Identifying sources of ozone to three rural locations in Nevada, USA, using ancillary gas pollutants, aerosol chemistry, and mercury

Matthieu B. Miller*, Rebekka Fine, Ashley M. Pierce, Mae S. Gustin *

Department of Natural Resources and Environmental Science, University of Nevada-Reno, 1664 N. Virginia St, Reno NV USA

*Corresponding authors: Matthieu B. Miller matthieu.b.miller@gmail.com and Mae S. Gustin mgustin@cabnr.unr.edu

Abstract:

Ozone (O_3) is a secondary air pollutant of long standing and increasing concern for environmental and human health, and as such, the US Environmental Protection Agency will revise the National Ambient Air Quality Standard of 75 ppbv to ≤ 70 ppbv. Long term measurements at Great Basin National Park (GBNP) indicate that O_3 in remote areas of Nevada will exceed a revised standard. As part of the Nevada Rural Ozone Initiative, measurements of O_3 and other air pollutants were made at 3 remote sites between February 2012 and March 2014, GBNP, Paradise Valley (PAVA), and Echo Peak (ECHO). Exceptionally high concentrations of each air pollutant were defined relative to each site as mixing ratios that exceeded the 90th percentile of all hourly data. Case studies were analyzed for all periods during which mean daily O_3 exceeded the 90th percentile concurrently with a maximum 8-h average (MDA8) O_3 that was "exceptionally high" for the site (65 ppbv at PAVA, 70 ppbv at ECHO and GBNP), and of potential regulatory significance. An $MDA8 \geq 65$ ppbv occurred only five times at PAVA, whereas this occurred on 49 and 65 days at GBNP and ECHO, respectively. The overall correlation between O_3 and other pollutants was poor, consistent with the large distance from significant primary emission sources. Mean CO at these locations exceeded concentrations reported for background sites in 2000. Trajectory residence time calculations and air pollutant concentrations indicate exceedances at GBNP and ECHO were promoted by air masses originating from multiple sources, including wildfires, transport of pollution from southern California and the marine boundary layer, and transport of Asian pollution plumes. Results indicate that the State of Nevada will exceed a revised O_3 standard due to sources that are beyond their control.

Keywords: National Ambient Air Quality Standards, criteria air pollutants, long-range transport, wildfire emissions

1. Introduction

Ozone (O_3) is an allotrope of oxygen (O), formed in the atmosphere through photochemical reactions. In the stratosphere, incident high-energy ultraviolet radiation ($\lambda < 242\text{nm}$) causes photo dissociation of O_2 into free oxygen radicals ($O_2 + h\nu \rightarrow O + O$) which rapidly react to form O_3 ($O_2 + O \rightarrow O_3$) (Chapman, 1930). Once formed, O_3 will itself dissociate under the impact of these high energy photons, producing a dynamic equilibrium that effectively blocks all radiation at this wavelength from reaching the lower atmosphere and earth surface. As a result of these stratospheric processes, tropospheric O_3 is naturally present only in small concentrations through either stratosphere-to-troposphere transport (STT), or in-situ photochemical oxidation of O_3 precursor molecules (Chameides et al., 1992; Finlayson-Pitts and Pitts, 2000; Stohl et al., 2003). Volatile organic compounds (VOCs) and nitrogen oxides (NO_x) are the main precursor emissions contributing to urban photochemical smog and ground level O_3 (Haagen-Smit, 1952; Chameides et al., 1992; Silliman, 2003).

Ozone is a strong oxidizing agent damaging to both environmental and human health (Chen et al., 2007; NRC, 2010). The United States Environmental Protection Agency (US EPA) currently maintains a National Ambient Air Quality Standard (NAAQS) of 75 ppbv for ground level O_3 over an 8-h period, and will revise this standard to between 60 – 70 ppbv (EPA, 2010). Long term monitoring of O_3 by the National Park Service (NPS) at Great Basin National Park (GBNP), a remote, high elevation ($> 2000\text{m}$) site in eastern Nevada, has demonstrated that maximum daily 8-h average (MDA8) O_3 at times exceeds the current NAAQS. Trend analyses by Fine et al. (this issue) have shown year-to-year increases in peak hourly O_3 at GBNP in late spring. Considering this trend, and known observations, GBNP has been non-compliant at the current NAAQS, and certainly will be, under a tighter regulatory standard, despite being far removed from any significant O_3 precursor emission sources. Similar remote, high elevation terrain throughout Nevada and the American west could also be affected by O_3 exceedances (Jaffe and Ray, 2007; Cooper et al., 2010; Gustin et al., this issue). Increases in baseline O_3 are due in large part to pollution transported in the free troposphere from Asian emission sources, a mechanism that contributes to observed O_3 mixing ratios in the Western United States (Zhang et al., 2008; Brown-Steiner and Hess, 2011; Lin et al., 2012b; Lin et al., 2014).

To address the lack of O_3 measurements in Nevada beyond the major urban areas of Reno-Sparks and Las Vegas, and an overall lack of data on baseline O_3 in much of the high elevation Western US, the Nevada Rural Ozone Initiative (NVROI) established a series of O_3 monitoring sites throughout rural areas

of the State in 2011 (Gustin et al., this issue). As part of this study, several sites were selected for additional instrumentation to help quantify air pollutant composition and identify potential sources of O_3 . One of these sites was GBNP, and the others were at Paradise Valley (PAVA) in north-central Nevada, and Echo Peak (ECHO) on the Nevada Nuclear Security Site (NNSS) in the south (Figure 1). Since ancillary air pollutants, aerosols, and mercury (Hg) species may enter Nevada by way of the free troposphere (Weiss-Penzias et al., 2009; Gustin et al., 2013; Huang and Gustin, 2012), we hypothesized that these in combination may be applied to understand sources of O_3 to Nevada. Long-range transport of Asian pollution contributes significantly to observed O_3 mixing ratios over the Western United States (Zhang et al., 2008; Lin et al., 2012b; Lin et al., 2014). Here we use multiple parameters including CO , SO_2 , NO , NO_x , NO_y , $PM_{2.5}$ and 10, Interagency Monitoring of Protected Visual Environments (IMPROVE) particulate chemistry, mercury, and detailed trajectory analyses. This paper summarizes the O_3 and ancillary pollutant data measured at these sites between February 2012 and March 2014, and identifies sources during exceptionally high O_3 observations that will have regulatory significance under the current and revised NAAQS.

