Tropospheric ozonesonde profiles at long-term U.S. monitoring sites: 2. Links between Trinidad Head, CA, profile clusters and inland surface ozone measurements

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Keywords/Index Terms

- Tropospheric Ozone – Surface Ozone – Ozonesondes – Self-Organizing Maps – Pollution – STE

Key Points

- Thin layers of high O\textsubscript{3} 1 – 4 km amsl are frequent over Trinidad Head, CA (TH)
- STE and pollution transport are difficult to distinguish with observations
- High TH O\textsubscript{3} coincides with +5 – 10 ppbv surface O\textsubscript{3} at high-elevation monitors

Abstract
Much attention has been focused on the transport of ozone \((O_3)\) to the Western U.S., particularly given the latest revision of the National Ambient Air Quality Standard (NAAQS) to 70 parts per billion by volume (ppbv) of \(O_3\). This makes defining a “background” \(O_3\) amount essential so that the effects of stratosphere-to-troposphere exchange and pollution transport to this region can be quantified. To evaluate free-tropospheric and surface \(O_3\) in the Western U.S., we use self-organizing maps to cluster 18 years of ozonesonde profiles (940 samples) from Trinidad Head, CA. Two of nine \(O_3\) mixing ratio profile clusters exhibit thin laminae of high \(O_3\) above Trinidad Head. A third, consisting of background (~20 – 40 ppbv) \(O_3\), occurs in ~10% of profiles. The high \(O_3\) layers are located between 1 and 4 km amsl, and reside above a subsidence inversion associated with a northern location of the semi-permanent Pacific subtropical high. Several ancillary data sets are examined to identify the high \(O_3\) sources (reanalyses, trajectories, remotely-sensed carbon monoxide), but distinguishing chemical and stratospheric influences of the elevated \(O_3\) is difficult. There is marked and long-lasting impact of the elevated tropospheric \(O_3\) on high-altitude surface \(O_3\) monitors at Lassen Volcanic and Yosemite National Parks, and Truckee, CA. Days corresponding to the high \(O_3\) clusters exhibit hourly surface \(O_3\) anomalies of \(+5 – 10\) ppbv compared to a climatology; the anomalies can last up to four days. The profile and surface \(O_3\) links demonstrate the importance of regular ozonesonde profiling at Trinidad Head.

1. Introduction

1.1. Free-Tropospheric \(O_3\) Contributions to Surface \(O_3\)
Contributions to the surface O₃ budget are the result of several natural and anthropogenic processes. Free-tropospheric O₃ increases from stratosphere-to-troposphere exchange (STE; Holton et al., 1995; Lin et al., 2012b; 2015; Langford et al., 2009; 2015), intercontinental pollution transport (Huang et al., 2010; Cooper et al., 2011), lightning (Pickering et al., 1998; Kaynak et al., 2008; Ott et al., 2010), and fires (Jaffe et al., 2004; Zhang et al., 2011; 2014) all modify surface O₃ when mixed into the boundary layer. Because these processes cannot be regulated, quantifying their influence is increasingly important given the recent lowering of the Environmental Protection Agency (EPA) National Ambient Air Quality Standard (NAAQS) from 75 ppbv to 70 ppbv O₃.

Quantitatively segregating contributions to surface O₃ from STE, transported pollution, and local emissions remains a challenge, especially from an observational standpoint. Furthermore, recent modeling studies show that STE may contribute to the surface O₃ budget much more than previously thought. Surface O₃ increases from STE can outweigh those from Asian pollution transport by up to a factor of three in the high altitudes of the Western U.S. (Lin et al., 2012a; b; Langford et al., 2015).

1.2. Ozonesonde Profile Links to Surface O₃

For the purpose of measuring O₃ entering the Continental U.S., ozonesondes have been launched at Trinidad Head, CA, approximately weekly since August 1997. Parrish et al. (2010) show a strong correlation between tropospheric O₃ from Trinidad Head sondes and surface O₃ at regional inland surface monitors. Knowledge of this relationship, however, yields little
information about the geophysical and chemical processes behind the observed O₃ profiles that have such a link to the surface. It also has not provided a clear definition of background O₃.

Stauffer et al. (2016) employed self-organizing maps (SOM) to cluster O₃ mixing ratio (O₃MR) profiles from Trinidad Head and three other Contiguous United States (CONUS) sites. Their study found that clusters of surface – 12 km O₃MR profiles were closely linked with large-scale meteorology, including tropopause and 500 hPa heights, potential vorticity (PV) anomalies/STE, and were not necessarily associated with a particular seasonality. Given the geophysical significance of O₃MR profile clusters and the ability to distinguish processes such as STE, we will employ the SOM technique to Trinidad Head surface – 6 km amsl O₃MR profiles. This narrowed altitude focus allows closer inspection of low to mid-tropospheric O₃ variability, and largely avoids the effect of tropopause O₃ gradients on the clusters. The Parrish et al. (2010) study used Trinidad Head ozonesonde data from June-July-August (JJA); we will extend our analysis to all months. In addition to examination of the links between the clusters of Trinidad Head O₃MR profiles and surface O₃ data, interpretation of the geophysical and chemical characteristics of the O₃ profile clusters adds significance to our results.

