Atmospheric Environment 82 (2014) 383–390

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Ozone in remote areas of the Southern Rocky Mountains

Robert C. Musselman*, John L. Korfmacher

US Forest Service, Rocky Mountain Research Station, 240 West Prospect Road, Fort Collins, CO 80526, USA

HIGHLIGHTS

- O_3 concentrations would contribute to NAAQS exceedances at most sites.
- Mid-level O_3 concentrations contributed to the high values of the W126 metric.
- There were significant year-to-year O_3 differences.
- O_3 was persistent at night, particularly at higher elevations.
- O_3 levels at high elevation sites suggested evidence of stratospheric intrusion.

ARTICLE INFO

Article history:
Received 17 June 2013
Received in revised form
21 October 2013
Accepted 24 October 2013

Keywords:
Air pollution
Forests
High elevation
NAAQS
Nighttime exposure
Stratospheric intrusion
W126

ABSTRACT

Ozone (O_3) data are sparse for remote, non-urban mountain areas of the western U.S. Ozone was monitored 2007–2011 at high elevation sites in national forests in Colorado and northeastern Utah using a portable battery-powered O_3 monitor. The data suggest that many of these remote locations already have O_3 concentrations that would contribute to exceedance of the current National Ambient Air Quality Standard (NAAQS) for O_3 and most could exceed a proposed more stringent secondary standard. There were significant year-to-year differences in O_3 concentration. Ozone was primarily in the mid-concentration range, rarely exceeding 100 ppb or dropping below 30 ppb. The small diel changes in concentration indicate mixing ratios of NO_x, VOCs, and O_3 that favor stable O_3 concentrations. The large number of mid-level O_3 concentrations contributed to high W126 O_3 values, the metric proposed as a possible new secondary standard. Higher O_3 concentrations in springtime and at night suggest that stratospheric intrusion may be contributing to ambient O_3 at these sites. Highest nighttime O_3 concentrations occurred at the highest elevations, while daytime O_3 concentrations did not have a relationship with elevation. These factors favor O_3 concentrations at many of our remote locations that may exceed the O_3 NAAQS, and suggest that exceedances are likely to occur at other western rural locations.
Published by Elsevier Ltd.

1. Introduction

Ozone is the most widespread phytotoxic air pollutant, causing injury to vegetation foliage and yield loss to crops and native vegetation in the US and Europe (US EPA, 2006, 2013). Vegetation is particularly sensitive to higher concentration levels of O_3 (Musselman et al., 2006; US EPA, 2013). Ozone is taken up into leaves through stomata and causes necrosis to plant tissue. The mechanisms of O_3 impact on plant tissue have been recently reviewed (US EPA, 2013). Cumulative O_3 exposure and leaf tissue injury can result in reduced growth. Reductions in growth can damage plants by reducing yield (Musselman et al., 2006). In addition, plants stressed from O_3 injury are more susceptible to damage from insects, diseases, and drought (US EPA, 2006, 2013).

The US EPA proposed (Federal Register January 19, 2010) strengthening the primary National Ambient Air Quality Standard (NAAQS) for O_3 and introduced a new form of the secondary standard (U.S. EPA, 2011). While the new primary and secondary standards for O_3 were proposed by the EPA, the Agency withdrew its proposal in 2011.[1] The proposed new primary O_3 NAAQS, designed to protect public health, was to change from 75 ppb to

* Corresponding author. Tel.: +1 970 498 1239; fax: +1 970 498 1212.
E-mail address: rmusselman@fs.fed.us (R.C. Musselman).

1352-2310/$ – see front matter Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.atmosenv.2013.10.051

[1] The proposed final rule was withdrawn by the President in 2011 to allow time for the current review to be completed (http://www.whitehouse.gov/the-press-office/2011/09/02/statement-president-ozone-national-ambient-air-quality-standards). For information on the proposed final rule for ozone before withdrawal see: (http://www.epa.gov/air/ozonepollution/pdfs/201107_OMBdraft-OzoneRIA.pdf). The new review is now completed (EPA 600/R-10/076F, February 2013) and the new final rule should be released in 2014.

70 ppb for the 3-year average of the 4th highest 8 h average concentration (U.S. EPA, 2011).

Scientific assessments have concluded that the primary NAAQS based on an hourly average concentration are inadequate to protect sensitive ecosystems (NRC, 2004). The EPA has indicated that a strengthened primary standard for ozone will not adequately protect sensitive tree species in higher elevation Western ecosystems where little O_3 data are available.[2]

The proposed new form of the secondary standard, which the Agency is still considering as a possible recommendation during its current review of the science, utilizes the W126, a peak-weighted cumulative parameter (Lefohn and Runeckles, 1987). The parameter focuses on the higher O_3 concentrations accumulated over a growing season which result in injury and damage to plant tissue. The W126 metric is calculated by weighting each hourly average with a peak-weighting parameter and then summing 12 weighted hourly values from 8 am to 8 pm each day, accumulating those daily sums for each month, accumulating three consecutive months averages, then averaging the highest annual three month averages over three years. The new secondary standard proposed was a W126 value that should not exceed 13 ppm-h (U.S. EPA, 2011).

Although the proposed new secondary standard recommended only the use of the W126 parameter, research has consistently shown that peak O_3 concentrations are necessary to negatively affect vegetation (Musselman et al., 2006). The W126 has been recommended to be used in conjunction with the N100 to more accurately assess vegetation sensitivity to O_3 (Lefohn and Foley, 1992; Davis and Orendovici, 2006; Musselman et al., 2006; Kohut et al., 2012).

Ozone is monitored primarily in urban areas and O_3 monitoring data are particularly sparse at rural, remote or high elevation sites. Typically, O_3 precursors are emitted from urban automotive and industrial sources. Nitrogen oxide is involved in O_3 titration and is often low at rural sites downwind of the emission sources (U.S EPA, 2006). Ozone concentrations are often greater at rural sites compared to urban locations (Logan, 1989). Ozone can be higher in rural than urban areas in the late evening and early morning hours; and vegetation at these sites may be sensitive to O_3 because native plants in natural ecosystems often have stomata partially open at night (Musselman and Minnick, 2000), particularly in plants exposed to O_3 (Dumont et al., 2013). Plant leaf defenses may be lower at night than during the day (Musselman et al., 2006; Heath et al., 2009). Ozone damage to vegetation is well documented for the eastern US and in California (US EPA, 2006, 2013) but little is known about O_3 concentrations or effects on vegetation at high-elevation sites in the Intermountain West.