2. Methods

2.1 Sites

For a detailed description of each site (Figure 1) and detailed site maps, see Gustin et al. (this issue).

Great Basin National Park (GBNP) is located on the central eastern edge of Nevada, in the southern Snake Range. The monitoring site (N39.0050 W114.2161, elev. 2060 m) is located within the park on the eastern lower slopes of the mountain range, overlooking the Snake Valley. The site is collocated with an NPS IMPROVE and CASTNET (Clean Air Status and Trends Network, GRB411) site. O_3 has been monitored at this location by the NPS since 1995, and mean hourly O_3 data were obtained from the NPS Gaseous Pollutant and Meteorological Data website (<http://ard-request.air-resource.com>). Particulate matter ($PM_{2.5}$) chemistry and concentration data from the IMPROVE network were obtained from <http://views.cira.colostate.edu/web/>. For criteria air pollutant measurements, a suite of Teledyne Advanced Pollution Instrumentation (TAPI) trace level gas analyzers was operated at GBNP from March 2012 to April 2014. These included CO (T300U), SO_2 (T100U), NO and NO_x (T200U), and NO and NO_y (T200UY). The NO_y measurement is the sum of NO_x ($NO + NO_2$) plus non- NO_x reactive nitrogen species, termed NO_z ($NO_x + NO_2 = NO_y$). NO_z includes a number of reactive oxidized nitrogen species, including

nitric acid (HNO_3) and peroxyacetyl nitrate (PAN), and these compounds can be potential interferences for the standard $\text{NO}/\text{NO}_2/\text{NO}_x$ measurement (Fahey et al., 1986; Dunlea et al., 2007).

In addition to the trace gas analyzers, several other instruments were operated intermittently at GBNP. An E-BAM particulate monitor (Environment-proof Beta Attenuation Monitor, Met One) was operated from November 2012 to August 2013 at the $\text{PM}_{2.5}$ size fraction. A Tekran 2537/1130/1135 Mercury Speciation System was operated at GBNP from September 2012 to July 2013. This instrument measures gaseous elemental Hg (GEM), gaseous oxidized Hg (GOM), and particulate bound Hg (PBM). Despite the fact that the Tekran GOM measurement collects different compounds of Hg(II) with different efficiency (Huang et al., 2013), and that the KCl coated denuder has interferences with O_3 and water vapor (Lyman et al., 2010; Gustin et al., 2013; Jaffe et al., 2014), these data are presented here because measurements from the Tekran instrument have been demonstrated to allow for identification of air from the free troposphere (Gustin et al., 2013). See Supplemental Information (SI) for instrument details.

Paradise Valley (PAVA) is located in central northern Nevada. The monitoring site (N41.5031 W117.4981, elev. 1385 m) is located on a private ranch within the valley, which is narrow and enclosed to the west and north by the Santa Rosa Range, and on the east by the Hot Spring Range. A suite of Thermo Fisher gas analyzers were operated at PAVA from February 2012 to April 2014. These included O_3 (49i), CO (48i), SO_2 (43i), and NO- NO_x (42i). A $\text{PM}_{2.5}$ E-BAM instrument was also operated at PAVA. See SI for instrument details.

Echo Peak (ECHO) is a NNSS radio and telecommunication station located on the southern edge of the Pahute Mesa in southwest Nevada (N37.2128 W116.3236, elev. 2286m). Due to the elevation, remoteness, and secure nature of this site, access was limited, and usually not possible during the winter months. At ECHO, a 2B Model 205 O_3 monitor was operated from May 2012 to April 2014 within an NNSS equipment shelter at the site. A Teledyne API T300U trace level CO analyzer was installed in June 2013 and was in operation until April 2014. See SI for instrument details.

2.2 Meteorology

Meteorological data collected at each site included temperature and relative humidity (CS HMP45C $\pm 0.2 - 0.3^\circ\text{C}$ and $\pm 2\%$), wind speed and direction (RM Young 05305 $\pm 0.2 \text{ m s}^{-1}$), and barometric pressure (Vaisala PTB110 $\pm 0.15 \text{ hPa}$). Data were recorded at 5 minute intervals using Campbell Scientific CR series data loggers, and hourly averages were calculated in post-processing. For GBNP, temperature and

relative humidity data were downloaded from the NPS Gaseous Pollutant and Meteorological Data website (<http://ard-request.air-resource.com>).

2.3 Quality Control

The array of instruments at GBNP and PAVA required site visits every 4-6 weeks for basic maintenance and calibration checks. ECHO was visited monthly (or as possible) by NNSS personnel, between major maintenance visits. Daily zero checks and weekly span checks were performed on an automated schedule using the on-site calibration systems. Data was manually retrieved at each site visit. A full description of the quality control, maintenance, and data processing procedures can be found in the SI.

