Available online at www.sciencedirect.com
ScienceDirect
Atmospheric Environment 41 (2007) 5452–5463
ATMOSPHERIC ENVIRONMENT
www.elsevier.com/locate/atmosenv

Increase in surface ozone at rural sites in the western US

Dan Jaffe[a,*], John Ray[b]

[a]University of Washington, 18115 Campus Way NE, Bothell, WA 98011, USA
[b]National Park Service, Air Resources Division, Denver, CO, USA

Received 13 October 2006; received in revised form 29 January 2007; accepted 8 February 2007

Abstract

We evaluated O_3 data for the period 1987–2004 from 11 rural and remote sites in the north and western US, including two sites in Alaska. All sites show a seasonal cycle with a spring or spring-summer maximum. By deseasonalizing the data, we are better able to identify seasonal and spatial patterns and long-term trends. For most of the locations in the western US that we considered, there are significant inter-site correlations in the deseasonalized monthly means. This indicates that there are large scale factors that influence the monthly mean O_3 concentrations across the western US. At seven out of nine sites in the western US, there is a statistically significant increase in O_3 with a mean trend of 0.26 ppbv year^{-1} (range at the seven sites is 0.19–0.51 ppbv year^{-1}). At three of the sites, we examined the data in more detail to find that the trends are present in all seasons. At the two sites in Alaska, no clear pattern was found. At the one ozonesonde site in the western US with long-term observations (Boulder, Colorado), no significant trend was identified. However, the statistical power in the ozonesonde analysis is limited due to the low frequency of ozonesonde launches. Temperature changes can explain only a fraction of the surface O_3 trend. We consider several possible explanations for these trends, including: increasing regional emissions, changes in the distribution of emissions, increasing biomass burning or increasing global background O_3. With the available data, we are not able to unambiguously identify the cause for increasing O_3 in the western US

Keywords: Ozone; National parks; Western US; Tropospheric chemistry

1. Introduction

O_3 plays a key role in the troposphere due to its chemical, human health, vegetation and climate influences. Tropospheric O_3 primarily comes from in situ production, supplemented by stratospheric exchange (IPCC, 2001). O_3 production depends on NO_x and non-methane hydrocarbons (NMHCs), along with other factors. NO_x is emitted mainly by fossil fuel combustion, but also from biomass burning, lightning and fertilized soils, so changes in any of these factors can influence the O_3 concentrations in the atmosphere.

For most of the 20th century, emissions of NO_x and NMHCs increased in North America, Europe and Asia as a result of increasing use of fossil fuels for combustion. In the US, emissions of NMHCs started to decline in the 1970s. For NO_x, the reported US emissions began a slower decline in the 1980s, due to increasingly tight controls under the US Clean Air Act (US EPA, 2003). Between 1983 and 2002, emissions of NO_x in the US, as reported in the EPA inventory, decreased by 15%

*Corresponding author. Tel.: +1425 352 5357; fax: +1425 352 5233.
E-mail addresses: djaffe@u.washington.edu (D. Jaffe), john_d_ray@nps.gov (J. Ray).

1352-2310/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.atmosenv.2007.02.034

and NMHC emissions decreased by 40% (US EPA, 2003). However, a recent analysis by Parrish (2006) suggests that US NO_x emissions from vehicles may have increased during the decade of the 1990s, in contrast to the EPA inventory. Within most urban areas of the US, there have been reductions in peak O_3 mixing ratios (Lin et al., 2001; US EPA, 2003, 2004), due mainly to NMHC reductions.

In less developed countries, rapid growth in emissions occurred in the later part of the 20th century. For example, in East Asia NO_x emissions grew by 4–6% $year^{-1}$ since 1980 (Akimoto and Narita, 1994; Streets et al., 2001). The increase in NO_x emissions is largest in China and appears to have continued into the 21st century based on emission inventories (Streets et al., 2001), satellite data (Richter et al., 2005), and other observations (Irie et al., 2005). However, in addition to industrial emissions, changes in biomass burning and climate may also play an important role in changing surface O_3 mixing ratios (Jaffe et al., 2004).