Federal Land Managers are mandated by the Clean Air Act to protect Air Quality Related Values in Class I areas and most of these areas are located at high elevation in the western U.S. However information about ambient O_3 concentrations at these remote locations is scarce. Some investigators have reported O_3 may be increasing in remote western U.S. areas (Jaffe and Ray, 2007), while others have indicated that O_3 has not experienced an increasing trend in recent years (Lefohn et al., 2010). While IPCC models have predicted that O_3 will increase in the future (Vingarzan, 2004) more recent models estimate O_3 may decrease (Coleman et al., 2013). Doherty et al. (2013) have shown that there is large variability in the amount and location of modeled surface O_3 changes and increases are related to surface temperatures and NO_x source emissions.

[2] Draft final Rule. National Ambient Air Quality Standard for Ozone (http://www.epa.gov/airquality/ozonepollution/pdfs/201107_OMBdraft-OzoneNAAQSpreamble.pdf).

Energy development often occurs in rural areas near national forests and national parks and at times near Class I wilderness areas protected from air pollutants by the US Clean Air Act. Oil and gas development has been intense in the Southern Rocky Mountains and episodic O_3 exposures have been observed at some of these locations (Schnell et al., 2009; Martin et al., 2012). Relatively remote areas with extensive energy development such as Pinedale, WY, the Uintah Basin of northeastern Utah, and the Pawnee National Grassland in Colorado, have been shown to be non-attainment for O_3. The O_3 levels are particularly high in these areas in winter when mixing ratios, snow cover, and local inversions favor O_3 formation and persistence.

Logan (1989) reported that O_3 concentrations above 80 ppb are unusual in the west, but provides data for only one year from three western rural sites. The highest elevation of the three sites was 1350 m (Evans, 1985). Other studies have shown that O_3 concentrations are often greater at higher elevations and downwind of urban areas, a result of transport from urban areas and/or lack of availability of NO for O_3 titration (Brace and Peterson, 1998; Barna et al., 2000; Evans et al., 1982; Logan, 1989; Wunderli and Gehrig, 1990; Aneja et al., 1991; Kley et al., 1994; Davies and Schuepbach, 1994; Peterson, 2000).

High-elevation remote sites in the western US may be exposed to high O_3 concentrations associated with stratospheric intrusions (Lefohn et al., 2011; U.S. EPA, 2013; Lin et al., 2012) associated with passage of a cutoff low pressure center causing tropospheric folding (Wooldridge et al., 1997; Schuepbach et al., 1999). Enhancements to surface O_3 affected by stratospheric transport to the surface are characterized by springtime occurrence, consistent mid- to high O_3 concentrations for many hours including nighttime hours, and occur more frequently at higher elevations where they are more likely to reach the surface (Wooldridge et al., 1997; Lefohn et al., 2011, 2012).

Several additional factors favor persistent O_3 occurrence at high elevation. 1) Higher rural O_3 concentrations can occur from transport downwind of urban areas. 2) Snow cover in high elevation ecosystems limits amount of soil and plant surface area available for degradation of O_3. There is often little diel variation in ozone concentration during winter at remote sites (Fehsenfeld et al., 1983; Wooldridge et al., 1997; Zeller and Hehn, 1996). Diel patterns indicate that O_3 concentrations seldom approach zero at night in remote areas (Logan, 1989; Wooldridge et al., 1997; Brodin et al., 2010; Zeller, 2000). 3) Air chemistry has lower NO_x precursors that results in less O_3 formation at remote western sites (Logan, 1989), but there are fewer NO_x compounds at remote sites for degradation of O_3 once it forms favoring persistence of O_3 at remote locations. 4) Wildfires in remote areas may contribute to higher ozone (Preisler et al., 2010; Bytnerowicz et al., 2013).

This study characterized ambient O_3 from 2007 to 2011 at remote sites in the Southern Rocky Mountains, and examined whether concentrations at these sites would contribute to violations of current and more stringent NAAQS. We discuss our findings in context of how processes such as stratospheric intrusions and rural background air chemistry might contribute to the current and future primary and secondary O_3 parameters used as metrics for the NAAQS.

2. Methods

The US Forest Service Rocky Mountain Research Station has monitored O_3 at remote high elevation sites in Colorado and northeastern Utah to determine O_3 levels in sensitive ecosystems near wilderness in national forests (Fig. 1 and Table 1). Because of limited access, monitoring is generally not possible at these locations before mid-June, and they seldom have access to electric

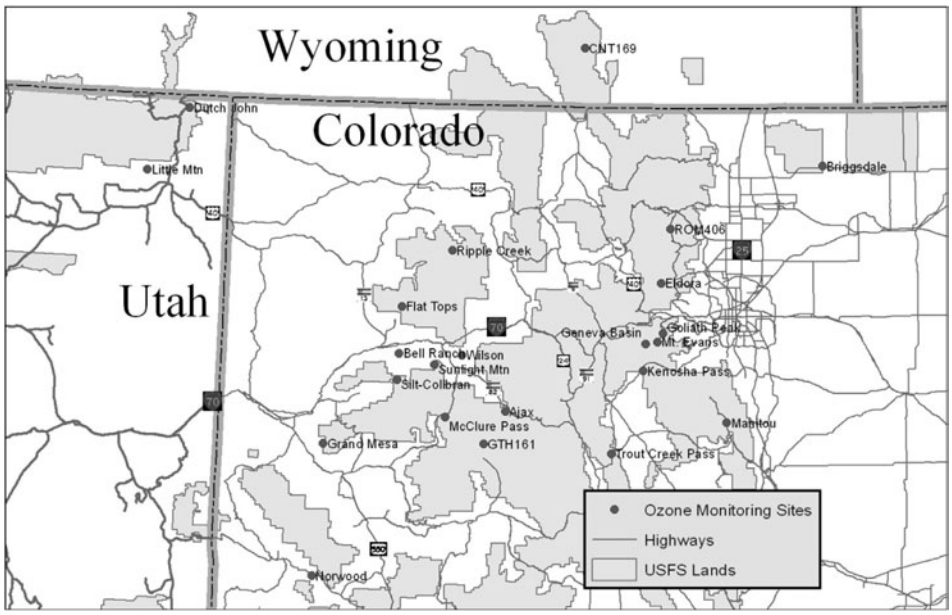

Fig. 1. Map of ozone monitoring sites in Colorado, NE Utah and SE Wyoming.

power or have facilities to house instrumentation. However, a few of the monitoring sites were established at ski areas and mountain passes that remain open year-round. Sites were located at least two tree heights distant from the nearest tree to allow a good exposure to the surrounding ambient air mass. Ogawa passive samplers (Koutrakis et al., 1993) provided initial regional data on biweekly average O_3 concentrations to identify sites with high O_3 loading where the continuous monitors were subsequently deployed to characterize hourly distributions.