2.4 Back Trajectory Modeling

Back trajectories were calculated using the HYSPLIT v.4 model (Hybrid Single Particle Lagrangian Integrated Trajectory, see Draxler and Hess, 1997) from the National Oceanic and Atmospheric Administration Air Resources Laboratory (NOAA ARL). Trajectories were calculated using National Centers for Environmental Prediction/National Center for Atmospheric Research (NCEP/NCAR) Reanalysis 1 Pressure Level Data, downloaded from the NOAA ARL Gridded Meteorological Data Archives (<http://www.ready.noaa.gov/archives.php>). The NCEP/NCAR Reanalysis is a 2.5 degree latitudinal-longitudinal global meteorological grid calculated at 17 pressure levels with a temporal resolution of 6 hours. Trajectory ensembles were initiated for dates of interest at 0000, 0600, 1200, and 1800 Pacific Standard Time (PST), and extended back in time 240 hours (10 days) from 9 points within a 0.5 x 0.5 degree grid, centered over each site at arrival heights of 500, 1000, 1500, and 2000 m (Fine et al, this issue). Total residence time (TRT) calculations were used for analysis of the trajectory data. The number of trajectory points within predefined source boxes (Figure SI 1) was divided by the total number of points in each trajectory ensemble to arrive at a percent TRT (Weiss-Penzias et al., 2009).

2.5 Data & Statistical Analyses

Statistical analyses were performed using Microsoft Excel and Sigmaplot. Correlative results were considered significant at a confidence level of 95% ($\alpha = 0.05$). Data are presented as mean $\pm$ standard deviation unless otherwise noted. The 90th percentile value was used to define exceptionally high mixing ratios of each measured air pollutant. Detailed case studies were developed for exceptionally high O₃ events. These exceptional events were defined periods during which mean daily O₃ exceeded

the 90th percentile at the same time that maximum 8-h average (MDA8) O₃ was equal to or greater than high values (65 ppbv at PAVA, 70 ppbv at ECHO and GBNP) that are of potential regulatory significance.

3. Results and Discussion

3.1 Ancillary Air Pollutants

Ancillary air pollutant data for PAVA, GBNP, and ECHO are summarized by year in Table 1. O₃ was not correlated with CO, SO₂, NO, NO_x, or NO_y on either a mean hourly or daily time step ($r^2 < 0.15$ for NO and NO_x and < 0.05 for all others). No correlations were observed when hourly data was binned into seasonal brackets, except in spring months at PAVA, there was a weak inverse relationship between NO and NO_x and O₃ ($r^2 = 0.17$ $n = 3231$, $r^2 = 0.16$ $n = 2469$, p -values < 0.001). At ECHO, mean hourly O₃ was not correlated with CO overall or seasonally (r^2 values < 0.05). Of particular interest were periods with exceptionally high O₃ and/or ancillary pollutant gases. The highest O₃ was typically observed in the months of May through August. Overall, the highest NO, NO_x, NO_y, and SO₂ values occurred primarily in the fall and winter without any correspondingly elevated O₃, and the highest CO events frequently occurred in the summer and fall (Figure 2). The highest peak hourly CO values typically correlated well with exceptionally high O₃, but all exceptionally high CO data together was not correlated with O₃.

3.1.1 Ozone

The mean O₃ mixing ratio at PAVA over the duration of measurement was 31 ± 12 ppbv, and O₃ followed a strong seasonal pattern, with higher mixing ratios observed in the summer and spring (37 ± 13 and 33 ± 13 ppbv) versus the winter and fall (28 ± 10 and 27 ± 11 ppbv). Hourly O₃ mixing ratios above the 90th percentile (> 47.7 ppbv) were observed approximately from late March to October, and these exceptionally high values showed a slight significant correlation with CO ($r^2 = 0.13$, $n = 1636$, p -value < 0.001). For comparable periods of data, approximately 19% of exceptionally high O₃ values occurred when CO was also elevated. High O₃ was not significantly correlated with the other measured pollutant gases (r^2 values < 0.05). A total of 5 days at PAVA had a MDA8 ≥ 65 ppbv over the entire period of measurement, and no days exceeded 70 ppbv. It should be noted that PAVA measurements were consistently lower than all other NVROI sites due to the location in a narrow valley and the influence of air masses from the north (Gustin et al., this issue).

The mean O₃ mixing ratio at GBNP was 46 ± 9 ppbv. Averaged seasonally, the highest O₃ was observed in the spring (54 ± 9 ppbv), followed by summer (49 ± 9 ppbv), then winter (43 ± 6 ppbv) and fall (41 ± 6

ppbv). Exceptionally high O₃ mixing ratios (> 61 ppbv) were observed primarily from late March to mid-August. Considering all 1-h O₃ mixing ratios above 61 ppbv, there was no significant correlation with the other measured criteria pollutant gases (r^2 values < 0.05). A total of 49 days at GBNP had an MDA8 $\geq$ 65 ppbv over the period of measurement, 42 of which were in the months May and June, and eight of those days exceeded an MDA8 of 70 ppbv.

At ECHO, the overall mean O₃ mixing ratio was 49 ± 9 ppbv. O₃ was highest in the summer and spring (55 ± 8 and 52 ± 7 ppbv, respectively), and lowest in the winter and fall (43 ± 5 and 45 ± 7 ppbv, respectively). Hourly O₃ data greater than the 90th percentile (> 61 ppbv) were not correlated with CO ($r^2 = 0.02$, $n = 290$). However, when both measurements were available, approximately 27% of exceptionally high 1-h O₃ mixing ratios occurred when CO was also elevated above the 90th percentile. A total of 65 days at ECHO had an MDA8 $\geq$ 65 ppb, and 7 of these exceeded 70 ppbv.

3.1.2 Carbon Monoxide

The mean CO mixing ratio at PAVA was 135 ± 50 ppbv over the duration of measurement. No distinct seasonal pattern was apparent in the CO data, except that large spikes in CO tended to occur in the summer months as a result of combustion from local and regional wildfires (see case study discussions below). CO mixing ratios above the 90th percentile (> 183 ppbv) were not significantly correlated with O₃ ($r^2 = 0.02$, $n = 1695$). For example, the highest observed CO was 967 ppbv (2100 PST, October 10, 2012). This was a night-time event which was not correlated with elevated O₃, but corresponded with a peak in NO and NO_x of 2.1 and 5.3 ppbv, respectively. The NO₂/NO_x ratio (0.60) for this event indicates incomplete plume oxidation and a local primary emission source.