Essentially, our methodology in this paper will be to re-examine the SOM at Trinidad Head, focusing on O₃MR from surface – 6 km amsl. The analyses will comprise two major efforts: 1) Infer meteorological and chemical characteristics of the SOM clusters using sonde measurements, reanalysis data, and remotely-sensed carbon monoxide (CO) and O₃ measurements. Evaluation of remotely-sensed measurements is contained in the Appendix to this paper. 2) Evaluate the correspondence of SOM nodes to nearby elevated surface O₃ monitors. Focus will mainly be on surface O₃ associated with SOM clusters that contain profiles with enhanced tropospheric O₃ values.
2. Data Sources and Methods

2.1. Clustering Ozonesonde Data with SOM

Ozonesonde and radiosonde profiles for Trinidad Head, CA, were obtained from the NOAA Earth System Research Laboratory Global Monitoring Division data archive (ftp://ftp.cmdl.noaa.gov/data/ozwv/Ozonesonde/). The data were averaged into 100 m bins for uniformity and compatibility with the SOM algorithm. Every profile set includes altitude, pressure, dry-bulb and potential temperature, relative humidity and frost point, O$_3$ partial pressure, and O$_3$MR. A total of 940 ozonesonde profiles from August 1997 – March 2015 are used in this study.

A very brief explanation of the SOM algorithm (Kohonen, 1995) is given here. For a complete discussion on SOM, its applications to O$_3$ profile data, and sensitivity tests comparing SOM and the similar k-means clustering algorithm, see Stauffer et al. (2016; details in Appendix). In the SOM application to O$_3$MR data, a 2-D array of initial nodes, which are comparable to cluster centroids, is defined, and the SOM algorithm is applied iteratively. After a number of iterations where the O$_3$MR data are input into the algorithm, the SOM converges to its solution. The O$_3$MR profiles are separated into exclusive clusters defined by their respective SOM nodes, which are equal to the mean of each cluster’s O$_3$MR profiles. An advantage of the SOM over other methods is the topographical ordering of clusters in the SOM. Similar nodes/clusters are arranged in adjacent positions in the map as will be seen in Results below.

Our prior work (Jensen et al., 2012; Stauffer et al., 2016) demonstrates that SOM provides
meaningful geophysical characterization of clustered O₃ data when compared to meteorological data.

The 100 m averaged surface – 6 km amsl O₃MR data for all profiles are input into the same batch SOM algorithm as in Stauffer et al. (2016). That is, we use a 3x3 SOM with nine clusters to allow direct comparisons with the surface – 12 km Trinidad Head, CA, clusters analyzed in that earlier study. The 940 O₃MR profiles are separated into nine exclusive clusters based on similarity in shape to one of the nine nodes.

2.2. Meteorological Data

Reanalysis data from the ERA-Interim (Dee et al., 2011) data set were obtained to aid meteorological interpretation of the ozonesonde profile clusters. Variables of geopotential height, temperature, PV, and cloud fraction were obtained at four pressure levels (250, 500, 700, 850 hPa), and variables of temperature (2 m), total cloud cover, and MSLP were obtained for the surface. The data are available for every six hours for the entire globe on approximately a 0.7° x 0.7° grid.

Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT; Draxler and Hess, 1997) 10-day forward and backward trajectories were calculated for every Trinidad Head ozonesonde profile. Kinematic trajectories ending at every km from 1 – 5 km at the time and location of ozonesonde launch were computed using meteorological data from the NCEP/NCAR Reanalysis Project (Kalnay et al., 1996).

2.3. Surface O₃ Data
To investigate links between tropospheric O₃ at the Trinidad Head ozonesonde site and regional surface O₃, data were obtained from high-elevation sites in CA with sufficient record lengths. Only monitors over 1 km amsl with O₃ data since 1997, the start of the Trinidad Head record, are considered. We require the 1 km elevation in an attempt to avoid effects from localized emissions sources from more populated lower elevation areas. This criterion also narrows our site candidates to those that are closer to the altitude of enhanced tropospheric O₃ layers over Trinidad Head. Three surface O₃ monitors in CA meet our constraints: Lassen Volcanic National Park (Lassen), White Cloud Mountain in Truckee, CA (Truckee), and Yosemite National Park – Turtleback Dome (Yosemite). Site metadata are listed in Table 1. The Lassen and Yosemite sites both operate year-round, while Truckee is typically operated from May – October, with a few years containing all months. Surface O₃ data were obtained from the Clean Air Status and Trends Network (CASTNET; http://java.epa.gov/castnet/clearsession.do; Lassen and Yosemite), and the EPA Air Quality System (AQS) database (https://aqs.epa.gov/api; Truckee).