A portable battery powered continuous O_3 monitor (2B Technologies, Boulder, CO[3]) was utilized at remote monitoring sites. At one site (Sunlight Mountain) where an electric powered temperature controlled building was available, O_3 was monitored with a TECO Model 49. The portable monitors were easily transported to remote areas and operated from a standard 12-V battery charged by a 40-W solar panel. Analyzers were programmed to sample at 1-min intervals. All data were stored as 15-min averages on a data logger (Campbell Scientific, Logan, UT) that also recorded air and instrument temperature and battery power. The monitor, battery and data logger were enclosed in a rainproof instrument shelter mounted along with the solar panel between two fence posts pounded into the ground about 80 cm apart. Sample inlets were located 2 m above the ground surface. An O_3 calibration source (2B Technologies Model 306) was included in the housing at some locations, programmed to conduct a calibration check at 0/200/100/50 ppb once every 7 days. Those locations without the O_3 source for automatic calibration were visited approximately monthly for a manual on-site calibration check. Sample inlets at all installations were protected by 0.5-μm PTFE particulate filters, which were changed monthly. A few installations were insulated to operate during winter, but most data were collected during the summer months when sites were accessible. Installation details, data reduction, calibration adjustment, and QA procedures are further described in Korfmacher and Musselman (unpublished manuscript).

[3] The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

When this study began the 2B portable O_3 monitor was not an EPA equivalency instrument, but it has now been listed by as a Certified Equivalent Method at 10–40 °C (Federal Register April 27, 2010). The remote monitoring locations do not always adhere to EPA Part 58 siting protocols, and temperatures at the remote monitoring sites are at times below 10 °C; thus the data cannot be used to certify compliance with the NAAQS. Nevertheless, the data provide an indication of locations where existing or more stringent standards might be exceeded.

Data were adjusted via linear regression and interpolation when calibration drift occurred. Most of the Colorado monitoring sites were field audited on site by the Colorado Department of Public Health and Environment – Air Resources Division. Data presented are primarily from O_3 monitoring only during the growing season, since many of our monitoring sites could not be accessed during the

Table 1
Rural monitoring sites collecting ozone data used in this study, and number of years with data. Rocky Mountain NP, Gothic, and Centennial are CASTNet sites.

Site name	State	County	Longitude	Latitude	Elevation (m)	Years of data
Briggsdale	CO	Weld	40.651	−104.335	1491	1
Bell Ranch	CO	Garfield	39.490	−107.660	1785	2
Dutch John	UT	Daggett	40.923	−109.396	1994	2
Norwood	CO	San Miguel	38.130	−108.287	2137	1
Manitou Exp. Forest	CO	Teller	39.100	−105.094	2354	2
Wilson	CO	Garfield	39.489	−107.168	2357	4
Silt–Collbran Pass	CO	Garfield	39.328	−107.671	2448	3
Little Mountain	UT	Uintah	40.538	−109.700	2621	2
Rocky Mountain NP	CO	Larimer	40.278	−105.545	2743	5
Flat Tops	CO	Garfield	39.774	−107.647	2869	3
Gothic	CO	Gunnison	38.956	−106.986	2926	5
Ripple Creek Pass	CO	Rio Blanco	40.085	−107.312	2929	3
McClure Pass	CO	Gunnison	39.110	−107.287	2933	2
Trout Creek Pass	CO	Chaffee	38.908	−105.991	3000	3
Grand Mesa	CO	Mesa	39.030	−108.225	3037	3
Kenosha Pass	CO	Park	39.411	−105.749	3110	5
Centennial	WY	Albany	41.364	−106.240	3178	5
Sunlight Mountain	CO	Garfield	39.426	−107.380	3224	5
Eldora Ski Area	CO	Boulder	39.941	−106.612	3272	4
Ajax Mountain	CO	Pitkin	39.154	−106.821	3414	4
Geneva Basin	CO	Clear Creek	39.575	−105.730	3474	2
Goliath Peak	CO	Clear Creek	39.638	−105.596	3518	5
Mount Evans	CO	Clear Creek	39.587	−105.641	4308	2

Table 2
Significance of elevation and year on ozone parameters using mixed-effects repeated measures linear model analysis. Elevation and year shown in **bold** are significant at $\alpha = 0.05\%$.

Response	Period	Covariate	Significance	Response	Month	Covariate	Significance	Response	Month	Covariate	Significance
Day W126	May–Jul	Elevation	0.407	Day Mean O_3	April	Elevation	0.211	Day Max O_3	April	Elevation	0.308
		Year	**0.017**			**Year**	**0.028**			**Year**	**<0.001**
	Jun–Aug	Elevation	0.579		May	Elevation	0.198		May	Elevation	0.895
		Year	**0.011**			**Year**	**0.001**			**Year**	**<0.001**
	Jul–Sep	Elevation	0.811		June	Elevation	0.742		June	Elevation	0.089
		Year	**0.046**			**Year**	**0.001**			**Year**	**0.002**
Night W126	May–Jul	**Elevation**	**0.002**		July	Elevation	0.124		July	Elevation	0.140
		Year	**0.026**			**Year**	**<0.001**			**Year**	**0.001**
	Jun–Aug	**Elevation**	**<0.001**		August	Elevation	0.159		August	Elevation	0.143
		Year	**0.010**			**Year**	**0.002**			**Year**	**0.015**
	Jul–Sep	**Elevation**	**<0.001**		September	**Elevation**	**0.009**		September	Elevation	0.693
		Year	0.492			Year	0.098			**Year**	**0.001**
Total W126	May–Jul	Elevation	0.093	Night Mean O_3	April	**Elevation**	**0.020**	Night Max O_3	April	**Elevation**	**0.013**
		Year	**0.019**			Year	0.066			**Year**	**<0.001**
	Jun–Aug	**Elevation**	**0.005**		May	**Elevation**	**0.005**		May	Elevation	0.143
		Year	**0.009**			**Year**	**0.003**			**Year**	**0.004**
	Jul–Sep	**Elevation**	**0.021**		June	**Elevation**	**0.001**		June	**Elevation**	**0.001**
		Year	0.254			**Year**	**<0.001**			**Year**	**0.002**
% Night W126	May–Jul	**Elevation**	**<0.001**		July	**Elevation**	**<0.001**		July	**Elevation**	**<0.001**
		Year	0.097			**Year**	**0.002**			**Year**	**0.020**
	Jun–Aug	**Elevation**	**<0.001**		August	**Elevation**	**<0.001**		August	**Elevation**	**<0.001**
		Year	0.366			**Year**	**0.001**			Year	0.256
	Jul–Sep	**Elevation**	**<0.001**		September	**Elevation**	**<0.001**		September	**Elevation**	**<0.001**
		Year	0.079			**Year**	**0.009**			**Year**	**0.030**

winter. Data are also presented here from a few of the sites that are accessible in winter and electric power and shelter are available. We also include in our analysis TECO O_3 monitor data from the CASTNet Centennial (CNT169), Gothic (CTH161) and Rocky Mountain National Park (ROM406) sites.

