundary ozone measured at 1.5 a.s.l. at Chews Ridge can serve as robust surrogates for concurrent inflows at Pt. Reyes at the same altitude.

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[41] Parrish, D.D., et al., (2010) Impact of transported background ozone inflow on summertime air quality in a California ozone exceedance area. *Atmos. Chem. Phys.*, 10, 10093–10109, doi: 10.5194/acp-10-10093-2010.

C. Huang et al. (2012) used advanced modeling techniques to determine that transboundary ozone and precursors were having a substantial impact on surface ozone concentrations in the Central Valley of California and the US West in general.[42]

1. As shown in **Figure B-21(a)**, the authors estimated that transboundary ozone was contributing between 28 to 32 ppbv to daily 8 hr. average concentrations in the San Joaquin Valley.

2. Assuming the estimated TAO fraction of 15 ppbv represents approximately 25 to 33% of the total transboundary ozone (45 to 60 ppbv) found in California's lower troposphere in summer, it is reasonable to conclude based on Huang et al.'s modeling that the TAO contribution to peak 1 hr. ozone concentrations to the central San Joaquin Valley is significantly larger than 3 ppb, the exceedance level registered at the Drummond Ave. monitor on Aug. 10, 2012.

IV. Fixed site and ozone sonde monitoring conducted by UC Davis (2012 and 2013) and by NOAA (2010) in central California provide further empirical support for the validity of ozone measurements at Chews Ridge as a surrogate measure of transboundary ozone flows to Fresno.

A. Ozone concentrations measured in transpacific, westerly airmasses at 1,500 m by the Pt. Sur and Pt. Reyes ozonesondes in 2010 are highly correlated with each other.

B. Furthermore, ozone observations of transpacific, westerly airmasses at 1,500 m by ozonesondes launched at Pt. Reyes are very highly correlated with concurrent observations of transpacific, westerly flows at 1,544 m made at the Chews Ridge field station located 30 km due east of Pt. Sur.

C. Chews Ridge concentration levels measured in August 2012 can thereby serve as a surrogate for the level of transboundary ozone found in the offshore airmasses at 1,500 to 2,500 m shown in **Figure B-4** that were transported to Fresno on Aug. 10, 2012.

V. Two ozone budget estimates conducted by UC Davis researchers each used conservative assumptions regarding the TAO fraction of the total transboundary ozone contribution to ground level ozone measured in Fresno on Aug. 10, 2012. In both cases the TAO fractional contribution to ground-level concentrations in Fresno exceeded the 3 ppbv margin of the exceedance recorded on that date.

A. The monthly mean concentration of nocturnal onshore airmasses measured at Chews Ridge for Aug. 2012 was 52 ppbv (see **Figure B-25**).

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[42] Huang et al. (2013) Impacts of transported background pollutants on summertime western US air quality: model evaluation, sensitivity analysis and data assimilation. *Atmos. Chem. Phys.*, 13, 359–391. doi:10.5194/acp-13-359-2013.

B. Ozone concentrations in nocturnal onshore winds at Chew Ridge during the 24 hours prior to the exceedance averaged 55 ppbv. Based on the accumulated evidence regarding the continuity between concentrations of transboundary ozone found at Chews Ridge and concentrations recorded by Pt. Reyes and Pt. Sur ozonesondes at the same altitude, these observations serve as representative surrogates for transboundary ozone found in air masses flowing over the San Joaquin Valley just above the daytime boundary layer (approximately 1 to 1.5 km).

C. Further evidence that the ozone concentrations observed at Chews Ridge are representative of the lower free troposphere over the San Joaquin Valley is found in the high correlation between the Chews Ridge ozone observations and observations made just above the daytime boundary layer by daily air flights over Fresno by CARB (see **Figure B-29**). Ozone profiles above Fresno during early morning and afternoon in summer of 2012 and 2013 reveal a consistent vertical ozone gradient above 1,500 m altitude with an average concentration is very similar to that observed at Chews Ridge (~55 +/-8 ppbv).

D. These correlations provide further evidence that transboundary ozone concentrations measured in onshore winds at Chews Ridge are representative of concentrations found in the Fresno Aug. 10, 2012 back trajectories to the Pt. Reyes/Carquinez gap at 1,500 to 2,500 m (**see Figure B-4**).

E. Using a model of daily ozone budget estimation derived from empirical evidence gained via an intensive flight campaign conducted in the SJV during the summer of 2013, two estimates of the TAO contribution to total transboundary ozone entrained into the Valley boundary layer were made. In each case the fractional contribution of TAO to ground level concentrations in Fresno exceeded the 3 ppbv exceedance margin registered at the Drummond Ave. monitor on Aug. 10, 2012.

    1. Both estimates are based on the assumption that the TAO fraction of total transboundary ozone flows to California can be derived with a high degree of assurance from the well-documented trend in ozone precursor growth in Asia over recent decades and the corresponding 15 ppbv growth in background ozone as documented by Cooper et al. (2010) since 1984 (see **Figure B-10** and related discussion).[43]

    2. The first estimate employed a more conservative assumption regarding the TAO fraction that was entrained into the SJV boundary layer--3 ppbv out of a total transboundary ozone estimate of 55 ppbv. Over the course of 5 midday hours when the entrainment is strongest and the exceedance event took place at the Fresno Drummond site, this amounted to a net contribution of 4.5 ppbv of ozone at the peak hour of 1300 PST.

    3. The second estimate is based on a more realistic entrained TAO fraction of 10 to 15 ppbv at the time of the exceedance. Applying this estimate to the same

[43] Cooper, O.R., et al. (2010) Increasing springtime ozone mixing ratios in the free troposphere over western North America. *Nature Letters*, Vol. 463, 21 January, doi:10.1038/nature08708.

entrainment formula, the hourly entrainment dilution over 5 hours results in a peak hour incremental contribution of 15 to 22.5 ppbv.

To conclude, an overall weight of evidence case has been made that the exceedance of the 1 hr. ozone standard at the Fresno Drummond Ave. monitor on Aug. 10, 2012 would not have occurred but for the contribution made by transboundary anthropogenic ozone from transpacific emission sources. In this document the District has sought to emphasize the broadest possible range of empirical elements that comprise our weight of evidence case, and their reinforcing logic. Compelling evidence has been documented, including a representative body of published research, two years of regional field observations, air flight campaign results, satellite retrievals, meteorological analyses, and ozone budget modeling of the event. As a result of this evidentiary process, a clear case has been made regarding the rising sources of TAO, the fractional contribution of TAO to transboundary ozone on the West Coast, the concentrations of transboundary ozone found in Valley airspace before and during the exceedance, and the transport processes that generated the ground level ozone enhancement.

In closing, the District recognizes the historical significance of a successful invocation of §179B on the basis of anthropogenic ozone from transpacific sources. This recognition is reflected in our prior research investments in the Chews Ridge field station and related aircraft observations. As EPA's anticipated ozone NAAQS reduction further encroaches upon background ozone concentrations, the District believes the foundation of scientific evidence put forward in support of this submission strikes an appropriate balance between feasibility and requisite rigor. In any case, weight of evidence-based quantification of TAO by western air districts will be an ongoing issue that will have increased significance under EPA's 2008 and 2015 8-hour ozone standards.