2.4. Atmospheric Infrared Sounder (AIRS) Data

The Atmospheric Infrared Sounder (AIRS; Aumann et al., 2003) launched on NASA’s Aqua satellite in May 2002, provides vertically-resolved measurements of temperature, humidity, and a number of trace gas species. Daily level 3, version 6, O₃ and CO data (http://acdisc.sci.gsfc.nasa.gov/opendap/Aqua_AIRS_Level3/AIRX3STD.006/) on a 1° x 1° horizontal grid that covers the globe assist our interpretation of the O₃ profile clusters at Trinidad
Head. Level 3 data are a quality-checked version of the level 2 swath products from AIRS, output on standard pressure levels. Only data from the ascending (daytime, equatorial crossing time of 1330 LST) node of the Aqua orbit are used here.

3. Results

The surface – 6 km amsl monthly-averaged O$_{3MR}$ climatology from Trinidad Head, CA (August 1997 – March 2015), is shown in Figure 1. In terms of O$_{3MR}$ averages, Trinidad Head exhibits a smaller seasonal cycle than other CONUS ozonesonde sites (Newchurch et al., 2003; Stauffer et al., 2016). A maximum in free-tropospheric O$_3$ is observed from April – August, when the combination of transported pollution, STE, and photochemical O$_3$ production has the greatest impact on the site. Ozone averages $\sim$55 – 60 ppbv from 2 – 4 km in April – August. At the surface, an O$_3$ minimum is observed in July with a maximum in MAM. Persistent inflow of marine boundary layer air from the Pacific keeps surface O$_3$ generally $\leq$ 50 ppbv at Trinidad Head year-round (Oltmans et al., 2008). This contrasts with the other CONUS stations where surface O$_3$ values, mostly in summer, frequently exceed 60 or 70 ppbv (Stauffer et al., 2016).

3.1. SOM Clusters

Climatological averages yield general information about a site’s typical O$_3$ variability, but often mask shorter-term events that occur throughout the year. The surface – 6 km amsl 3x3 SOM O$_{3MR}$ profile clusters (Figure 2) reveal a more realistic depiction of the O$_3$ profile variability over Trinidad Head and simple data visualization. Each node in Figure 2 contains a
distinct profile shape, with related clusters holding adjacent positions in the SOM manifold. In contrast, the mean, 20th and 80th percentile O3 for the whole data set is shown in cyan with each cluster in Figure 2. Nodes 1, 4, and 7 include very low amounts (< 40 ppbv) of lower tropospheric O3, nodes 2, 5, and 8 contain near average (~50 ppbv) O3 amounts in the low to mid-troposphere, and nodes 3, 6, and 9 contain high (> 60 ppbv) O3 amounts in layers at progressively higher altitudes.

The disparity between the monthly-averaged O3MR profiles (Figure 1) and the profile nodes (Figure 2) illustrates how much information is lost using simple ozonesonde averages at Trinidad Head. Monthly-averaged O3MR below 4 km peaks at 62 ppbv in May at Trinidad Head. However, average O3 in three of the nodes (3, 6, and 9) all exceed this value at some point below 4 km, with node 6 exhibiting a maximum of 76 ppbv at 3.2 km amsl, and several profiles with > 100 ppbv O3MR. Nodes 3, 6, and 9 encompass a significant percentage, 26%, of total Trinidad Head profiles, with cluster-average O3 amounts far exceeding that of any monthly average.

The remainder of this paper describes geophysical interpretations of the profiles and links to surface O3 at the monitoring sites for the SOM nodes. All nine SOM nodes are examined, but our main focus is on nodes 3 and 6, which contain locally high amounts of O3 in the lower troposphere, node 1, which is very clean throughout the troposphere, and nodes 7 and 9, which appear to have stratospheric influence and very high O3 amounts above 5 km.

3.2. Seasonality and Meteorological Analyses

The seasonality of O3 profiles (Figure 3) reveals results similar to the Stauffer et al. (2016) finding that O3MR SOM clusters often do not correspond to distinct seasons. Nodes 1, 2,
4, and 5 favor certain months, but every month of the year is represented in these clusters. Other nodes contain sharper peaks in the distribution of months. Nodes 3 and 6, which contain high O$_3$ amounts, generally occur in spring and summer. Newchurch et al. (2003) noted that STE events and intrusions of high O$_3$ into the troposphere were much more frequent at Trinidad Head compared to other CONUS sites, especially in the summer. This may explain the seasonality of profiles in nodes 7 and 9, which are most common between April and August. The cleaner nodes 1 and 4 are analogous to node 7 in Stauffer et al. (2016). Profiles in those clusters are likely affected by subtropical air, and represent baseline/background O$_3$ amounts over Trinidad Head that are observed during several months of the year.