The 8-h average O_3 values were calculated for the monitoring sites and the data are presented for comparison to the current 75 ppb primary standard in effect since 2008 and the 70 ppb proposed new primary standard. The W126 values were calculated according to the EPA proposed method (US EPA, 2012) and are shown for each site using both the proposed standard 12-h daytime and the 24-h total daily exposure window. Additional data presented are the N60, N70, N80, N90, and N100 metrics, where the Nxx is the number of hours of $O_3 \geq$ xx ppb. A mixed-effects repeated measures linear model (SAS PROC GLIMMIX) was run to determine the importance of year and elevation (fixed effects) and their interaction on O_3 concentration parameters. Analysis used restricted maximum likelihood as the estimation method, the Kenward–Roger method for degrees of freedom calculation, a compound-symmetry covariance matrix structure, and Tukey–Kramer adjustments for multiple LS means comparisons. Differences were considered significant at the 0.05 confidence level.

3. Results and discussion

The data available show that more than 60% (14 of 23) of the remote sites had O_3 concentrations from 2007 to 2011 where the 4th highest 8-h average was $\geq$75 ppb and would contribute to exceedance of the current primary NAAQS for O_3; and more than 78% (18 of 23) had values that would contribute to exceedance of the proposed more stringent primary O_3 NAAQS of $\geq$70 ppb (Supplementary Tables S1 and S2). Nine of the 11 sites with complete datasets (90% completeness for 3 consecutive months for three or more years) had a year with the 4th highest 8-h average values above 75 ppb. The 8-h average concentrations were as high as 101.5 ppb and eight sites had values above 80 ppb. Concentrations of the 4th highest and the highest 8-h values were similar in value, indicating consistency in O_3 concentrations at these sites.

All seven sites with complete datasets and 69% of all sites (16 of 23) had at least one year with a three-month 12-h W126 value greater than 13 ppm-h (Supplementary Tables S3 and S4), contributing to exceedance of the proposed new secondary standard. The three month 12-h W126 values were as high as 25 ppm-h, and the 24-h W126 values were as high as 52 ppm-h. Five of the seven sites with complete datasets had three month 12-h W126 value of >21 ppm-h. The 24-h W126 values were twice as high as

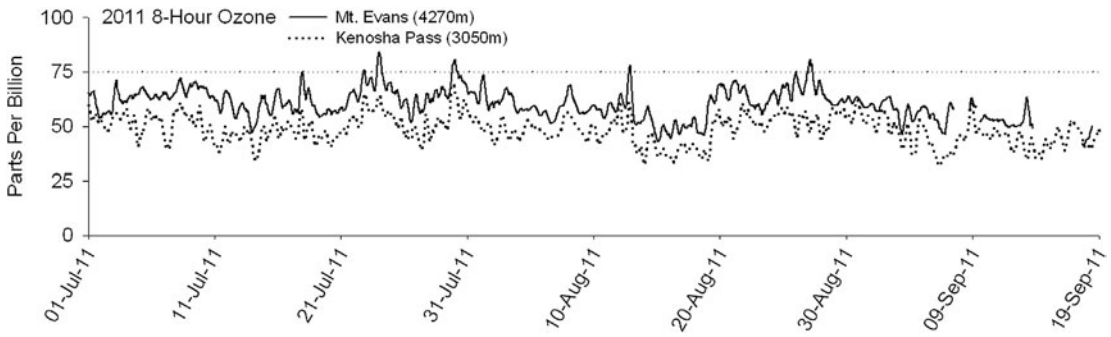

Fig. 2. Ozone at two sites only 21 km apart, Front Range, Colorado. Dotted line indicates current NAAQS ozone standard. Concentrations are consistently higher at the higher elevation site.

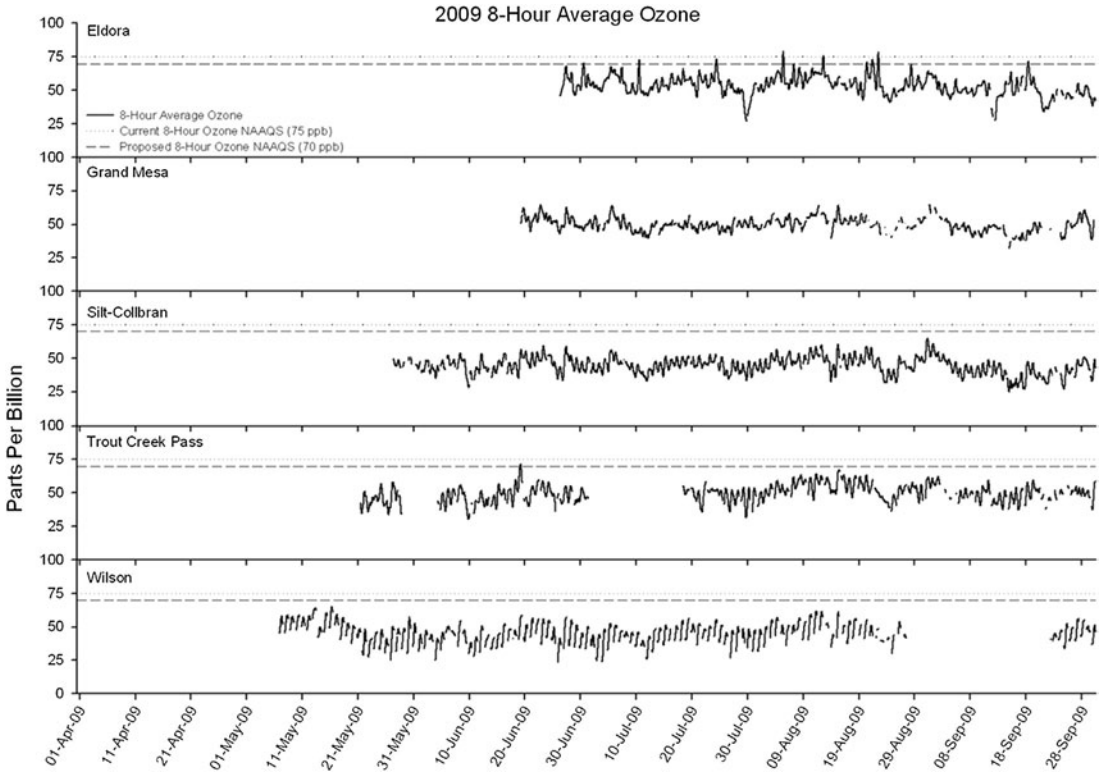

Fig. 3. Rural sites with summer data showing seasonal 8-h average ozone concentration for 2009. Hatched lines indicate 70 and 75 ppb 8 h average.

