A Study of Long Range Transport of Ozone and Aerosols to the San Joaquin Valley

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Background

~~Increasing a~~Atmospheric emissions in other parts of the world, especially in developing Asian countries, are rising and contributing to increases in background levels of criteria pollutants entering California, including ozone and PM. The San Joaquin Valley (SJV) is one of the most air polluted regions in the state. Recent federal, state, and local (SJV Air Pollution~~s~~ Control District) regulations have lowered pollutant concentrations in the SJV but these early gains are becoming more difficult to continue, possibly due to increasing background pollutants. This study aims to investigate the long term behavior and impacts of exogenous air pollution on the SJV.

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Accomplishments

The extreme environmental conditions and remote location of Chews Ridge required the construction of a utility structure to house sensitive instruments and equipment. A new 10-battery bank was installed inside the shed to provide the continuous power needed to run all equipment from the on-site wind turbine and photovoltaic panel generation facilities, operated by the Monterey Institute for Research in Astronomy (MIRA). 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) have all been installed and operated successfully for over 14 months and have withstood the extreme conditions present seasonally at Chews Ridge with no compromise in function. Remote access to the on-site computer and instruments has been established and procedures are in place to ensure proper instrument function and facilitate access to data, with site visits occurring every 5-6 weeks or as needed for maintenance and RDI impactor film replacement. Over one year's worth of ozone and aerosol data has been collected and initial findings are presented in this report. Six months of RDI aerosol samples have been analyzed via synchrotron X-ray fluorescence, with analysis on further samples ongoing. This data is currently being analyzed and is not included in this report, but will be incorporated into future reports. Four airborne surveys have also been conducted and provide additional information on vertical patterns of ozone offshore and upwind of the site, above Chews Ridge, and within the SJV.

Initial Results

Analysis has been conducted on data gathered at Chews Ridge as well as two ARB sites of interest, Arvin-Di Giorgio (ARB site number 15249) and Fresno-Skypark (ARB site number 10245). These sites were selected due to their geographic location as well as their exceedance history. Figure 1 illustrates the three sites considered.

Figure 1. Map of southern San Joaquin Valley illustrating the locations of the ARB sites examined in relation to the Chews Ridge monitoring site.

Figure 2 shows the average diurnal ozone profiles for Chews Ridge, Arvin, and Fresno for the ozone season, defined here as June 1 - September 30, from 2012. Both sites within in the SJV display a diurnal ozone profile typical of most urban environments: photochemical production dominates during the daytime, while reaction of ozone (titration with fresh NO emissions and dry deposition) under a shallow nocturnal boundary layer prevails at night. In contrast, the Chews Ridge diurnal profile sees a 6-8 ppb decrease in concentration during the daytime. The lack of any significant sources of NO_x at Chews Ridge prevents any significant photochemical production of ozone during the day, and stomatal uptake by vegetation most likely dominates the budget.