To remove the effects that different seasons may have on meteorological analyses, results here are presented in terms of both SOM node means and anomalies from climatology (1981 – 2010 base period). The ERA-Interim 500 hPa height means and anomalies corresponding to each SOM cluster are shown in Figure 4, revealing typical large-scale mid-tropospheric patterns. The polluted nodes 3 and 6 are under, or just downstream of a synoptic-scale ridge, where one would expect subsidence. The large-scale pattern corresponding to node 2 is nearly identical to nodes 3 and 6. However, node 2 seasonality (Figure 3) is essentially the opposite of nodes 3 and 6, explaining the O$_3$ differences among those nodes found in the lower troposphere in Figure 2. Nodes 7 and 9, hypothesized to be impacted by STE, are associated with influence from a trough centered directly over the site. In Stauffer et al. (2016), we showed a strong correlation between 500 hPa troughs and O$_3$ enhancement from STE events. The baseline nodes 1 and 4 exhibit a dichotomy in 500 hPa anomaly patterns, indicating that background tropospheric O$_3$ mixing ratios can occur under a variety of synoptic conditions at Trinidad Head.
The ERA-Interim MSLP means and anomalies (Figure 5) show the influence the position of the semi-permanent Pacific subtropical high has on the Trinidad Head O₃ profiles. Clusters 2, 3, and 6 all show MSLP anomalies of +1 – 3 hPa extending into the Pacific Northwest of North America. This is a stark contrast to the MSLP fields corresponding to clusters 1 and 7. Except for cluster 9 (34.7° N), cluster 6 (34.1° N) is the farthest north position of the center (‘H’ on Figure 5) of the Pacific subtropical high of all the SOM nodes, with other nodes (2, 4, 5, 7) centered 1.5 – 2° latitude farther south. The 500 hPa and MSLP patterns for node 6 are similar to conditions associated with O₃ maxima described during past campaign studies (e.g. Kloesel et al., 1992; Huang et al., 2010; Cai et al., 2016) along the CA coastline and at inland surface sites. Specifically, the CA coast is situated downstream of a 500 hPa ridge, upstream or along a 500 hPa trough axis, and influenced by an anomalously positioned Pacific subtropical high that extends higher surface pressures into the Pacific Northwest. The relationship between subsidence presumed from ERA-Interim analyses and high O₃MR₄ over Trinidad Head warrants further investigation.

A side-by-side comparison of SOM node average O₃MR₄, relative humidity (RH), and potential temperature (θ) in Figure 6 shows clear signs of subsidence influencing the high O₃ profiles in nodes 3 and 6. Nodes 3 and 6 exhibit inflection points in the θ profiles and are 3 – 10 °C warmer at 1 km amsl than all other clusters. The subsidence interpretation is further supported by cluster 3 and 6 RH that averages > 10% lower than all other clusters in the 2 – 4 km layer. A decrease in RH is expected if water vapor is conserved in a subsiding, warming air parcel. The layers of high O₃ reside above the strong inversion layer at 1 km, evidence that the enhanced O₃ values were transported with the air masses from higher altitudes. Figure 6 also displays a prominent anti-correlation between O₃ and RH.
The contoured maps of backward and forward trajectories from HYSPLIT (Figure 7a, b) give a general sense of the transport pathway for each of the SOM clusters. The backward (forward) trajectories end (start) at 3 km amsl, near the altitude of the O$_{3\text{MR}}$ maxima in clusters 3 and 6. Though most of the back trajectories are zonal, anti-cyclonic curvature can be visualized, especially in cluster 3. The trajectories also have a more northerly approach along the CA coast in clusters 3 and 6, associated with the mid-tropospheric ridge and the Pacific subtropical high influence extending farther northeast (Figures 4 and 5). Most of the trajectories approach Trinidad Head from higher altitudes, much like those computed in Oltmans et al. (2008). Forward trajectories show a tendency for transport to continue in a meridional direction from Trinidad Head in many clusters, but zonal directions are dominant. The HYSPLIT trajectories did not indicate STE or potential pollution transport from specific regions corresponding to observed high O$_3$ in clusters 3 and 6.

The meteorological evidence presented clearly shows that large-scale synoptic influence and associated subsidence affect the Trinidad Head O$_3$ profiles. However, distinguishing STE and pollution transport contributions to O$_3$ in the lower troposphere over Trinidad Head remains difficult with available reanalyses and observations, particularly with this large data set. Analyses of remotely-sensed data from AIRS and a description of our effort to separate pollution transport and STE are presented in the Appendix. In general, analyses of stratospheric (PV) and pollution (CO) indicators yielded mixed and unconvincing results on influences on the profiles.

### 3.3. SOM Links to Surface O$_3$ Data
The monthly-averaged diurnal surface $O_{3MR}$ over the 18 year record for the three CA surface sites is shown in Figure 8. Lassen is the cleanest site by a large margin, with a maximum in hourly $O_{3MR}$ of 57 ppbv in July and August. Truckee maximizes at 65 ppbv in July, and Yosemite is, on average, the most polluted, with an hourly maximum of 68 ppbv in both July and August. Lassen and Yosemite both show some influence presumably from regional NO$_x$ emissions sources. This is manifest as a larger diurnal range in $O_{3MR}$ from NO$_x$ titration at night. More removed from regional influences, Truckee exhibits a minimal diurnal range. As with the Trinidad Head ozonesonde profiles, we find that surface $O_3$ variability at the three monitoring sites is best understood through links to the Trinidad Head SOM clusters, rather than with simple climatology, because SOM also discriminates subtle but important differences among the three surface sites.

3.3.1. Sonde/Surface $O_3$ Correspondence

The relationship between the $O_{3MR}$ measured by the Trinidad Head ozonesondes and $O_{3MR}$ at the three surface sites is shown in Figures 9 – 11. At each site, average diurnal $O_{3MR}$ was calculated for days corresponding to each SOM node (black lines), with the average $O_{3MR}$ from the sonde plotted in black dots. The sonde $O_{3MR}$ presented in Figures 9 – 11 is from the same altitude as each respective surface monitor.