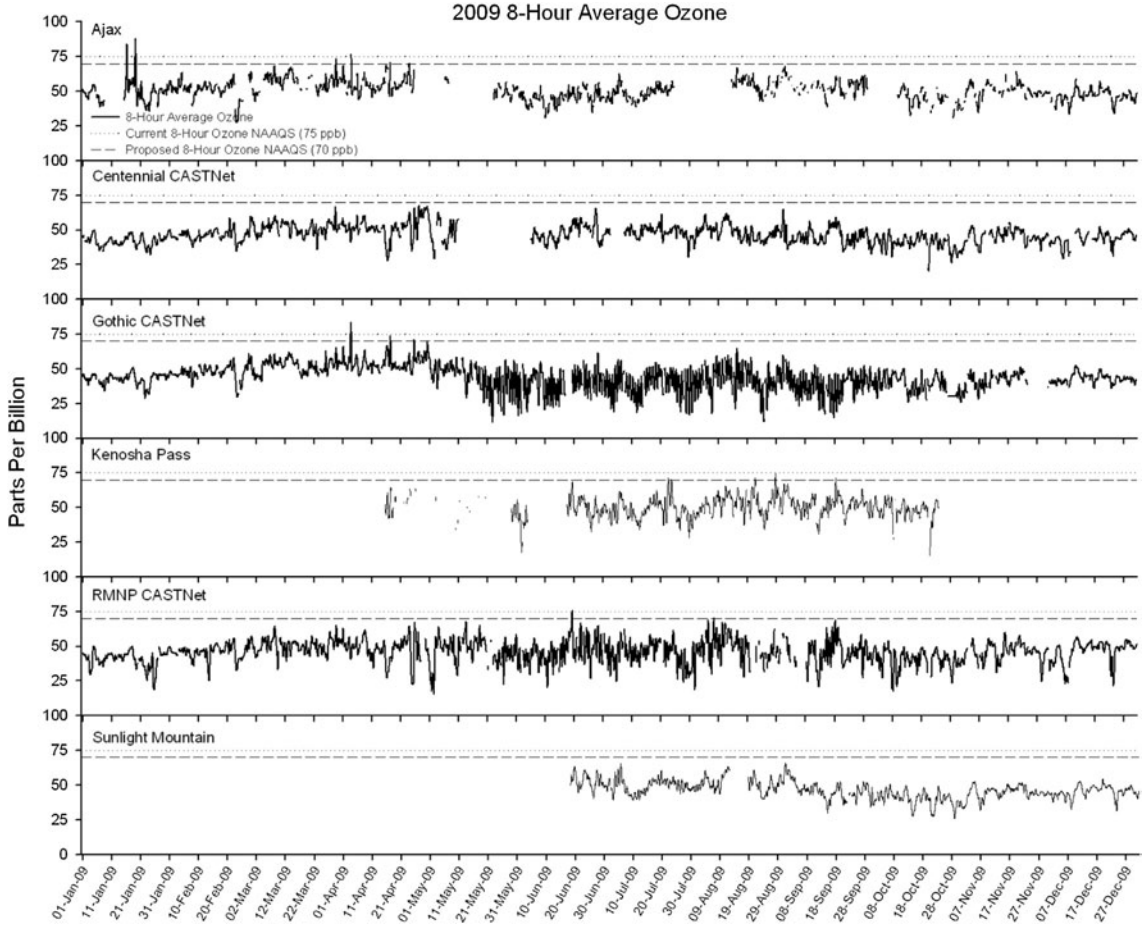

Fig. 4. Rural sites with year-round data showing 8-h average ozone concentration for 2009. Hatched lines indicate 70 and 75 ppb 8 h average.

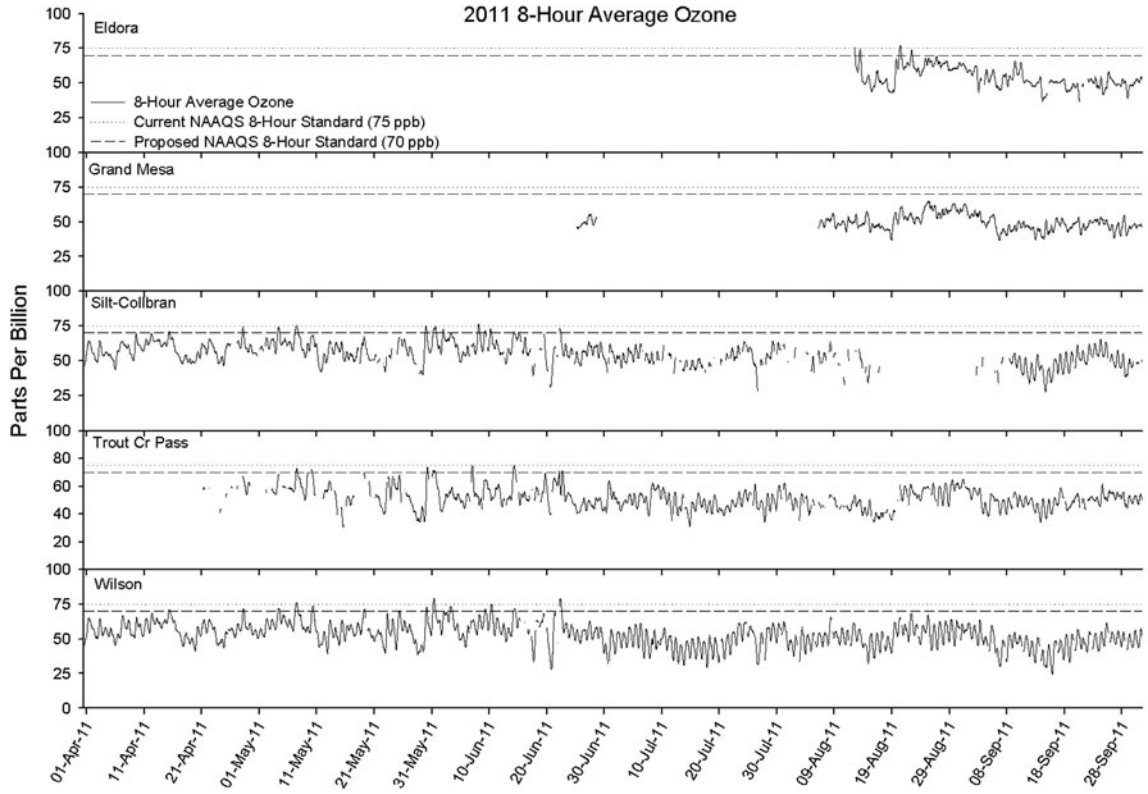

Fig. 5. Rural sites with summer data showing seasonal 8-h average ozone concentration for 2011. Hatched lines indicate 70 and 75 ppb 8 h average.

the 12-h values at some sites, particularly at the higher elevations, a result of increased nighttime persistence of O_3 at these sites compared to lower elevation sites. The mixed model analyses found that the nighttime W126 values were more related to elevation than were the daytime values (Table 2 and Supplementary Fig. S1).