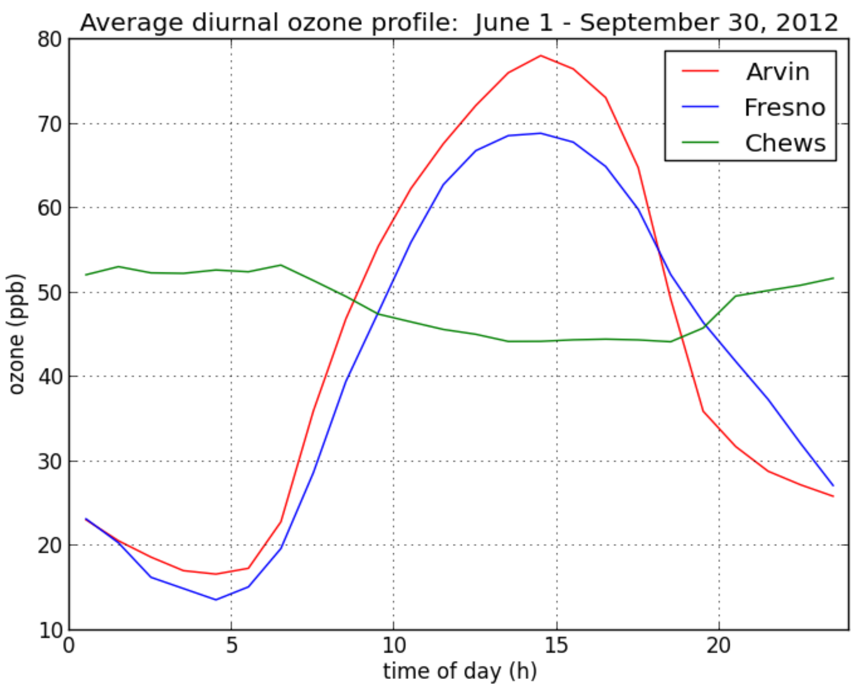

Figure 22. Average diurnal ozone profiles for the three sites. June 1 - September 30, 2012.

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Figure 3 shows the mean diurnal changes of wind speed, specific humidity, and ozone for July. A similar pattern is seen in each of the summer months, one that is consistent with the development of a convective boundary layer on the mountainous terrain in the daytime. The convective coupling in general increases surface drag, slowing the winds, while the sunshine promotes stomatal conductance and thus evapotranspiration leading to a rise in specific humidity and fall in ozone concentration due to dry deposition. We believe 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.

Evidence of the absence of a diurnal trend in the winds can be seen in Figure 4, which shows the "pollution roses" segregated into daytime (defined as 06:00 - 20:00 PST) and nighttime hours, for both hourly ozone concentration and total aerosol number concentration measured by the SMPS. The first feature of note in Figure 4 is that there are similar distributions of northeasterly and southwesterly flow at the site during both day and night. Thus there is not simply a thermally forced circulation driving the local winds. NCAR/NCEP reanalysis data of the region (not shown) 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

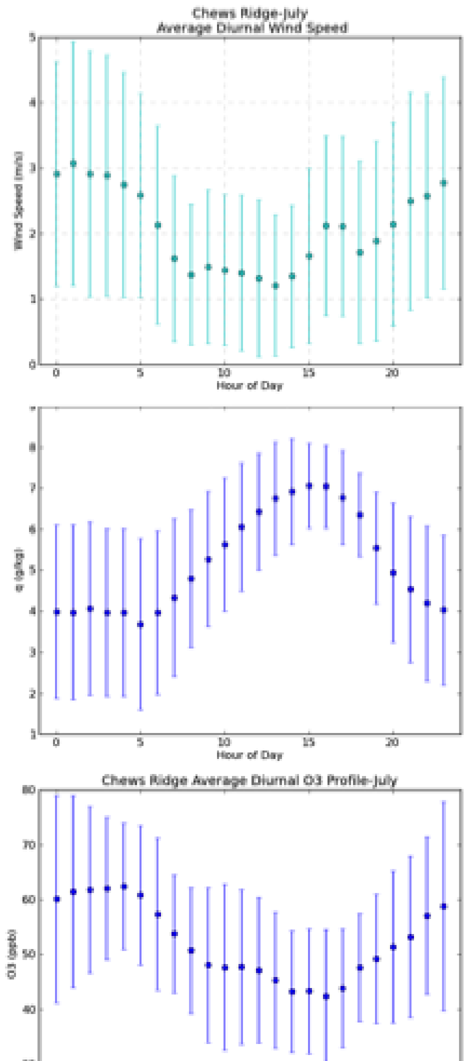

Figure 3. Diurnal variations of wind speed (top), specific humidity (middle), and ozone (bottom) for July at Chews Ridge. Filled circles are the averages for each hour of the day and bars represent +/- 1 standard deviation within each bin.

influenced by the local topography. Although westerly and southwesterly flows do exhibit a primary mode of the observed winds, there is also a persistent mode from the northeast which would be coming up the wall of the Salinas Valley bringing anthropogenic emissions. The second salient feature of Figure 4 is that the total number concentration of (small, submicron) particles exhibits its largest peaks during the continentally influenced northeasterly flow periods, but the highest ozone measurements tend to occur during the onshore, west-southwesterly flow. This finding supports the hypothesis that the higher ozone concentrations found at this altitude are indeed transboundary and are not influenced by North American emissions. Further, it is strongly suggestive that the inflow at this altitude has the potential to bring elevated ozone into the air above the SJV, on the downwind side, and influence the surface exceedance levels at times.