As in Parrish et al. (2010), our results show that Trinidad Head ozonesondes are representative of regional $O_3$ levels. There is generally strong agreement (on average ±5 ppbv) between $O_{3MR}$ from Trinidad Head sondes and the surface monitors for most SOM clusters, particularly at Truckee (Figure 10) and Yosemite (Figure 11). The Lassen site (Figure 9) is
cleaner, with average surface \( O_{3MR} \) that is consistently below that measured at Trinidad Head, and rarely exceeds the Trinidad Head value during peak \( O_3 \) later in the afternoon. Two exceptions to the agreement between sonde and surface are found in nodes 1 and 7 at all sites. These two clusters at Trinidad Head contain profiles with very low \( O_{3MR} \) in the low to mid-troposphere, but often occur in the summer months. This outcome is similar to that found in Brodin et al. (2011) and Oltmans et al. (1996) – that agreement between ozonesonde and surface data is seasonally dependent. Generally the best agreement occurs when \( O_3 \) is low in the winter, and worst in the summer when local photochemistry often causes differences between the surface and free troposphere.

SOM nodes 3 and 6, the two polluted Trinidad Head sonde clusters, are associated with the highest surface \( O_3 \) at all three monitoring sites. Node 3 and 6 average surface \( O_{3MR} \) are quite similar to the maximum monthly averages from Figure 8. Lassen node 3 and 6 \( O_{3MR} \) maxima are 59 and 60 ppbv, compared to the 57 ppbv maximum in July and August. Truckee node 3 and 6 \( O_{3MR} \) maxima are 70 and 68 ppbv, compared to 65 ppbv (July). Yosemite node 3 and 6 \( O_{3MR} \) maxima are 69 and 67 ppbv, compared to 68 ppbv (July and August). However, these results are somewhat misleading because cluster 3 and 6 ozonesondes are not exclusive to the summer months when photochemical \( O_3 \) production is highest. Therefore, we choose to calculate surface \( O_3 \) anomalies from monthly averages to better assess the impact of the increased tropospheric \( O_3 \) in nodes 3 and 6.

Each day of surface \( O_{3MR} \)s corresponding to a SOM node is compared to its respective monthly climatological \( O_{3MR} \) (measurement – climatology), and the results are averaged for each SOM node. The results of these calculations are shown in Figure 12. In addition to surface measurements for the same day as the Trinidad Head sondes, measurements for one, two, and
three days after the sonde date are illustrated to estimate how long O₃ anomalies persist. Ozone anomalies are 5–10 ppbv above monthly climatology the same day as the ozonesondes in clusters 3 and 6 at all three sites. In the afternoon and evening hours, Truckee surface O₃ anomalies peak at +12 ppbv the same day as node 3 profiles. Conversely, surface O₃ associated with node 7 falls well below (-5 to -10 ppbv) climatology. The synoptic-scale meteorology associated with node 7 is hostile to surface O₃ production.

Significant positive O₃ anomalies of +5 ppbv associated with node 3 and 6 profiles at Trinidad Head linger up to three days after the ozonesonde launch date. Considering that the Yosemite site is 515 km SE of Trinidad Head, this suggests that the Trinidad Head ozonesondes can predict surface O₃ conditions up to four days for an extensive area of CA.

3.3.2. Potential Implications for NAAQS

The large positive anomalies in surface O₃ at these sites associated with Trinidad Head sondes have significant implications for compliance with the 8-hr NAAQS standard of 70 ppbv. The U.S. NAAQS for 8-hr surface O₃ was revised in October 2015 from the previous value of 75 ppbv, to 70 ppbv. The California Air Resources Board (CARB) already approved a statewide 70 ppbv O₃ standard equal to the current NAAQS in April 2005. Compliance with the NAAQS, set by the Environmental Protection Agency (EPA), is determined by a region’s “design value.” The design value is calculated as the three-year running average of the fourth highest maximum daily 8-hr average O₃ (MDA8). Because of the implications for environmental regulation, we evaluate the link between Trinidad Head SOM nodes and MDA8/NAAQS at the surface O₃ sites.
The frequency and total number of exceedances of the current NAAQS/CARB O₃ standard (70 ppbv) for each Trinidad Head SOM node for the three surface O₃ sites is shown in Table 2. Given the possibility of future, stricter standards, results for a hypothetical 60 ppbv standard are also presented. Results for the surface sites correspond to the same day as the ozonesonde launches. Not surprisingly, the frequency of exceedances corresponding to polluted ozonesonde profiles in clusters 3 and 6 are much higher than the other nodes, maximizing at nearly a 50% frequency at Truckee (70 ppbv standard) on node 3 profile days. Almost 2/3 of node 7 profiles at Trinidad Head are from JJA. However, the exceedance frequency in node 7 at Truckee and Yosemite is half that of the polluted nodes 3 and 6, and there has never been a 70 ppbv exceedance at Lassen on the day a node 7 profile was observed. Extending this analysis to a stricter 60 ppbv standard shows a dramatic jump in exceedance rates. Under a 60 ppbv standard, the cleaner Lassen site exhibits exceedance rates similar to that of Truckee and Yosemite for the 70 ppbv standard, and there are no 0% exceedance nodes. The two polluted sites both display four SOM nodes containing ≥50% exceedance frequency for a 60 ppbv standard. The links between free-tropospheric and surface O₃ must be considered for NAAQS policy discussions as air quality regulations become ever more stringent.