The overall mean CO mixing ratio at GBNP was 108 ± 32 ppbv. Seasonal mean CO values were not significantly different (102 to 120 ppbv). CO above the 90th percentile (> 140 ppbv) showed no correlation with O₃ ($r^2 < 0.01$, $n = 1188$). For example, the highest observed CO mixing ratio was 580 ppbv (July 22, 2013). This was a night event lasting from 1900 to 0700 PST, and was not associated with elevated O₃ (mean 45 ± 4.5 ppbv), but directly corresponded to an increase in NO_x and NO_y (max 5.5 and 5.7 ppbv, respectively). These high mixing ratios were related to nighttime subsidence of smoke emissions from the Black Fire, burning 18.8 km² in the Highland Ridge Wilderness approximately 18 km to the south of GBNP. Back trajectory calculations indicate air flow below 500 m was from the south-southwest in the 24 hours preceding this event, and surface winds at the site were dominated by a down-canyon wind with an average vector of 226 degrees during the event.

The CO record at ECHO included only part of summer 2013 and winter 2013-2014, however, the mean mixing ratio (130 ± 34 ppbv) was similar to GBNP and PAVA. The highest recorded CO value was 259 ppbv (1400 PST, March 23, 2014), but this is likely a low bias due to the shorter data record. CO above the 90th percentile (> 172 ppbv) showed no correlation with O_3 ($r^2 = 0.02$, $n = 392$). Mean CO concentrations at all sites exceeded the range in concentrations for background locations given by Finlayson-Pitts and Pitts (2000) demonstrating the impact of increasing anthropogenic emissions from the Asian continent on the Western United States (Table 1).

3.1.3 Sulfur Dioxide

The mean SO_2 mixing ratio at PAVA was 0.17 ± 0.34 ppbv over the duration of measurement, with a maximum recorded mixing ratio of 9.3 ppbv (November 5, 2013). The majority of SO_2 observations were below the minimum detection limit of the analyzer (< 0.2 ppbv). SO_2 above the 90th percentile (> 0.41 ppbv) showed no correlation with O_3 ($r^2 = 0.01$, $n = 1764$). There was not a distinct seasonal pattern in SO_2 , however the highest SO_2 mixing ratios were observed in the months of November through January (Fig. 2a).

The mean SO_2 mixing ratio at GBNP was 0.05 ± 0.09 ppbv, with a maximum recorded mixing ratio of 0.74 ppbv (June 2, 2012). SO_2 above the 90th percentile (> 0.16 ppbv) showed no correlation with O_3 ($r^2 = 0.024$, $n = 419$). Data collection was intermittent due to repeated component failures. The limited dataset indicated SO_2 was below 1 ppbv even during peak events, and due to the operational difficulties this analyzer was taken offline on June 5, 2013. While SO_2 gas mixing ratios tended to be low, sulfate is usually the dominant component of fine mass measured at the GBNP IMPROVE site (SI Figure 12). This indicates substantial oxidation of SO_2 in aged pollution plumes, consistent with long-range transport from distant combustion sources, the primary emitter of SO_2 and accounting for an estimated 72% of all sulfate aerosols in the atmosphere (Haywood and Boucher, 2000).

3.1.4 Nitrogen Oxides

At PAVA, the mean NO and NO_x mixing ratios were 0.4 ± 0.6 and 2.1 ± 1.8 ppbv over the duration of measurement. These values are indicative of background concentrations (Table 1) and the overall NO_2/NO_x ratio of 0.82 indicates a high degree of oxidation and limited nearby primary NO emissions. However, the peak hourly NO and NO_x recorded was 9.9 and 22.0 ppbv (1800 PST, October 27, 2012), with an NO_2/NO_x ratio of 0.55 indicating a substantial percentage of un-oxidized NO, suggesting local emission sources sometimes contribute to exceptionally high NO_x mixing ratios.

For the NO_x measurements available at GBNP (March 2013 to March 2014), mean NO and NO_x mixing ratios were 0.06 ± 0.24 and 0.46 ± 0.68 ppbv, respectively. NO and NO_y (T200UY) measurements were available from March 2012, with overall mean mixing ratios of 0.15 ± 0.32 and 0.70 ± 0.87 ppbv, respectively, and a maximum observed hourly NO_y concentration of 41.7 ppbv (December 11, 2013). The overall NO_2/NO_x ratio was 0.72, indicating some local primary NO sources. The mean hourly NO_x/NO_y ratio of 0.65 indicated a significant percentage of NO_2 species was normally present. However, while the highest O_3 mixing ratios were observed in May and June, the mean NO_y mixing ratio during this time was lower than average at 0.59 ± 0.26 ppbv, as was NO_x at 0.32 ± 0.18 ppbv (data available 2013 only). This suggests that nitrogen oxides, including PAN, a major chemical transport mechanism for O_3 precursor emissions (Fischer et al. 2011; Lin et al., 2012a), were not a strong driver of exceptionally high O_3 at GBNP in spring 2013.

3.1.5 Fine Particulate Matter & Mercury

The overall mean daily $\text{PM}_{2.5}$ concentration at PAVA was $7.4 \mu\text{g m}^{-3}$ with a maximum daily concentration of $54 \mu\text{g m}^{-3}$ observed in August 2013. Mean daily $\text{PM}_{2.5}$ at PAVA was not correlated with mean daily O_3 ($r^2 = 0.01$) or with any other gas parameter except for a weak significant correlation with mean daily CO ($r^2 = 0.21$, $p < 0.01$). However, mean daily $\text{PM}_{2.5}$ concentrations above the 90th percentile ($10.7 \mu\text{g m}^{-3}$) were moderately correlated with CO ($r^2 = 0.36$, $p < 0.01$) and with mean daily O_3 ($r^2 = 0.16$, $p < 0.01$). This reflects the influence of wildfire smoke on CO and $\text{PM}_{2.5}$ concentrations at PAVA, and the tendency for the highest O_3 to occur during such conditions (discussed below).