An autocorrelation analysis, presented in Figure 5, of the ozone data from Chews Ridge, Arvin, and Fresno further points to the difference between the ozone profiles at the mountaintop inflow site and the surface sites in the SJV. The autocorrelation coefficient falls off faster initially at Chews Ridge, and is less Gaussian than the other sites. The longer decorrelation time observed for Fresno, in the center of the valley, is likely a result of the longer residence time of air in the bottom of the valley due to the incomplete ventilation of the valley boundary layer. Although the autocorrelation falls off faster initially for the mountain site because it is typically ventilated by free tropospheric air, it does not decorrelate completely until about 3 days. The Arvin data appears to decorrelate the most rapidly, at approximately 2 days. This may be the result of the site's proximity to the very bottom of the valley, where flow may be sufficiently ventilated out through the Tehachapi Pass during the day, and is inundated by downslope (katabatic) flow at night from many different directions.

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However, this aspect of the Arvin O_3 data should be investigated further, particularly in light of the fact that some of the most severe exceedances are found at this site at the downwind end of the San Joaquin Valley.

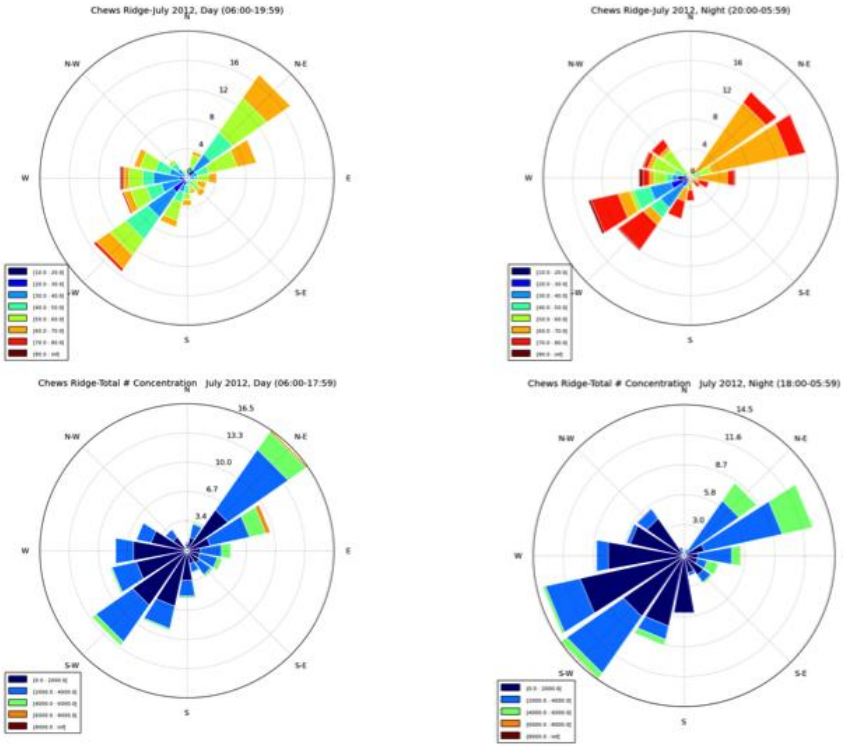

Figure ~~5~~4. Day (left) and night (right) pollution roses of ozone (top) and accumulation mode aerosols (bottom) for July 2012 at Chews Ridge. Concentration bins are represented by the colors for each of 12 sector wind

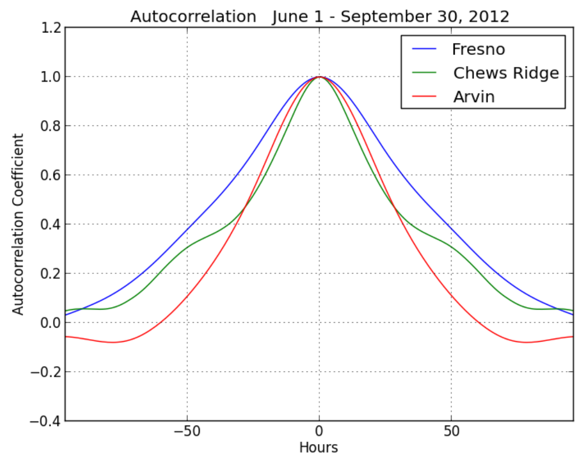

Figure ~~4~~5. Autocorrelation plot of ozone data from the three sites for the period from June 1 - September 30, 2012.