4. Summary/Conclusions

We performed SOM clustering analysis on the lower tropospheric segment (surface – 6 km amsl) of the Trinidad Head ozonesonde dataset, consisting of 940 profiles from 1997 – 2015. As with our prior study of Trinidad Head ozone profiles from the surface to 12 km, we found strong connections between overall O₃ structure and certain meteorological conditions. We also
found that most SOM nodes included profiles from a range of seasons. Specifically, polluted O₃ profile clusters at Trinidad Head occur when the site is situated in a downstream position from a 500 hPa ridge, and subsiding air in an anti-cyclonic pathway around the semi-permanent Pacific subtropical high. These conditions lead to the highest surface O₃ values at three elevated air quality monitoring sites (Lassen, Truckee, and Yosemite) downwind of Trinidad Head; this relationship holds for several days after the sounding is made. The clear links among ozonesonde clusters, diurnal surface O₃, and MDA8/exceedance frequency at these locations have strong implications for the effectiveness of emissions controls and future policy considerations. For example, with a 60 ppbv MDA8 O₃ standard, several polluted ozonesonde SOM nodes are associated with an exceedance on more than half of days at Truckee and Yosemite.

The SOM allows identification of baseline O₃ amounts and their associated meteorological conditions, as it does not rely on the simple averaging that generates climatological O₃ values. Background O₃ of ~20-40 ppbv in cluster 1 occurred throughout the year when Trinidad Head was situated between a 500 hPa trough and ridge, and was likely influenced by a subtropical air mass. With the elevated O₃, nominally polluted in a few nodes, the SOM cannot distinguish imported O₃ from long-range transport or STE (see Appendix). However, it is safe to conclude that cases where high tropospheric O₃ is caused exclusively by one process or the other are rare. Profiles will need to be evaluated in conjunction with chemical model output on a case-by-case basis to determine dominant signals affecting the O₃ profile.

**Appendix A**
We describe efforts to combine analysis of the Trinidad Head SOM ozonesonde record with remotely-sensed CO and O₃ measurements from AIRS to distinguish STE and transported pollution contributions to O₃ profiles over the 14.5 year record. Stratospheric intrusions of air deep into the troposphere typically contain low amounts of CO and water vapor, and high amounts of O₃ and PV (Browell et al., 1996; Ott et al., 2016). Layers of transported pollution generally contain higher CO compared to typical tropospheric concentrations in conjunction with high O₃. Lin et al. (2012a) were able to use AIRS CO to detect influence from Asian emissions during the CalNex campaign in May – June 2010.

Data from AIRS was analyzed at 700 hPa (~3 km amsl, near the altitude of maximum O₃ in nodes 3 and 6) to identify potential pollution signatures in the Trinidad Head profiles. The same SOM output from the body of this paper is used, truncated to the AIRS data record length (September 2002 – March 2015). There is a distinct seasonal cycle of CO, so we present results in terms of anomalies from monthly means from the AIRS record.

The SOM node-averaged CO anomalies (Figure A1) provide compelling evidence for only a few of the Trinidad Head O₃ clusters. For example, node 1 exhibits an average CO anomaly of -4 ppbv. This is characteristic of clean, subtropical air influencing Trinidad Head given the low O₃MRs throughout the surface – 6 km profile in node 1. The highest CO anomalies occur in node 6, averaging 5 ppbv above climatology, indicating frequent pollution events on those days. The Trinidad Head site lies directly between a dipole of negative and positive CO anomalies in node 3, so we examine the individual cases to determine if separating influence from pollution and STE in the O₃ profiles is possible.

Figure A2 shows an analysis of CO, PV, and O₃MR at 700 hPa over the Trinidad Head site. Nodes 3 and 6, which contain the highest O₃MRs at this level, are distinguished from the
other nodes on the plot. One might expect an inverse relationship between PV and CO, but no such relationship is evident in Figure A2. There are individual cases that suggest low CO/high PV STE cases and vice versa, but there are also exceptions. Using RH and CO as a proxy for STE (not shown) also yields inconclusive results. Thus, the low altitudes where we observe high O₃ over Trinidad Head may be too far removed from both pollution and STE sources to separate them.

