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Characterizing the impacts of vertical transport and photochemical ozone production on an exceedance area

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HIGHLIGHTS

- Observation-based analysis of ozone (O_3) in California and consequences for air quality policy.
- Assessment of the seasonality of O_3 production above California's San Joaquin Valley.
- Evidence that free tropospheric air affects ground-level O_3.
- Insights into O_3 transport which is difficult to identify by traditional modeling-based approach.

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ABSTRACT

Offshore and inland vertical profiles of ozone (O_3) were measured from an aircraft during 16 flights from January 2012 to January 2013 over the northern San Joaquin Valley (SJV) and over the Pacific Ocean. Analysis of in situ measurements presents an assessment of the seasonality and magnitude of net O_3 production and transport within the lower troposphere above the SJV. During the high O_3 season (May–October), the Dobson Unit sum of O_3 in the 0–2 km above sea level (km.a.s.l.) layer above the SJV exceeds that above the offshore profile by up to 20.5%, implying net O_3 production over the SJV or vertical transport from above. During extreme events (e.g. Stratosphere-to-troposphere transport) vertical features (areas of enhanced or depleted O_3 or water vapor) are observed in the offshore and SJV profiles at different altitudes, demonstrating the scale of vertical mixing during transport. Correlation analysis between offshore O_3 profiles and O_3 surface sites in the SJV lends further support the hypothesis of vertical mixing. Correlation analysis indicates that O_3 mixing ratios at surface sites in the northern and middle SJV show significant correlations to the 1.5–2 km.a.s.l. offshore altitude range. Southern SJV O_3 surface sites show a shift towards maximum correlations at increased time-offsets, and O_3 surface sites at elevated altitudes show significant correlations with higher offshore altitudes (2.5–4 km.a.s.l.).

1. Introduction

The United States Environmental Protection Agency (EPA) sets National Ambient Air Quality Standards (NAAQS) for ground-level ozone (O_3). The 2008 NAAQS for O_3 requires that the 3-year average of the annual 4th-highest daily maximum 8-h mean mixing ratio be less than or equal to 75 parts per billion by volume (ppb) (US EPA, 2006). The California Air Resources Board (CARB) sets more stringent 1-h and 8-h O_3 standards at 90 ppb and 70 ppb respectively to better address longstanding O_3 problems (CARB, 2005). The formulation of attainable O_3 standards relies on the accurate identification of a representative baseline mixing ratio of O_3 that would occur in the United States in the absence of recent, locally emitted or produced anthropogenic pollution, as defined by the Task Force on Hemispheric Transport of Air Pollution (Dentener et al., 2011). Current baseline O_3 mixing ratios are estimated to be in the range of 15–60 ppb, with estimates varying based on model and experimental uncertainties, season, location and elevation (Fiore et al., 2003; Lefohn et al., 2011; Zhang et al., 2011; Lin et al.,

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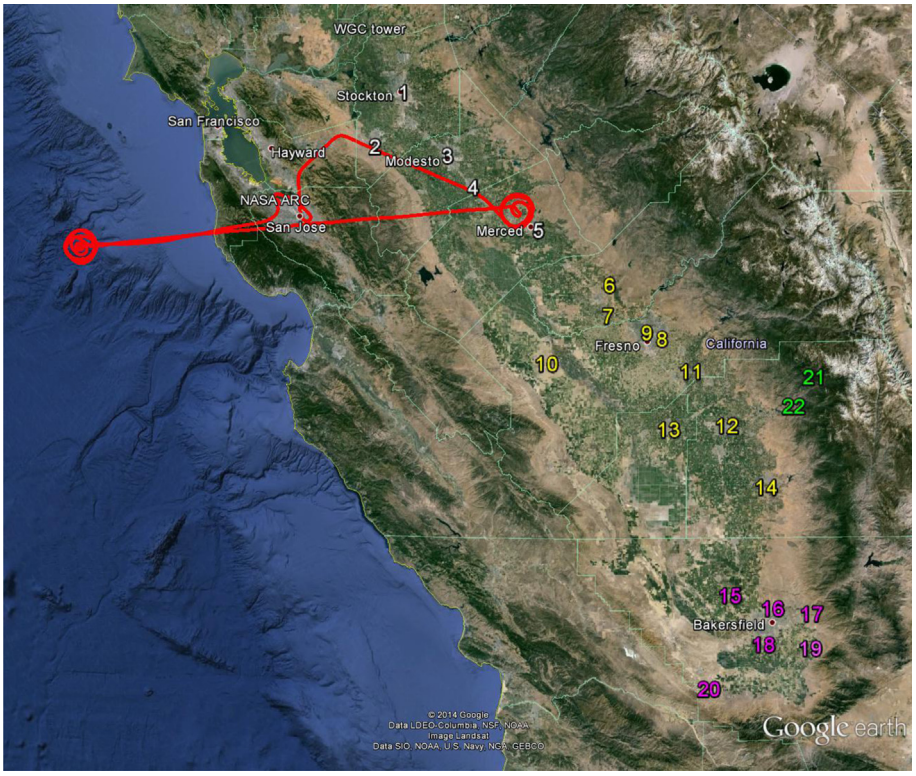