The maximum daily 8-h average (MDA8) ozone concentrations are used in the comparative analysis between sites in order to de-emphasize the influence of local effects and diurnally recycled ozone. Figure 6a shows the MDA8 correlation between Chews Ridge and the Fresno-Sierra Sky Park monitoring site. The highest correlation is found at an offset of 9 hours yielding an $r^2 = 0.4012$. Similarly, Figure 6b

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shows the MDA8 correlation between Chews Ridge and the Arvin DiGiorgio monitoring site, where the maximum correlation is observed with an offset of 12 hours, with $r^2 = 0.3751$. Finally, the same analysis is carried out for Chews Ridge and the ARB monitoring site at Lower Kaweah in the Sequoia/Kings Canyon National Park, situated 50 km northeast of Visalia at an elevation of 1890 m asl. All of the SJV surface sites seem to correlate similarly to Chews Ridge with correlation coefficients of about 0.60. These are, in fact, slightly greater than most of the correlations found in the work by Parrish et al. (2010) looking at ozone sonde data 1.5 - 2.0 km above Trinidad Head with surface sites on the interior of the Northern Sacramento Valley - an analogous situation. These correlations may be evidence that the background ozone sampled at Chews Ridge is responsible for a significant portion of the ozone variation in the SJV during the crucial summer ozone season, when air quality standard exceedances are an issue. The intercepts of these linear fits may be considered to some degree a relevant background of ozone in the region, which in the lower SJV sites appears to be between 20-25 ppbv.

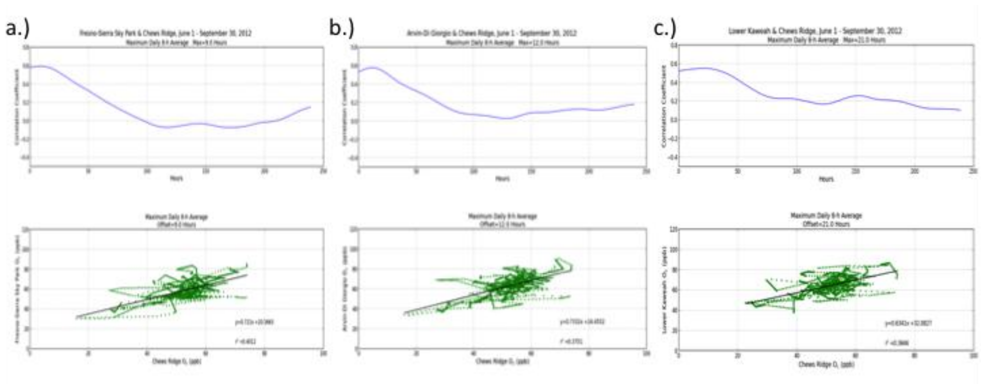

Figure 46. Correlation lag times for MDA8 ozone concentrations (June 1 - September 30, 2012) between Chews Ridge and three SJV surface sites: (a) Fresno - Sierra Sky Park, (b) Arvin - DiGiorgio, and (c) Lower Kaweah. Bottom panel figures are the scatter plots of the interpolated MDA8 values at the optimum lag times.

The lag times of maximum correlation of 9-21 hours for the ozone data at Chews Ridge and the SJV surface sites, are also comparable to, but slightly shorter than, those of the Parrish et al. (2010) study, which the authors argue is representative of the transit time between airmasses at aloft (1.5-2.0 km) along the coast to the valley bottom. As might be expected for average transport patterns, the maximum correlation times increase from Fresno, 9 hours, to Arvin, 12 hours.

Over the course of the 2012 summer ozone season, four research sorties were flown down the SJV and over Chews Ridge to profile the air above the valley floor and at the coast near Monterey. Flight reports for each sortie can be found in the appendix of this report, but the results from the two main profiles measured are presented in Figure 7a for ozone and 7b for methane, which is likely a good tracer of SJV influence. The blue lines represent the coastal profiles and the light green those over the SJV with the solid to varying qualities of dashing representing the different dates of the flights that spanned from mid June to mid September.