Possible trends in tropospheric O_3 have been examined by numerous researchers (Fusco and Logan, 2003; Lee et al., 1998; Logan et al., 1999; Oltmans et al., 1998, 2006; Vingarzan, 2004). A recent analysis of ozonesonde data identified a complex pattern of changes with a decrease in upper tropospheric O_3 over most regions and an increase in middle and lower tropospheric ozone over Europe and East Asia. The complex pattern of O_3 changes was attributed to changes in stratospheric O_3, emissions and/or climate (Fusco and Logan, 2003). Evaluation of data at Okinawa, Japan from 1989 to 1997 indicates an O_3 increase of 2.5% $year^{-1}$ in Asian continental air during the winter–spring period (Lee et al., 1998). At a rural station near Hong Kong, Chan et al. (2003) found an O_3 increase of 1.5% $year^{-1}$ for the period of 1984–1999, which was attributed to increasing emissions from China. Naja and Akimoto (2004) report that regionally polluted airmasses in East Asia have experienced an 11–20% increase between the 1970s and the 1990s. At Mace Head, background O_3 appears to have risen 0.5 ppbv $year^{-1}$ in the past two decades and in all seasons (Simmonds et al., 2004). The authors attribute this change to increasing global emissions (Simmonds et al., 2004).

In North America, a similar background change has been suggested by several studies. At Lassen National Park in Northern California, a 15-year record of surface O_3 was evaluated using back-trajectories. A positive trend in O_3 was found in both the Pacific-marine and continental air masses (Jaffe et al., 2003). However, analysis by Oltmans et al. (2006), found no trend at a coastal California site or several National Parks in the western US. In Canada, a positive trend was seen at rural sites in the Province of British Columbia (Vingarzan and Taylor, 2003). Lin et al. (2000) examined O_3 trends using the database of EPA monitoring sites in the US. They found that the distribution of O_3 had shifted over time, with the highest percentile concentrations showing a decrease and the lowest percentile showing an increase. The authors attributed this effect to an increase in background O_3, largely due to increasing emissions from Asia (Lin et al., 2000; Berntsen et al., 1999; Fiore et al., 2002; Jacob et al., 1999; Parrish et al., 2004; Vingarzan, 2004).

If global background O_3 is increasing, then we would expect this change to be most evident at cleaner sites in the western US. Nonetheless, sites that receive significant regional pollution, such as in the east, southeast or southwestern US, may still be affected by this change (Fiore et al., 2002). However, it will be much more difficult to separate the local from global influence at these regionally polluted sites. For this study, we will examine O_3 trends at background sites in the western US and Alaska. This extends our earlier work, which focused on only one site along the west coast of the US (Jaffe et al., 2003).

2. Methods

We have examined O_3 records in relatively remote locations in the US, which are mostly unaffected by nearby pollution sources. We considered only sites with at least 12 years of data and sites that have no major gaps in the data record. These sites are located in the western US and Alaska. Most sites have 15–18 years of data and most are managed by the US National Park Service (NPS). Table 1 gives information about each site, and Fig. 1 shows a map marked with the locations of the sites used for trend analysis. Of the 11 sites considered only two, Rocky Mountain National Park (RMNP) and Lassen National Park (LNP), have had any recorded days with an 8-h daily maximum O_3 concentration greater than 0.08 ppmv. These two sites are adjacent to major metropolitan regions, so are more affected by regional pollution.

Data for this analysis has come from several different sources. Surface O_3 data are collected at

Table 1
Sites used in O_3 trends analysis

Location	Site type	Lat. (°N)/Long. (°W)/elevation (m)	Data record (mm/yy–mm/yy)	# days > 0.08 ppmv in data record[a]
Lassen N.P., CA	NPS	40.5°N, 121.6°W, 1756 m	10/87–8/04	6
Rocky Mt. N.P., CO	NPS	40.3°N, 105.6°W, 2743 m	1/87–11/04	19
Yellowstone N.P., WY	NPS	44.6°N, 110.4°W, 2400 m	4/87–8/04	0
Glacier N.P., MT	NPS	48.5°N, 114.0°W, 976 m	4/89–10/04	0
Denali N.P., AK	NPS	63.7°N, 149.0°W, 661 m	7/87–11/04	0
Barrow, AK	NOAA/CMDL	71.3°N, 156.6°W, 11 m	3/73–12/03	0
Pinedale, WY	CASTNET	42.9°N, 109.8°W, 2388 m	1/89–12/04	0
Gothic, CO	CASTNET	39.0°N, 107.0°W, 2926 m	7/89–12/04	0
Centennial, WY	CASTNET	41.4°N, 106.2°W, 3178 m	7/89–12/04	0
Craters of the Moon, ID	NPS	43.5°N, 113.6°W, 1815 m	10/92–12/04	0
Canyonlands N.P., UT	NPS	38.5°N, 109.8°W, 1809 m	8/92–12/04	0

[a]This column gives the number of days in the data record with 8-h daily maximum O_3 concentrations greater than 0.08 ppmv.