Fig. 1. AJAX flight track (red line, profiles over Merced and RAINS) and location of the CARB O_3 surface sites plotted in Google™ Earth. White numbers represent northern SJV sites (1 = Stockton, 2 = Tracy, 3 = Modesto, 4 = Turlock, 5 = Merced), yellow numbers represent mid-SJV sites (6 = Madera, city, 7 = Madera, Pump Yard, 8 = Clovis, 9 = Fresno, 10 = Tranquility, 11 = Parlier, 12 = Visalia, 13 = Hanford, 14 = Porterville), pink numbers represent southern SJV sites (15 = Shafter, 16 = Oildale, 17 = Edison, 18 = Bakersfield, 19 = Arvin-Di Giorgio, 20 = Maricopa) and green numbers represent sites located within the Sierra Nevada mountain range (21 = Sequoia National Park, Ash Mountain, 22 = Sequioa National Park, Lower Kaweah).

2012). Current literature indicates increasing levels of baseline O_3 due to increasing global emissions (Cooper et al., 2010, 2011; Parrish et al., 2012, 2013; Gratz et al., 2015). At the same time, the NAAQS O_3 standard has been reduced several times over the last few decades, with decision on a further reduction of the NAAQS O_3 target to 60–70 ppb due (US EPA, 2010). This has resulted in an increasing emphasis on understanding the contributions and processes which impact surface O_3 in the western US (Jaffe, 2011; Parrish et al., 2012; Lefohn et al., 2014).

Understanding the atmospheric composition of air coming into the western United States is important for air quality issues. Previous studies have highlighted the importance of characterizing O_3 aloft, reporting that downward mixing of free tropospheric O_3, long range transport of O_3 and its precursors, and lofting and subsequent entrainment of regional emissions affect surface O_3 (e.g. Sahu and Lal, 2006; Langford et al., 2012; Lin et al., 2012; Neuman et al., 2012 and references therein). In addition, the positive vertical gradient for O_3, complex mountainous terrain of the Western US, uncertain boundary conditions and variations due to exceptional events (e.g. stratosphere-to-troposphere transport (STT) and biomass burning) complicate efforts to model O_3. Previous studies, using different models, report underestimations of O_3 mixing ratios in the western US (Tong and Mauzerall, 2006; Reidmiller et al., 2009; Jaffe, 2011; Zhang et al., 2011; Koumoutsaris and Bey, 2012). The challenges of modeling O_3 in the western US highlight the importance of O_3 observations and exploring alternative analysis methods, which can contribute towards the understanding of tropospheric O_3 in this region. Some alternative methods are discussed herein.

Most of our knowledge of O_3 in California is based on long-term surface O_3 sites, such as those maintained by CARB, ozonesondes from Trinidad Head (Parrish et al., 2010), short-term aircraft/multi-intensive campaigns such as ARCTAS-CARB, CalNex and IONS-2010 (Neuman et al., 2012; Singh et al., 2012; Cooper et al., 2011; Pfister et al., 2011) and long-term MOZAIC profiles at airport locations (Cooper et al., 2005). This manuscript reports in situ O_3 vertical profile measurements over California's San Joaquin Valley (SJV) and offshore, during 16 flights from January 2012 to January 2013. The overall aim of this study is to gain a greater understanding of the processes contributing to surface O_3 in California's SJV; an extreme exceedance area, with local meteorology and topography presenting significant challenges for O_3 attainment (e.g. Bao et al., 2008; CARB, 2007). This study specifically aims to: 1) characterize O_3 inflow to the SJV, 2) assess the magnitude and seasonality of net O_3 production within the lower troposphere above the SJV, and 3) determine the effects of vertical transport on O_3 mixing ratios at SJV surface sites.

2. Experimental approach: airborne instrumentation

Airborne in situ measurements of O_3 were performed as part of the Alpha Jet Atmospheric eXperiment (AJAX), which is based at and operated from NASA Ames Research Center at Moffett Field, CA (37.415° N, 122.050° W).

O_3 mixing ratios were measured using a commercial O_3 monitor (2B Technologies Inc., model 205) based on ultraviolet (UV) absorption techniques and modified for flight worthiness. Details of the modification, calibration and sampling system are reported by Yates et al. (2013).