With the exception of the flight of August 30 which saw anomalous southerly flow throughout the region, it is apparent that the profiles appear to be of common composition somewhere between 1000 - 1500 m altitude, and that the measurements at Chews Ridge (1550 m) capture the variability of these airmasses well. Below this altitude there are appreciable elevations of both ozone and methane indicating the influence of internal California sources. Moreover, the ozone gradients between the valley boundary layer and the common layer aloft are not conducive to downward transport of ozone to the valley surface because there typically is more in the boundary layer at least during the middle of the day (these profiles were all conducted between 11:00 - 12:30 PST.) Caution should be made, however, in generalizing these profiles because on all these dates aside from the Aug 30 flight noted above, the winds observed at Chews Ridge were easterly during the daytime, which is not consistent with systematic westerly transport over the ridge and into the valley.

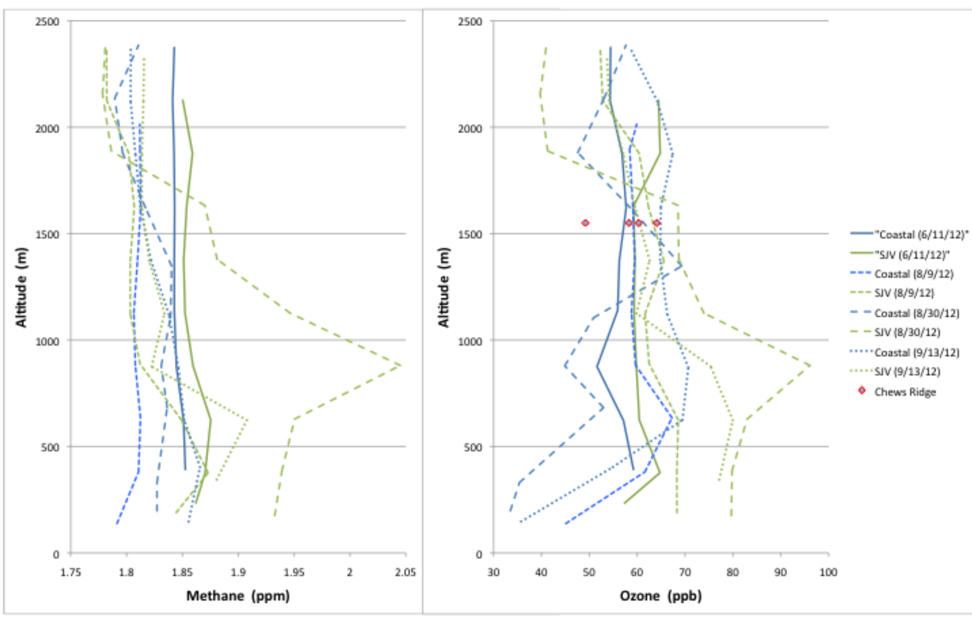

Figure 57. Methane (left) and ozone (right) profiles observed during the four research flights. Blue colors indicate coastal profiles and light green are over the center of the SJV.

Although not shown here graphically, selecting the conditions when the wind at Chews Ridge is approximately onshore (310 > wdir > 170) does not reduce the correlation coefficients of Figure 6 significantly (e.g. 0.38 to 0.34 at Arvin.) Moreover, the peak correlations found always occurred when the surface sites were considered ***after*** the Chews Ridge data, indicative of an average transport pattern from the west to the east. Thus the majority of the correlation observed between the mountaintop monitoring site and the valley floor appears to be due to the hypothesis that transboundary air observed at Chews Ridge is being carried to the SJV and influencing the surface ozone conditions.