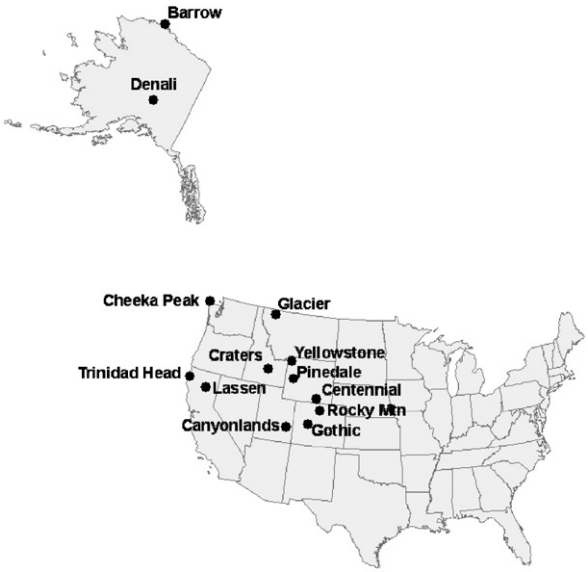

Fig. 1. Map showing location of the observation sites.

many National Parks in the US; however at most of these sites the data record is relatively short. We have used data from National Parks in the western US with 12 or more years of O_3 data. Details on the NPS O_3 monitoring program can be found at: ⟨http://www2.nature.nps.gov/air/Monitoring/network.cfm⟩. We have also used data from three sites in the Clean Air Status and Trends Network (CASTNET) and data from the NOAA-CMDL Barrow observatory in Alaska. In total, we have examined data from nine sites in the continental US and two sites in Alaska.

At these sites, O_3 has been measured using UV absorption and has followed consistent calibration procedures using NIST traceable standard photometers and based on US EPA protocols. Except for Barrow, the data were obtained as hourly averages and the data records were screened to ensure that only reasonable values were included in the analysis. Especially for the CASTNET data, there are a number of unrealistic O_3 values in the data record that must be removed prior to statistical analysis, but these constitute less then 1% of the data record. These were identified by extended periods (>6 h) when O_3 mixing ratios remained unchanged to three significant figures at either very high or very low values (<10 or >100 ppbv). For Barrow, the data were obtained as monthly means. The long-term monthly uncertainty is believed to be less than 2% (Oltmans et al., 2006).

We also used Electrochemical Concentration Cell (ECC) ozonesonde data for Boulder, Colorado and Trinidad Head, California. These measurements were made by the NOAA Climate Monitoring and Diagnostics Laboratory (Boulder, CO), and the data were provided by Bryan Johnson (NOAA-CMDL/ESL). Starting in July 1997, the ozonesondes used an ECC cathode solution consisting of 2% unbuffered KI (Newchurch et al., 2003). Prior to this date the ECC cathode solution was 1% buffered KI solution, which could overestimate the O_3 mixing ratios, although this should not have a large effect on tropospheric values (Johnson et al., 2002). The data from Boulder extend back to 1979 so can be used for trend analysis, with some caveats. For comparison purposes, we also used surface O_3

data from Cheeka Peak, Washington (Jaffe et al., 1999).

Detection of trends in geophysical data is complicated by a number of factors, including natural variability and changes in site or operating procedures. Generally, the greater the natural variability, the longer it takes to detect a trend (Weatherhead et al., 1998). There are a variety of methods that have been employed to detect trends, some of which are better than others (Hess et al., 2001). In our analysis, we have used ordinary least squares (OLS) regression on the deseasonalized monthly means, which is one of the more robust methods (Hess et al., 2001). We also computed trends using Theil's method (Conover, 1980; Hoaglin et al., 1983). Theil's method calculates the slope from the median of every combination of paired data points. The confidence interval for Theil's method is calculated by a non-parametric method. This results in a trend estimate that is less sensitive to outliers than OLS. Theil's method has been used previously in many geophysical analyses and has been used by the NPS to evaluate changes in air quality in the US National Parks (NPS, 2006a, b). We have also used a multiple regression model, which incorporates both time and temperature as independent variables. Statistical analyses were conducted primarily with SPSS software (Chicago, IL) versions 12 and 13. The Theil's method slopes and confidence intervals were calculated using a FORTRAN program written by the authors.

Ideally, we would like sites with long data records that have remained unchanged over many years. Unfortunately, perfect data records rarely exist. For many of these sites, a change in site location or inlet height was made in the mid-1990s. At Lassen, Rocky Mountain, Yellowstone, Glacier, Denali and Canyonlands National Parks, the inlet height was changed from 3.5 to 10 m in the mid-1990s. The site at Yellowstone National Park also was moved 1.5 km. While for many pollutants these changes would be relatively minor, for O_3 this may not be the case. This is because O_3 has a relatively large deposition to the surface, so that during nighttime inversions, a significant vertical gradient can result. Thus it is possible that the inlet height change may have an influence on O_3 mixing ratios, especially at night. Given the much stronger vertical mixing, we expect the influence of inlet height will be much less during the daytime.