At GBNP, the mean $\text{PM}_{2.5}$ concentration over the period of measurement was $4.9 \mu\text{g m}^{-3}$, with a maximum daily mean value of $13.0 \mu\text{g m}^{-3}$, and $\text{PM}_{2.5}$ was not well correlated (r^2 values < 0.1) with any other measured parameters. Hg data was available at GBNP between September 2012 to January 2013, and April to July 2013. Overall, mean concentrations of GEM, PBM, and GOM were $1.2 \pm 0.4 \text{ ng m}^{-3}$, $15 \pm 11 \text{ pg m}^{-3}$, and $24 \pm 19 \text{ pg m}^{-3}$, respectively. The mean spring and summer GEM concentration ($1.4 \pm 0.4 \text{ ng m}^{-3}$) was statistically significantly higher than mean fall and winter concentration ($0.9 \pm 0.4 \text{ ng m}^{-3}$, t-test, $p < 0.001$), which supports greater interception of polluted air at GBNP during the spring months.

3.2 Identification of Sources Contributing to Exceptional Ozone Events: Case Studies

3.2.1 Paradise Valley

Exceptionally high O₃ events at PAVA were observed on 10 days exceeding the 90th percentile O₃ mixing ratio of 47.7 ppbv, and five days in which the O₃ MDA8 exceeded 65 ppbv. As mentioned, the lower O₃ values for this site relative to other locations are due to its location in a narrow, steep valley affecting convective boundary layer mixing, resulting in less impact from the free troposphere, and the influence of air masses from more northerly areas, compared to more southerly sites in the State (see Gustin et al., this issue). The majority of exceptionally high O₃ events, as well as the highest individual O₃ mixing ratios, corresponded directly with visible smoke from local or regional wildfires, and high concentrations of CO, SO₂, NO_x, and PM_{2.5}. Wildfires have previously been identified as contributing sources for elevated O₃ (Jaffe et al., 2008; Jaffe and Widger 2012). Calculated trajectory residence times indicated little input from Asia or transport over the marine boundary layer for these events (Table SI 1).

During the period August 6 to 21, 2012, three days were above the mean 90th percentile for O₃ at PAVA, and four days exceeded an MDA8 of 65 ppbv. The elevated O₃ was attributable to smoke plumes from several regional wildfires (primarily the Holloway Fire of August 6 to 7, to the west-northwest of PAVA on the Oregon-Nevada border; and the Hanson Fire of August 10-25, approximately 12 km due west). On August 6, the O₃ MDA8 reached 65 ppbv while mean daily CO, NO, and NO_x reached 190, 0.9, and 4.7 ppbv, respectively. The highest O₃ observed at PAVA occurred on August 11 while the site was directly within the smoke plume from the Hansen Fire (Figure 3, SI Figures 2-3), with an MDA8 of 67 ppbv and hourly mean O₃ values that exceeded 80 ppbv simultaneously with peak values in CO, SO₂, NO, and NO_x (709, 1.1, 0.7, and 8.2 ppbv, respectively). During the day while relative humidity (RH) was below 20% (10:00-23:00), O₃ was well correlated with CO ($r^2 = 0.79$), SO₂ ($r^2 = 0.80$), and NO_x ($r^2 = 0.67$, p-values < 0.001).

Wildfire activity also contributed to exceptionally high O₃ events observed at PAVA in the summer of 2013. Diffuse amounts of smoke from the Rim Fire, burning west of Yosemite National Park in central California from August 17 to October 24, were first evident at PAVA beginning on August 18. When the main plume of the fire descended over PAVA on August 23 (SI Figure 4), mean daily CO reached 367 ppbv, with a peak hourly mixing ratio of 620 ppbv. On August 24, mean hourly O₃ peaked at 73 ppbv concurrently with a peak in NO and NO_x of 0.44 and 2.32 ppbv, respectively, and the MDA8 was 68 ppbv, the highest observed at PAVA and the only other day with an MDA8 ≥ 65 ppbv. CO mixing ratios

remained elevated through September and into October serving as a conservative tracer for the fire. However, NO and NO_x were only intermittently elevated during this time period, presumably related to the progression of the Rim Fire and less consumption of vegetation as the fire became contained.

The only exceptionally high O₃ days at PAVA not related to wildfire (but not exceeding ≥ MDA8 65 ppbv) occurred April 30 to May 6, 2013. The sources of exceptionally high O₃ during this time period resulted from two separate mechanisms. From April 30 to May 2, 2013, daily mean O₃ values were exceptionally high (49 to 51 ppbv). This event was associated with the passage of a cold front, the leading edge of which moved across northern Nevada on April 30. Mean daily CO dropped sharply from 140 ppbv on April 29, down to 114 ppbv on April 30 following passage of the front. Mean daily NO_x also decreased from 0.6 ppbv to 0.2 ppbv. On May 2, mean hourly O₃ peaked at 64 ppbv at 17:00-18:00 PST, and the MDA8 reached 61 ppbv. This elevated O₃ event is attributed to deep down mixing of stratospheric air to the surface (Lin et al., 2012a), as indicated by the high barometric pressure (873 mbar versus mean daily pressure of 863 ± 5 mbar) and the extremely low RH (minimum 5.4%). Back-trajectory and TRT calculations from May 1-2 support this interpretation, indicating a uniform air stream descending from altitudes above 5 km from the north-northwest, with zero percent of trajectory points passing through any delineated source region (SI Table 1, SI Figure 5).