The SOM node-averaged O₃ anomalies (Figure A3) display the inability of AIRS to detect the thin layers of high O₃ observed in nodes 3 and 6 at Trinidad Head. In fact, AIRS reports negative O₃MR anomalies at 700 hPa in nodes 3 and 6. The true O₃MR anomalies as measured by the ozonesondes average between 8 – 15 ppbv above the monthly climatology. The O₃ distributions in Figure A3 appear to be tuned toward O₃MRs found at higher altitudes near 5 – 6 km amsl (see Figure 2). Nodes 1, 7, and 9, which all have notably high or low O₃MR at 5 – 6 km, also display large AIRS O₃ anomalies. This effect likely arises because of the vertical sensitivity of the AIRS instrument. AIRS is most sensitive in the mid-troposphere, generally between 300 – 600 hPa (Warner et al., 2007; Thonat et al., 2012). Thus, the majority of information input into the retrieval algorithm comes from above the O₃ maxima found in SOM nodes 3 and 6. The fact that the thin layers of high O₃ above Trinidad Head are unnoticed by AIRS shows that the satellite is no substitute for ozonesonde profiling.

The likelihood that many profiles contain elements of both STE and pollution make definitive characterization of the SOM nodes difficult. Additional information from chemical transport model output will be analyzed in future studies to determine the frequency and magnitude of STE and pollution effects on the Trinidad Head ozonesonde profiles.
Acknowledgments

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Table 1: Information on sites used in this study.

<table>
<thead>
<tr>
<th>Monitoring Site</th>
<th>Lat/Lon(°)</th>
<th>Altitude (m)</th>
<th>Dates Used</th>
<th>Distance to Trinidad Head (km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trinidad Head</td>
<td>40.8/-124.2</td>
<td>20</td>
<td>1997 – 2015</td>
<td>N/A</td>
</tr>
<tr>
<td>Lassen</td>
<td>40.5/-121.6</td>
<td>1756</td>
<td>1997 – 2015</td>
<td>219</td>
</tr>
<tr>
<td>Truckee</td>
<td>39.3/-120.8</td>
<td>1335</td>
<td>1997 – Oct. 2014</td>
<td>327</td>
</tr>
<tr>
<td>Yosemite</td>
<td>37.7/-119.7</td>
<td>1605</td>
<td>1997 – 2015</td>
<td>515</td>
</tr>
</tbody>
</table>
Table 2: Surface O$_3$ site frequency of exceeding the 70 ppbv NAAQS/CARB MDA8 surface O$_3$MR standard, and a hypothetical 60 ppbv standard, coincident with each SOM node from Trinidad Head, CA, O$_3$ profiles. Statistics for the surface sites are for the same day as the ozonesonde profile. Values $\geq$40% are in bold.