There were year-to-year differences in O_3 concentration at each site; O_3 was generally lower in 2009 compared to 2011. Results of the mixed-effects model analysis determined that year-to-year differences were generally significant for nearly every O_3 exposure index (Table 2). Yearly differences were more evident in the early and mid-season data and they were not significantly different by September. The percent of O_3 accumulated at night also showed no significant year-to-year differences. Elevation was significant for most nighttime O_3 parameters including night W126, % of W126 occurring at night, mean night O_3, and max night O_3. Elevation was not significant for most daytime O_3 parameters.

Stratospheric intrusion may have contributed to high O_3 concentrations at some of the remote sites. Evidence at specific sites supporting the importance of stratospheric inputs of O_3 include: 1) higher O_3 concentrations at the higher elevation sites, 2) highest 8-h averages at night, and 3) highest O_3 values occurring during springtime (April–May). Several recent studies have noted the importance of stratospheric O_3 affecting surface O_3 (Lefohn et al., 2012; Lin et al., 2012). Additional trajectory and meteorological analyses beyond the scope of this study could provide evidence of a stratospheric source of the ground level O_3.

Only four sites (Kenosha Pass, Ajax, Goliath Peak, and Mount Evans) had hourly O_3 concentrations above N100 (Supplementary Table S5). These sites were located at high elevation, and the hourly peaks at Ajax were during April when the enhancements may have been associated with stratospheric O_3. Monitoring at Goliath and Evans was limited to mid-summer and additional high concentrations may have occurred earlier in the season. The lack of a large number of high O_3 concentrations and the high 24-h W126 values indicate that mid-level values were the primary contributor to the W126 metric.

Most sites had higher O_3 concentrations in 2011, a year with higher summer temperatures and more wildfires. Ozone is often higher when temperatures are higher, and investigators have reported a relationship of O_3 to wildfires (Altshuller and Lefohn, 1996; Bytnerowicz et al., 2013). Kenosha Pass, Goliath Peak, and Mt Evans (all above 3100 m elevation) had consistently high values for most years and had 8-h average concentrations above 90 ppb (Supplementary Tables S1 and S2). These sites are east of the continental divide and closer to the Front Range Denver urban area (Fig. 1). Ajax, located on the slopes above the City of Aspen, CO, also had high O_3 values (Supplementary Table S1). The more remote Grand Mesa and Ripple Creek Pass sites had consistently lower values, but data were unavailable for both of these sites during April–May when O_3 values were relatively high at the other sites. Ozone was often greater at higher elevation sites (Fig. 2), a result of increasing nighttime accumulation with elevation.

Year-round and seasonal observations of O_3 patterns indicate consistencies demonstrated by data shown in Figs. 3–6 for 2009 and 2011. Most sites had an 8-h average value that exceeded 75 or 70 ppb (when springtime data were available), even in years where O_3 values were lower (2009 compared to 2011). Diel variation was somewhat higher during the summer, but O_3 concentrations seldom dropped below 30 ppb indicating the lack of titration and mixing ratios of NO_x, VOCs, and O_3 that favor persistence of O_3. Ozone peaks occurred throughout the spring and summer; and the elevated spring-time values suggest a stratospheric source of O_3.

Several of the monitoring sites (Bell Ranch, Wilson, Sunlight, Silt–Colbran, Flat Tops, Ripple Creek Pass, and Briggsdale) are close to or downwind from oil and gas development. All of these sites had 8-h O_3 concentrations greater than 70 ppb (Supplementary Tables S1 and S2). Silt–Collbran had 12-h W126 values exceeding 22 ppb-h, and Briggsdale and Sunlight had 12-h W126 value above

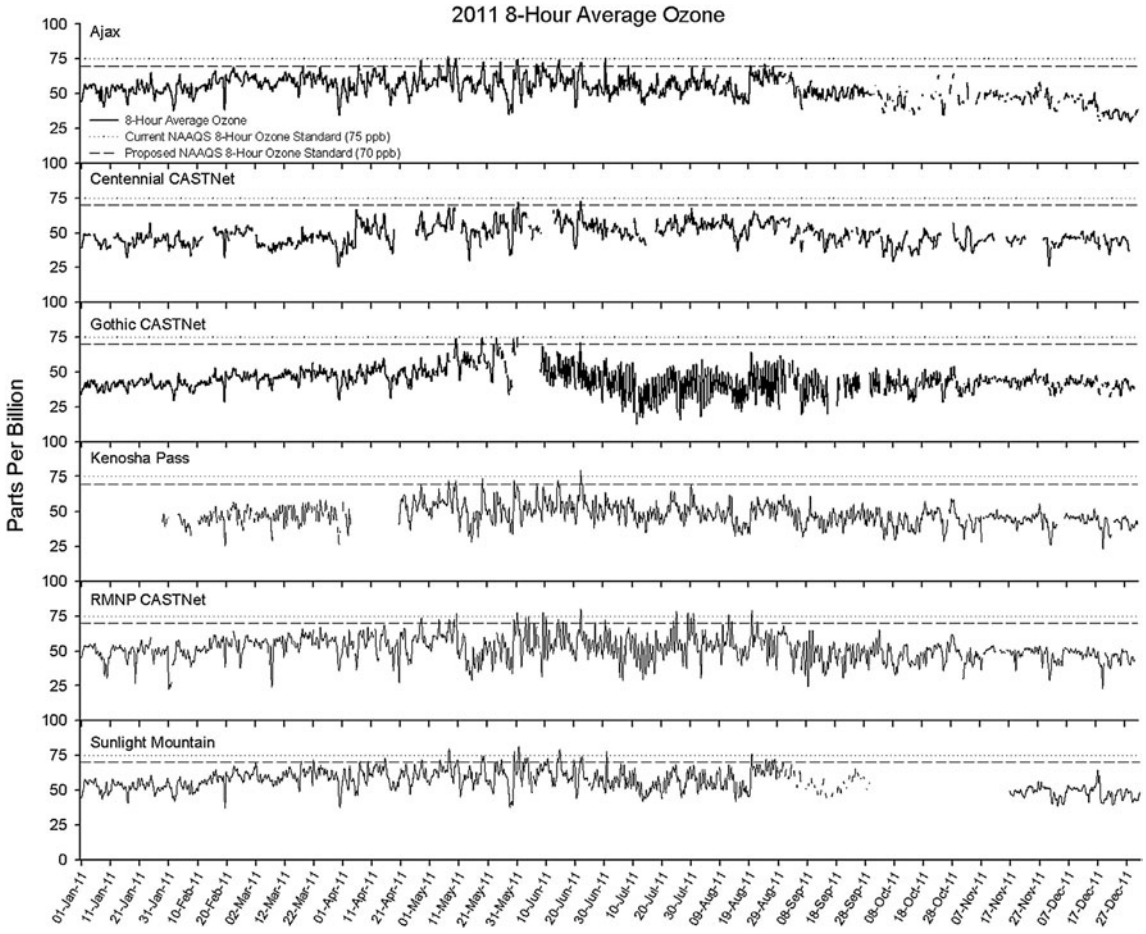

Fig. 6. Rural sites with year-round data showing 8-h average ozone concentration for 2011. Hatched lines indicate 70 and 75 ppb 8 h average.