Mean daily O₃ again exceeded the 90th percentile on May 4-6, with peak O₃ occurring at 15:00 PST on all days. From May 3 to May 6, a surface low pressure trough moved across Northern California into Nevada following the cold front. Over this period, mean daily CO increased sharply from 124 ppbv on May 3 to 174 ppbv on May 6, and NO and NO_x increased up to 0.3 and 1.4 ppbv, respectively. This O₃ event was also observed slightly earlier at both ECHO and GBNP (May 5, MDA8 of 71 and 76 ppbv, respectively, discussed in detail below). Elevated O₃ during this period was attributed to regional transport of polluted air parcels from southern California and southern Nevada. Back-trajectory calculations indicated an enhanced number of trajectory points passing through the LA and LV source boxes versus the median percentile range for this season (SI Table 1, SI Figure 6). The exceptionally high CO signal observed during this event is attributed to smoke from the Springs Fire, which burned 24,000 acres in the Santa Monica Mountains of southern California between May 2 and May 12.

3.2.2 Great Basin & Echo Peak

Unlike PAVA, exceptionally high O₃ events at GBNP and ECHO were relatively large and frequent (21 and 14 days, respectively, Table 2). For both ECHO and GBNP, the 90th percentile O₃ mixing ratio was 61

ppbv. Trajectory residence times (Table SI 2 and SI 3) for exceptionally high events at GBNP and ECHO indicate significant transport over the marine boundary layer, indicating the importance of long range transport from the Asian continent. MDA8 O₃ at GBNP was analyzed in detail by Fine et al. (this issue). During 2012, there were 15 days exceeding an MDA8 of 70 ppbv at GBNP (Table 2). At ECHO, 9 days in 2012 were recorded with MDA8 values greater than 70 ppbv in June and July, and all of these days occurred within the same exceptional event periods identified at GBNP. However, no criteria pollutant data was available for the months of May to July at GBNP, and CO data was only available after July 8 at ECHO. Back trajectory and TRT calculations indicated that similar transport patterns were in place for both sites in 2012, with a significant percentage of air moving through and over the marine boundary layer (MBL) (SI Figures 7-11). IMPROVE data from GBNP during this time period indicated that in the majority of these exceptional events fine mass was dominated by total sulfate (SO₄ + NH₄SO₄, mean 40.5%, SI Figure 12), an indicator of long-range pollution transport (Brown-Steiner and Hess, 2011; Lin et al. 2012b). During 2013, four exceptionally high O₃ events occurred simultaneously at both GBNP and ECHO, for which ancillary pollutant and other tracer data enabled a more detailed study on a case by case basis (Table 2).

O₃ values at GBNP rose sharply during May 5, 2013, to a peak of 80 ppbv at 1700 PST, exceeding the NAAQS, and remained exceptionally high into May 6. Exceptionally high O₃ was also observed at ECHO on May 5 (Table 2). At GBNP this event was characterized by a concurrent rise and peak in CO (145 ppbv) and PM_{2.5} (19 µg m⁻³). For the whole period of May 5-6, O₃ was well correlated with CO ($r^2 = 0.58$, p -value < 0.001) and PBM ($r^2 = 0.42$, p < 0.01), and weakly significantly correlated with PM_{2.5} ($r^2 = 0.16$, p < 0.01) and SO₂ ($r^2 = 0.17$, p < 0.01). There was an inverse correlation with GEM ($r^2 = 0.47$, p < 0.01), as well as a weak inverse correlation with NO_x ($r^2 = 0.17$, p < 0.01) and NO_y ($r^2 = 0.10$, $p = 0.03$). The mean hourly NO₂/NO_x ratio was 0.86 ± 0.04 (range 0.71-0.93), indicating that NO₂ was the dominant nitrogen species. Back-trajectory calculations illustrate that a majority of the air mass impacting GBNP and ECHO descended from above 3 km, but a significant fraction of trajectory points passed through the Los Angeles (LA) and MBL boundary layers (Figure SI 13, SI Table 2). The relatively high CO mixing ratio and the correlations between O₃, CO, and PM_{2.5} suggests a component of wildfire smoke, and this event is attributed to the Springs Fire in southern CA superimposed upon Asian pollution, a source that is consistent with back trajectory calculations. GEM clearly decreased concurrently with increasing O₃ during this event, possibly converted to GOM (not adequately captured by the denuder, see Gustin et al., 2015) or PBM in the presence of a strong oxidant plume and fine particulate matter.

During the period of May 21 to 26, 2013, both GBNP and ECHO had exceptionally high O₃ mixing ratios (Table 2). On May 25-26 in particular, MDA8 O₃ at GBNP exceeded 70 ppbv. CO was only weakly correlated ($r^2 = 0.16$, $p = 0.01$) with O₃ on these days, and while slightly elevated above the overall springtime seasonal mean (114 versus 102), did not exceed 90th percentile levels. However, SO₂ was moderately well correlated ($r^2 = 0.39$, $p < 0.001$) and reached peak values around 0.2 ppbv during the same hours that O₃ was at its peak (77 to 79 ppbv, 0800 to 1000 PST, May 25). GEM was moderately inversely correlated with O₃ ($r^2 = 0.49$, $p < 0.001$), and while PM_{2.5} and PBM showed no relationship with O₃ ($r^2 < 0.01$), GOM was moderately positively correlated with O₃ ($r^2 = 0.63$, $p\text{-value} = 0.01$) suggesting that the high O₃ mixing ratios during this event directly contributed to formation of GOM through oxidation of GEM. Back trajectory calculations indicated that most of the air impacting GBNP on these days had moved southeastward from the Arctic and Alaska, over the Gulf of Alaska and eastern Pacific at altitudes below 1.5 km, and recently passed through major parts of the MBL, San Francisco, San Joaquin, or Los Angeles source areas (SI Table 2, Figure SI 14). IMPROVE data for May 25 shows that sea salt and total sulfate accounted for relatively high percentages of total fine mass (3.1% and 57.5% versus seasonal means of 1.3% and 35%, respectively, SI Figure 12). These aerosol data suggest a maritime source, such as oxidation of SO₂ emissions from diesel vessels (Cooper et al., 2011), or possibly biogenic dimethyl sulfide emissions from marine plankton (Bates et al., 1992). The NO₂/NO_x ratio of 0.86 and the NO_x/NO_y ratio of 0.57 indicated a significant amount of oxidation of NO to NO₂ to NO_z species, supporting an aged plume and transport (Slowik et al., 2011).