Figure 8 illustrates the average diurnal size distribution profile for aerosol data at Chews Ridge during the summertime ozone season. Throughout the morning and early afternoon the particle profile is relatively steady. However, at around 14:00 PST, the profile shifts rather suddenly and there is a significant increase in the concentration of smaller sized particles. Then, As the afternoon progresses, the aerosol sizes appear to grow. This may be indicative of nucleation events occurring at Chews Ridge, and thus could have bearing on issues of particle number concentrations in the SJV. Such secondary aerosol production could be the result of important ozone precursors being generated in the high VOC/low NO_x environment of the coastal range. In principle the free tropospheric air that feeds this region is efficiently decoupled from the ocean surface during the summer months, meaning that in the absence of high dust or biomass burning events, the air could be very low in existing condensation nuclei, further increasing the chances for new particle production. Nucleation of new particles in this location, establishing a sort of air quality boundary condition for North America, might further exacerbate the ozone/aerosol problems in the SJV. This behavior in the aerosol size distribution deserves to be the focus of further investigation in the aerosol composition (RDI) and continued analysis of the unique data set being collected at Chews Ridge.

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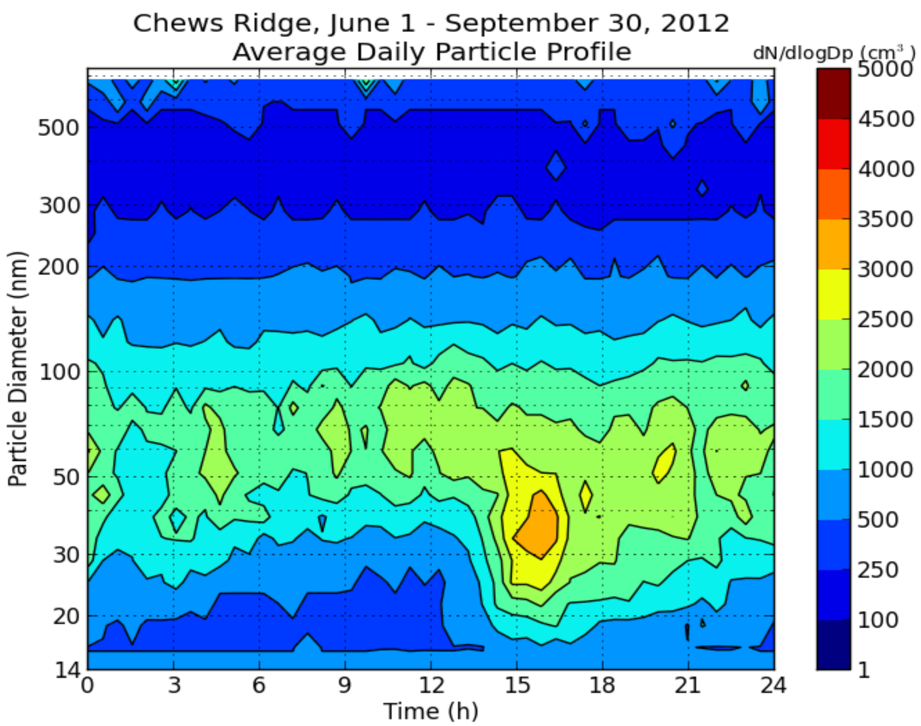

Preliminary Conclusions

Initial findings during the first year of operation support the initial hypothesis that background exogenous pollutants sampled at Chews Ridge have an impact on air in the SJV, as indicated by the correlation analysis presented. As more data is collected, through a second summertime ozone season (2013), the data will provide a better understanding of the long term trends of background pollutants entering California.

Further Research Plan

Further analysis of this aerosol data in conjunction with the recently received RDI aerosol chemical speciation data will allow for a better understanding of these recurring events as well as singular, large scale deviations from the average aerosol profile.

Ongoing analysis of the RDI aerosol data will provide many new insights, including a better understanding of the possible origins of the sampled air mass at Chews Ridge which will in turn help identify possible sources of increased background ozone entering California. Additionally, this understanding of the origins of the sampled air mass may well provide unique insights into ozone and PM exceedance periods in the SJV.

Continued analysis will include:

> Analysis of the RDI aerosol size-segregated composition data to better fingerprint airmasses influenced by long range transport

> Compile the ARB aircraft ozone data taken above Fresno to try to develop a better climatology of the vertical structure of ozone above SJV and thereby improve the estimates of downward transport.

> Conditional analysis of back trajectories from Chews Ridge indicating a lack of continental influence.