13 ppb-h. Only one of these sites, Ripple Creek Pass where access limited collection to summer-only data, had W126 values that did not exceed 13 ppm-h.

Only one site with three years of data, Grand Mesa, did not have O_3 levels that would contribute to exceedance of the proposed secondary NAAQS for O_3 and data were limited for that site (Figs. 3 and 5 and Supplementary Table S4). The large number of mid-level O_3 concentrations contributed substantially to the higher W126 values, and few sites had high O_3 values as indicated by the small number of N100s (Supplementary Table S5).

O_3 is a regional pollutant influenced by air patterns and is generally consistent over large geographic areas with uniform terrain. However the complex terrain and airflow patterns, the large changes in elevation, and the point sources of precursors from energy development might limit extrapolation beyond our monitoring sites in the Southern Rocky Mountains. Nevertheless, our data suggest that exceedance of the NAAQS for O_3 may occur in many remote high elevation areas of the Southern Rocky Mountains, and compliance with the current primary and proposed secondary O_3 standard may be difficult to achieve. The proposed new rule called for additional O_3 monitoring in rural areas. While the exceedance of the NAAQS had been considered an urban problem, our results indicate that exceedance of the current primary proposed more stringent primary and new secondary standard NAAQS may also be a problem in non-urban rural, high-elevation, and remote areas.

Even though the number of areas with potential for exceeding NAAQS is a concern, much of the O_3 that contributed to the exceedance was not peak, but mid-level concentrations. The lack of nighttime scavenging of O_3 at remote high elevation sites allow for the large number of mid-level concentration values that can be accumulated into the summation of the W126 value, as evidenced by the high 24-h and nighttime W126 values. Few sites had a large number of high O_3 values, as indicated by the small number of N100s, suggesting that exceedance of the current primary and proposed secondary O_3 NAAQS would seem to be less likely to have an impact on vegetation, particularly if they occur at nighttime. Yet the persistence exposure of plants to mid-level O_3 at night should not be discounted, since stomata of many native plants are partially open at night when detoxification potential is lower, and O_3 can delay stomatal closing allowing additional uptake. Plant energy is expended to detoxify O_3 or to produce additional antioxidants. Even though this response may difficult to quantify there is increased potential for tissue injury or plant damage and nighttime O_3 uptake should not be ignored for plants already growing under stress at high elevation. Daytime O_3 could be preferentially weighted but nighttime O_3 should also be included in a NAAQS metric for O_3.

Acknowledgments

We acknowledge the statistical advice of L. Scott Baggett, RMRS Biometrician. We thank numerous field technicians for assistance in maintaining the monitoring network. We thank John Frank, RMRS, for technical assistance. We thank US Forest Service Regions 2 and 4 air resources managers, especially Jeff Sorkin, Debra Miller, Andrea Holland-Sears, Helen Kempenich, and Eric Schroder, for support of this research. The Friends of Mount Evans and Lost Creek

Wildernesses also provided support for the research. We thank Roger Wilson, Glenwood Springs, CO, for allowing us to place a monitor at his residence.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2013.10.051.

References

Altshuller, A.P., Lefohn, A.S., 1996. Background ozone in the planetary boundary layer over the United States. J. Air Waste Manag. Assoc. 46, 134–141.

Aneja, V., Businger, S., Li, Z., Claiborn, C., Murthy, A., 1991. Ozone climatology at high elevations in the Southern Appalachians. J. Geophys. Res. 96 (D1), 1007–1021.

Barna, M., Lamb, B., O'Neill, S., Westberg, H., 2000. Modeling ozone formation in the Cascadia Region of the Pacific Northwest. J. Appl. Meteorol. 39, 349–366.

Brace, S., Peterson, D.L., 1998. Spatial patterns of tropospheric ozone in the Mount Rainier Region of the Cascade Mountains, U.S.A. Atmos. Environ. 32, 3629–3637.

Brodin, M., Helmig, D., Oltmans, S., 2010. Seasonal ozone behavior along an elevation gradient in the Colorado Front Range Mountains. Atmos. Environ. 44, 5305–5315.

Bytnerowicz, A., Burley, J.D., Cisneros, R., Preisler, H.K., Schilling, S., Schweizer, D., Ray, J., Dulen, D., Beck, C., Auble, B., 2013. Surface ozone at the Devils Postpile National Monument receptor site during low and high wildland fire years. Atmos. Environ. 65, 129–141.

Coleman, L., Martin, D., Varghese, S., Jennings, S.G., O'Dowd, C.D., 2013. Assessment of changing meteorology and emissions on air quality using a regional climate model: impact on ozone. Atmos. Environ. 69, 198–210.

Davies, T.D., Schuepbach, E., 1994. Episodes of high ozone concentrations at the earth's surface resulting from transport down from the upper troposphere/lower stratosphere: a review and case studies. Atmos. Environ. 28, 53–68.

Davis, D.D., Orendovici, T., 2006. Incidence of ozone symptoms on vegetation within a National Wildlife Refuge in New Jersey, USA. Environ. Pollut. 143, 555–564.

Doherty, R.M., Wild, O., Shindell, D.T., Zeng, G., MacKenzie, I.A., Collins, W.J., Fiore, A.M., Stevenson, D.S., Dentener, F.J., Schultz, M.G., Hess, P., Derwent, R.G., Keating, T.J., 2013. Impacts of climate change on surface ozone and intercontinental ozone pollution: a multi-model study. J. Geophys. Res. Atmos. 118, 3744–3763.

Dumont, J., Spicher, F., Montpied, P., Dizengremel, P., Jolivet, Y., Le Thiec, D., 2013. Effects of ozone on stomatal responses to environmental parameters (blue light, red light, CO_2 and vapour pressure deficit) in three *Populus deltoides x Populus nigra* genotypes. Environ. Pollut. 173, 85–96.

Evans, G., Finkelstein, P., Martin, B., Possiel, N., Granves, M., 1982. The National Air Pollution Background Network 1976–1980. Project Summary. EPA-600/S4-82-058. 7 pg.

Evans, G.F., 1985. The National Air Pollution Background Network Final Project Report. EPA/600/S4–85/038.

Federal Register 75, No. 11/Tuesday January 19, 2010/Proposed Rules, pp. 2938–3052.

Federal Register 75, No. 80/Tuesday April 27, 2010/Notices, pp. 22126–22127.