On June 2, mean hourly O₃ reached 85 ppbv at ECHO (1400 PST) and 83 ppbv at GBNP (2000 PST) and MDA8 values over 70 ppbv (Table 2). Additionally, the Clark County Department of Air Quality (which includes the Las Vegas metropolitan area) reported an MDA8 of 73 ppbv for June 2 (http://airquality.clarkcountynv.gov/cgi-bin/aqi_map.pl). At GBNP, the peak in O₃ was coincident with a spike in other pollutant gases, lasting from 1900 to 2400 PST (Figure 4). During this 6-h time period, O₃ was strongly correlated with CO ($r^2 = 0.90$), SO₂ ($r^2 = 0.79$), NO_x ($r^2 = 0.86$), and NO_y ($r^2 = 0.85$), and was well correlated with PM_{2.5} ($r^2 = 0.62$, all $p\text{-values} < 0.001$). Concentrations of all parameters decreased dramatically as RH increased above 20% after 2400 PST. No Hg data was available for this time. Back trajectory calculations for June 2 indicated the majority of trajectories traveling at altitudes greater than 5 km over Asia and the northern Pacific before descending in a clockwise spiral above southern Nevada (Figure SI 15). Exceptionally high CO values observed at GBNP during this plume (316 ppbv) are similar to those observed in other known smoke plumes, and this is attributable to emissions from the Powerhouse Fire, which began May 30 in the San Gabriel Mountains north of Los Angeles. MODIS

imagery clearly revealed smoke from this fire moving northeast over southern Nevada on June 2 (Figure SI 16). Thus, this event is attributable to both long-range transport and regional pollution.

June 16 to 18 was the last event in 2013 with exceptionally elevated O_3 at GBNP, with MDA8 values reaching 74 and 76 ppbv on June 17 and 18, respectively. This event was less pronounced but also apparent at ECHO (Table 2). At 1100 PST June 17, barometric pressure began to decrease sharply from 796 mbar down to a low of 785 mbar on June 18. At the same time, O_3 increased sharply from 61 ppbv at 1200 to 77 ppbv at 1700 PST, and CO showed a simultaneous rise from 81 ppbv to 116 ppbv. Both O_3 and CO remained elevated until 1800 June 18, at which time mixing ratios declined sharply to 51 and 70 ppbv, respectively. Though not occurring simultaneously with the increase in O_3 and CO, two spikes in NO_x and NO_y (up to 1.5-1.8 ppbv) occurred during the morning (0600 – 1000 PST) of June 18, with the NO_x/NO_y ratio (0.52) indicating a substantial NO_2 component. No exceptional $PM_{2.5}$ peaks were observed, with a mean concentration during this time of $4 \mu g m^{-3}$. IMPROVE data for June 18 indicates that total sulfate and nitrate were slightly higher than average at 37.1 % and 8.7% of total fine mass, respectively, and total fine mass was not different from the monthly mean (Figure SI 12). Back trajectory calculations from GBNP indicate 1% of trajectory points passed through the Asia source area, and that a combined 13% of trajectory points passed through the SF, SJV, LA, and LV source areas (SI Table 2, SI Figure 17). The origin of this air mass and sharp increase in pollutant concentrations indicates long-range transport of pollution from regional sources and Asian.

4.0 Conclusions

This study used multiple pollutants to understand the sources of ozone to remote locations in the State of Nevada. With the exception of CO, ancillary pollutant gases analyzed in this paper were on the low end of estimated background concentrations (Finlayson-Pitts and Pitts, 2000), even below instrument detection limits in some cases, and were not correlated with O_3 except in specific, discreet events. As defined here, exceptionally high O_3 events in Nevada were restricted to May through August. At the low elevation PAVA site in the northern part of the state, an atypical Basin and Range valley closed on three sides, the highest O_3 events were infrequent and not of regulatory significance. When they did occur, they were often related to precursor emissions from local and regional wildfires and pollution. At higher elevations in the southern part of the state at GBNP and ECHO, mean O_3 mixing ratios were significantly greater and exceptionally high O_3 events reached higher values, exceeding the current NAAQS 7 times at GBNP and 5 times at ECHO. Two out of four exceptionally high O_3 events captured at GBNP and ECHO in 2013, with $MDA8 \geq 70$ ppbv, were attributable to wildfire emissions superimposed upon that derived

from Asian emissions. Along with wildfires, exceptionally high O₃ events for Nevada are also impacted by pollution in the marine boundary layer and California, and as such, are not controllable by the State. Multiple sources are attributed to high exceedance events.

Ancillary pollutant concentrations were lower on average at GBNP than at PAVA, consistent with the remote and relatively pristine environment of the GBNP site. However, the low elevation of PAVA insulates it from consistent interception of free tropospheric air, and thus long-range pollution transport, whereas the higher elevation and more southerly latitude of GBNP and ECHO facilitates interception of high O₃ air masses transported over marine boundary layer air and across California. This was readily apparent in the downwind dispersion of smoke from wildfires in southern California, visible in satellite imagery, and was supported by the nearly identical incidence of high O₃ events between GBNP and ECHO, sites separated by a distance of 260 km, but often directly in line with prevailing air movement from the southwest (Douglas et al., 1993). Spring-summer (2013) GEM concentrations were significantly higher at GBNP than in the fall and winter, supporting more interception of polluted air during these months. Although mean spring NO_x and NO_y mixing ratios were lower than average, discrete peaks were observed during this time with large NO_z fractions (up to 0.48), supporting periodic interception of long-range pollution. Results support our hypothesis that using multiple air pollutant indicators allows for better understanding of sources of O₃ to remote locations. This data can be used to validate chemical transport modeling that can quantitatively assess the relative contribution from each of the sources identified here.