<table>
<thead>
<tr>
<th>Node</th>
<th>Lassen Volcanic</th>
<th>Truckee</th>
<th>Yosemite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(&gt;70 ppbv)</td>
<td>(&lt;70 ppbv)</td>
<td>(&lt;70 ppbv)</td>
</tr>
<tr>
<td>1</td>
<td>2.5%, (2 days)</td>
<td>16.4%, (9 days)</td>
<td>21.3%, (17 days)</td>
</tr>
<tr>
<td>2</td>
<td>0.6%, (1 day)</td>
<td>31.7%, (20 days)</td>
<td>13.6%, (21 days)</td>
</tr>
<tr>
<td>3</td>
<td>12.0%, (10 days)</td>
<td><strong>47.7%</strong>, (31 days)</td>
<td>37.3%, (31 days)</td>
</tr>
<tr>
<td>4</td>
<td>0.0%, (0 days)</td>
<td>10.0%, (7 days)</td>
<td>5.1%, (9 days)</td>
</tr>
<tr>
<td>5</td>
<td>0.9%, (1 day)</td>
<td>14.8%, (8 days)</td>
<td>11.5%, (13 days)</td>
</tr>
<tr>
<td>6</td>
<td>12.5%, (10 days)</td>
<td>39.7%, (27 days)</td>
<td><strong>40.0%</strong>, (32 days)</td>
</tr>
<tr>
<td>7</td>
<td>0.0%, (0 days)</td>
<td>17.9%, (7 days)</td>
<td>17.8%, (8 days)</td>
</tr>
<tr>
<td>8</td>
<td>1.6%, (2 days)</td>
<td>9.3%, (7 days)</td>
<td>14.7%, (19 days)</td>
</tr>
<tr>
<td>9</td>
<td>6.2%, (5 days)</td>
<td>29.4%, (20 days)</td>
<td>29.6%, (24 days)</td>
</tr>
<tr>
<td></td>
<td>(&gt;60 ppbv)</td>
<td>(&lt;60 ppbv)</td>
<td>(&lt;60 ppbv)</td>
</tr>
<tr>
<td>1</td>
<td>6.3%, (5 days)</td>
<td>34.5%, (19 days)</td>
<td><strong>42.5%</strong>, (34 days)</td>
</tr>
<tr>
<td>2</td>
<td>7.1%, (11 days)</td>
<td><strong>54.0%</strong>, (34 days)</td>
<td>25.3%, (39 days)</td>
</tr>
<tr>
<td>3</td>
<td>28.9%, (24 days)</td>
<td><strong>80.0%</strong>, (52 days)</td>
<td><strong>61.4%</strong>, (51 days)</td>
</tr>
<tr>
<td>4</td>
<td>4.0%, (7 days)</td>
<td>25.7%, (18 days)</td>
<td>14.3%, (25 days)</td>
</tr>
<tr>
<td>5</td>
<td>4.4%, (5 days)</td>
<td>37.0%, (20 days)</td>
<td>28.3%, (32 days)</td>
</tr>
<tr>
<td>6</td>
<td><strong>40.0%</strong>, (32 days)</td>
<td><strong>64.7%</strong>, (44 days)</td>
<td><strong>62.5%</strong>, (50 days)</td>
</tr>
<tr>
<td>7</td>
<td>17.8%, (8 days)</td>
<td>33.3%, (13 days)</td>
<td><strong>51.1%</strong>, (23 days)</td>
</tr>
<tr>
<td>8</td>
<td>12.4%, (16 days)</td>
<td>36.0%, (27 days)</td>
<td>34.9%, (45 days)</td>
</tr>
<tr>
<td>9</td>
<td>28.4%, (23 days)</td>
<td><strong>50.0%</strong>, (34 days)</td>
<td><strong>56.8%</strong>, (46 days)</td>
</tr>
</tbody>
</table>
Figure 1: Monthly-averaged O$_3$MR profiles for Trinidad Head, CA, from surface to 6 km amsl.
Figure 2: 3x3 SOM surface – 6 km amsl O$_{3}$MR output for Trinidad Head. The SOM nodes (cluster average O$_{3}$) are shown in black, with the individual O$_{3}$MR profiles in gray. The overall mean O$_{3}$MR (cyan), 20$^{th}$ and 80$^{th}$ percentile O$_{3}$MR (dashed cyan) are shown on all plots. The percentage of the total profiles and number of profiles in each SOM node appear on the figures.
Figure 3: Seasonality corresponding to each SOM node from Trinidad Head, shown as the relative frequency of months within each SOM node. Each histogram totals 100%.
Figure 4: Contoured map of average ERA-Interim 500 hPa geopotential heights and height anomalies from climatology corresponding to each SOM node. Anomaly data are contoured every 10 m from -60 to 60 m. Averaged data are contoured every 6 dm. Blue colors represent negative anomalies and red colors represent positive anomalies. The green dot represents the Trinidad Head site location.
Figure 5: Contoured map of average ERA-Interim MSLP and MSLP anomalies from climatology corresponding to each SOM node. Anomaly data are contoured every 1 hPa from -5 to 5 hPa. Averaged data are contoured every 2 hPa. Blue colors represent negative anomalies and red colors represent positive anomalies. The green dot represents the Trinidad Head site location.
Figure 6: Profiles of average O$_{3MR}$ (equivalent to SOM node), RH, and potential temperature ($\theta$) corresponding to each SOM node at Trinidad Head.
Figure 7: Contoured maps of HYSPLIT 10-day backward (A, top) and forward (B, bottom) trajectories terminating/starting at 3 km at time and location of O₃ profiles corresponding to each SOM node. Data are contoured based on the fraction of trajectories passing through 1° x 1° grid boxes. Contours are drawn every 0.01 from 0.05 to 0.40.
Figure 8: Monthly-averaged diurnal O₃MRs for each surface monitoring site. LST hour 04 was removed from Truckee because of lack of data.
Figure 9: Mean diurnal surface O$_{3MR}$ at Lassen Volcanic National Park corresponding to each SOM node. All surface O$_{3MR}$ average values are shown, with values corresponding to the SOM node of interest highlighted by the black line. Black dots represent the SOM node average ozonesonde O$_{3MR}$ corresponding to the same altitude as each surface O$_3$ site. Lines marking ±1 standard deviation beyond average ozonesonde O$_{3MR}$ and ozonesonde launch time are also shown. The number of days of surface O$_3$ data corresponding to each SOM node is shown in each frame.
Figure 10: As in Figure 9, but for the Truckee surface O₃ monitor. LST hour 04 was removed because of lack of data.
Figure 11: As in Figure 9, but for the Yosemite National Park – Turtleback Dome surface O₃ monitor.
Figure 12: Average diurnal surface O$_3$MR anomalies corresponding to each SOM node. Data from each site (columns) is given for the same day as the ozonesonde profile, up to three days after the profile date (rows).
Figure A1: Contoured map of average AIRS 700 hPa CO anomalies from monthly climatology corresponding to each SOM node. Data are contoured every 1 ppbv from -8 to 8 ppbv. Blue colors represent negative anomalies and red colors represent positive anomalies. The green dot represents the Trinidad Head site location.
Figure A2: Scatterplot of 700 hPa AIRS CO anomaly (ppbv) and ERA-Interim PV (PVU), with 700 hPa O₃MR from Trinidad Head ozonesondes in colors. Node 3 points are large circles, node 6 points are large squares, and the remaining nodes’ points are small circles.
Figure A3: Contoured map of average AIRS 700 hPa O$_3$ anomalies from monthly climatology corresponding to each SOM node. Data are contoured every 1 ppbv from -6 to 6 ppbv. Blue colors represent negative anomalies and red colors represent positive anomalies. The green dot represents the Trinidad Head site location.
Fraction of Trajectories Passing Through 1°×1° Boxes

Trajectories Terminate at 3 km

Legend:
0.4 0.35 0.3 0.25 0.2 0.16 0.1 0.05