Fehsenfeld, F.C., Bollinger, M.J., Liu, S.C., Parrish, D.D., McFarland, M., Trainer, M., Kley, D., Murphy, P.C., Albritton, D.L., Lenschow, D.H., 1983. A study of ozone in the Colorado mountains. J. Atmos. Chem. 1, 87–105.

Heath, R.L., Lefohn, A.S., Musselman, R.C., 2009. Temporal processes that contribute to nonlinearity in vegetation responses to ozone exposure and dose. Atmos. Environ. 43, 2919–2928.

Jaffe, D., Ray, J., 2007. Increase in surface ozone at rural sites in the western US. Atmos. Environ. 41, 5452–5463.

Kley, D., Geiss, H., Mohnen, V.A., 1994. Tropospheric ozone at elevated sites and precursor emissions in the United States and Europe. Atmos. Environ. 28, 149–158.

Kohut, R., Flanagan, C., Cheatham, J., Porter, E., 2012. Foliar ozone injury on cutleaf coneflower at Rocky Mountain National Park, Colorado. West. North Am. Nat. 72, 32–42.

Korfmacher, J.L., Musselman, R.C., A Portable Battery Powered Ozone Monitoring System for Use in Remote Areas (US Forest Service unpublished manuscript).

Koutrakis, P., Wolfson, J.M., Bunyaviroch, A., Froelich, S.E., Hirano, K., Mulik, J.D., 1993. Measurement of ambient ozone using a nitrite-saturated filter. Anal. Chem. 65, 210–214.

Lefohn, A.S., Foley, J., 1992. NCLAN results and their application to the standard-setting process: protecting vegetation from surface ozone exposures. J. Air Waste Manag. Assoc. 42, 1046–1052.

Lefohn, A.S., Runeckles, V.C., 1987. Establishing standards to protect vegetation – ozone exposure/dose considerations. Atmos. Environ. 21, 561–568.

Lefohn, A.S., Shadwick, D., Oltmans, S.J., 2010. Characterizing changes in surface ozone levels in metropolitan and rural areas in the United States for 1980–2008 and 1994–2008. Atmos. Environ. 44, 5199–5210.

Lefohn, A.S., Wernli, H., Shadwick, D., Limbach, S., Oltmans, S.J., Shapiro, M., 2011. The importance of stratospheric – tropospheric transport in affecting surface ozone concentrations in the western and northern tier of the United States. Atmos. Environ. 45, 4845–4857.

Lefohn, A.S., Wernli, H., Shadwick, D., Oltmans, S.J., Shapiro, M., 2012. Quantifying the importance of stratospheric–tropospheric transport on surface ozone concentrations at high- and low-elevation monitoring sites in the United States. Atmos. Environ. 62, 646–656.

Lin, M., Fiore, A.M., Cooper, O.R., Horowitz, L.W., Langford, A.O., Levy II, H., Johnson, B.J., Naik, V., Oltmans, S.J., Senff, C.J., 2012. Springtime high surface ozone events over the western United States: quantifying the role of stratospheric intrusions. J. Geophys. Res. 117, D00V22. http://dx.doi.org/10.1029/2012JD018151.11.

Logan, J.A., 1989. Ozone in rural areas of the United States. J. Geophys. Res. 94, 8511–8532.

Martin, R., Moore, K., Mansfield, M., Hill, S., Harper, K., Shorthill, H., 2012. Final Report: Uinta Basin Winter Ozone and Air Quality Study. December 2010–March 2011. Energy Dynamics Laboratory, Utah State University. EDL/11–039 http://rd.usu.edu/files/uploads/ubos_2010-11_final_report.pdf.

Musselman, R.C., Lefohn, A.S., Massman, W.J., Heath, R.L., 2006. A critical review and analysis of the use of exposure- and flux-based ozone indices for predicting vegetation effects. Atmos. Environ. 40, 1869–1888.

Musselman, R.C., Minnick, T., 2000. Nocturnal stomatal conductance and ambient air quality standards for ozone. Atmos. Environ. 34 (5), 719–733.

NRC, 2004. Committee on Air Quality Management in the United States. National Research Council. Air Quality Management in the United States. National Academy of Sciences, Washington, D.C.

Peterson, D.L., 2000. Monitoring air quality in mountains: designing an effective network. Environ. Monit. Assess. 64, 81–91.

Preisler, H.K., Zhong, S., Esperanza, A., Brown, T.J., Bytnerowicz, A., Tarnay, L., 2010. Estimating contribution of wildland fires to ambient ozone levels in National Parks in the Sierra Nevada, California. Environ. Pollut. 158, 778–787.

Schnell, R.C., Oltmans, S.J., Neely, R.R., Endres, M.S., Molenar, J.V., 2009. Rapid photochemical production of ozone at high concentrations in a rural site during winter. Nat. Geosci. 2, 120–122.

Schuepbach, E., Davies, T.D., Massacand, A.C., Wernli, H., 1999. Mesoscale modelling of vertical atmospheric transport in the Alps associated with the advection of a tropopause fold – a winter ozone episode. Atmos. Environ. 33, 3613–3626.

U.S EPA, 2006. Air Quality Criteria for Ozone and Related Photochemical Oxidants, vol. III, 424 pp. EPA600/R-05/004cF. Volume III of the Criteria Document chapters on "Environmental Effects of Ozone and Other Photochemical Oxidants". Published online as "Air Quality Criteria for Ozone and Related Photochemical Oxidants" http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=149923.

U.S. EPA, 2011. Regulatory Impact Analysis. In: Final National Ambient Air Quality Standard for Ozone. http://www.epa.gov/air/ozonepollution/pdfs/201107_OMBdraft-OzoneRIA.pdf.

U.S EPA, 2012. Welfare Risk and Exposure Assessment for Ozone. EPA 452/P-12-004. July. http://www.epa.gov/ttn/naaqs/standards/ozone/data/20120816welfarerea.pdf.

U.S EPA, 2013. Integrated Science Assessment for Ozone and Related Photochemical Oxidants. EPA/600/R-10/076F. Office of Research and Development, Research Triangle Park, NC. February.

Vingarzan, R., 2004. A review of surface ozone background levels and trends. Atmos. Environ. 38, 3431–3442.

Wooldridge, G., Zeller, K., Musselman, R., 1997. Ozone concentration characteristics at a high-elevation forest site. Theor. Appl. Climatol. 56, 153–164.

Wunderli, S., Gehrig, R., 1990. Surface ozone in rural, urban and alpine regions of Switzerland. Atmos. Environ. 24, 2641–2646.

Zeller, K., 2000. Wintertime ozone fluxes and profiles above a subalpine spruce–fir forest. J. Appl. Meteorol. 39, 92–101.

Zeller, K., Hehn, T., 1996. Measurements of upward turbulent ozone fluxes above a subalpine spruce-fir forest. Geophys. Res. Lett. 23 (8), 8.