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Table 2. Exceptional O₃ events at GBNP and ECHO for 2012 and 2013, in both daily mean and MDA8 O₃ (all values ppbv). Grey numbers indicate a value that did not exceed the thresholds considered for an exceptional event (≥ 61 ppbv daily, ≥ 70 ppbv MDA8) but that are included in reference to larger events, dashes indicate non-exceptional data.

Figure 1. Location map of monitoring sites at Paradise Valley (PAVA), Great Basin National Park (GBNP), and Echo Peak (ECHO), which are part of the greater NVROI monitoring network.

Figure 2. Mean hourly values of gas pollutants at: A) PAVA B) GBNP C) ECHO. Medium gray symbols represent all hourly value, superimposed black symbols are values above the 90th percentile (value in upper right). Light gray symbols represent all NO values for respective GBNP NO_x and NO_y instruments.

Figure 3. Exceptional O₃ and other air quality parameters at PAVA, August 11-13, 2012.

Figure 4. Exceptional O₃ and other air quality parameters at GBNP, June 2, 2013.

Table 1. Summary of air pollutants at Great Basin National Park (GBNP), Paradise Valley (PAVA), and Echo Peak (ECHO) by year (all values in ppbv). UV is ultra-violet, IR is infra-red. Background estimates from Finlayson-Pitts and Pitts (2000). Minimum detection limits (MDL) are reported by manufacturer.

Site	Year	Ozone		CO	SO ₂	NO-NO _x		NO-NO _y
		Method	UV fluorescence	IR spectro-photometry	UV fluorescence	Chemiluminescence		Chem iluminescence
		Background	30-40	50-100	< 1.0	0.2 - 10		0.2 - 10
GBNP	2012	MDL	< 1.0 ppbv	20 ppbv	0.05 ppbv	0.05 ppbv		0.05 ppbv
		Mean ± StDev	50 ± 10	112 ± 38	0.07 ± 0.13			0.2 ± 0.43
		Median	49	106	0.06	no data		0.12
		Range	20 - 99	22 - 375	0 - 0.72			0 - 12.43
	2013	Mean ± StDev	45 ± 9	105 ± 29	0.04 ± 0.05	0.07 ± 0.3	0.40 ± 0.70	0.15 ± 0.30
		Median	44	103	0.03	0.03	0.35	0.10
		Range	14 - 83	20 - 581	0.0 - 0.40	0.0 - 16.1	0.0 - 30.9	0.0 - 17.43
	2013	MDL	< 1.0 ppbv	40 ppbv	0.4 ppbv	0.4 ppbv		
		Mean ± StDev	30 ± 13	139 ± 56	0.1 ± 0.2	0.1 ± 0.6	2.3 ± 1.9	
		Median	30	131	0.1	0.1	2.0	
		Range	1.0 - 84	32 - 967	0 - 2.3	0 - 9.9	0 - 21.8	
		Mean ± StDev	33 ± 12	127 ± 44	0.2 ± 0.4	0.5 ± 0.5	2.0 ± 1.8	
		Median	34	127	0.1	0.4	1.5	
		Range	4 - 73	0.0 - 620	0.0 - 9.3	0.0 - 7.3	0 - 19.3	
ECHO	2012	MDL	< 1.0 ppbv	20 ppbv				
		Mean ± StDev	50 ± 9					
		Median	49	no data				
		Range	39 - 84					
	2013	Mean ± StDev	49 ± 8	131 ± 33				
		Median	48	129				
		Range	18 - 85	25 - 259				

Table 2. Exceptional O₃ events at GBNP and ECHO for 2012 and 2013, in both daily mean and MDA8 O₃ (all values ppbv). Grey numbers indicate a value that did not exceed the thresholds considered for an

exceptional event (≥ 61 ppbv daily, ≥ 70 ppbv MDA8) but that are included in reference to larger events,
dashes indicate non-exceptional data.

2012		April		May		May		May		May		May		June		June		June		June-July		July		July							
		23	2	3	7	8	14	15	16	17	21	22	23	24	25	26	29	2	3	4	9	19	20	21	22	23	24	30	1	15	29
GBNP	Daily	62	63	67	61	64	64	69	69	62	55	61	63	61	71	72	70	-	56	69	59	61	43	56	73	62	63	60	64	62	62
	MDA8	67	66	68	63	67	68	76	74	64	70	67	68	72	80	72	77	-	73	71	78	71	46	71	75	67	64	73	71	65	64
ECHO	Daily	no data																67	67	-	62	69	48	72	65	-	-	72	70	-	68
	MDA8	no data																73	74	-	70	73	56	80	69	-	-	77	77	-	70

2013		May 5 6		May 14 15 16			May 21 22 23			May 24 25 26			June 2 16		June 17 18	
GBNP	Daily	64	62	63	61	63	50	62	54	56	72	67	63	65	65	74
	MDA8	76	68	67	69	69	69	67	64	64	76	72	71	67	74	76
ECHO	Daily	66	55	67	59	61	65	59	60	66	76	62	68	66	67	65
	MDA8	71	58	65	69	64	71	61	67	78	77	67	74	67	70	69

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Figure 2. Mean hourly values of gas pollutants at: A) PAVA B) GBNP C) ECHO. Medium gray symbols represent all hourly values, superimposed black symbols are values above the 90th percentile (value in upper right). Light gray symbols represent all NO values for respective GBNP NO_x and NO_y instruments.

Figure 3. Exceptional O₃ and other air quality parameters at PAVA, August 11-13, 2012. Time is Pacific Standard.

Figure 4. Exceptional O_3 and other air quality parameters at GBNP, June 2, 2013. Time is Pacific Standard.