To evaluate the influence from inlet height, we examined the monthly means for daytime (10am–6pm, local time) and nighttime (10pm–6am, local time) data. For every month, we compared data from the same month in the 2 years before and after the inlet change took place. At most parks where this inlet change occurred, the nighttime data showed a statistically significant jump of several ppbv following the inlet height change. The daytime data did not show any systematic change. This is what would be expected, since a strong vertical gradient in O_3 often develops at night but is less prevalent during the day. So to minimize the influence from the inlet height change, we will focus our trend analysis on only the daytime data.

3. Results

Fig. 2 shows the monthly average O_3 mixing ratio as seen at five surface sites, plus data from the Trinidad Head ozonesondes. Most sites experience a spring maximum in O_3. This peak is seen throughout the lower troposphere of the Northern Hemisphere and reflects the influence from global background O_3. Some sites also show a summer peak which is due to photochemical O_3 production from regional NO_x and NMHC emissions. This is most apparent for Rocky Mt. N.P. and Lassen N.P., both of which are adjacent to major metropolitan regions. As seen in Table 1, these two sites occasionally exceed an 8-h average concentration of 0.08 ppmv. Fig. 2 also shows the influence of altitude on O_3. Elevated sites generally have higher O_3 mixing ratios (e.g., Centennial compares well with the Trinidad Head 1.5–3.5 km data). In fall

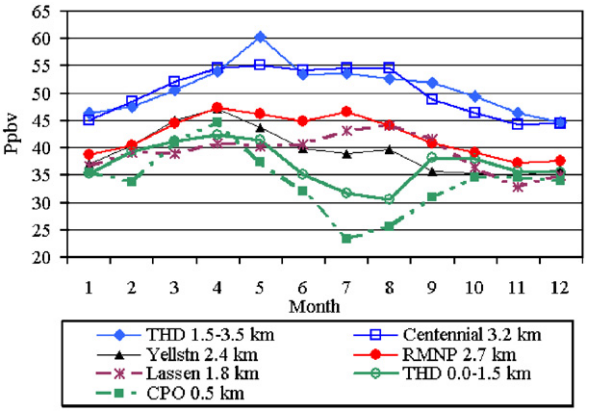

Fig. 2. Monthly average O_3 at seven sites in the western US. The sites are Trinidad Head (THD, average of ozonesonde data from 0 to 1.5 km and 2.5–3.5 km asl); Cheeka Peak (CPO); Yellowstone N.P. (Yellstn); Rocky Mt. N.P. (RMNP); Lassen N.P.; and Centennial. The elevation of each site is given in the caption.

through spring, concentrations are similar at most of the lower elevation sites. For example, the difference in monthly mean concentrations between Cheeka Peak, Trinidad Head at 0–1.5 km and the other sites is only about 5 ppbv through most of the year, whereas in summer this difference becomes 15–20 ppbv. This argues that the background influence at the inland sites is strongest in fall, winter and spring, and reduced in summer as regional photochemical pollution becomes more important at the inland sites.

3.1. Trend analysis

Hourly averages were converted into daytime (10:00–18:00 local time) monthly means. The seasonal component was removed from the monthly means using the seasonal decomposition procedure in SPSS software, which uses the "Census I" method (Wheelwright and Makridakis, 1985). The deseasonalized monthly means (DSMM) values have the same long-term average as the original data. OLS analysis was then conducted on the DSMM values. This procedure will give a robust measure of the annual trend, so long as the trend is present and relatively uniform in all seasons. In a later section, we show that this assumption appears to be valid.

Figs. 3a–c show a time series of the deseasonalized monthly means for three of the sites: Rocky Mountain, Yellowstone and Lassen Volcanic National Parks with OLS regression lines. Table 2 gives the trend analysis on the DSMM values using both OLS and Theil's method for all 11 sites.

Trend analysis using the OLS and Theil's methods give very similar results. Both analysis methods yield trends that are positive and statistically significant at most sites in the western US, the only exceptions being Pinedale and Glacier N.P. At Denali N.P., OLS yields a marginally significant trend ($P = 0.06$), whereas the Theil's method yields a significant trend ($P = 0.01$), but in both cases the magnitude of the trend is very small.

Of the nine sites in the continental US, seven have a statistically significant trend. For the nine western US sites, the OLS trends range from 0.0–0.51 ppbv year^{-1}, with a mean of 0.26 ppbv year^{-1}. For the 18-year period between 1987 and 2004, this corresponds to an average O_3 increase of 5 ppbv. This result is similar to the one we reported previously for Lassen Volcanic National Park using 1988–2002 data (Jaffe et al., 2003). In that analysis, we found a statistically

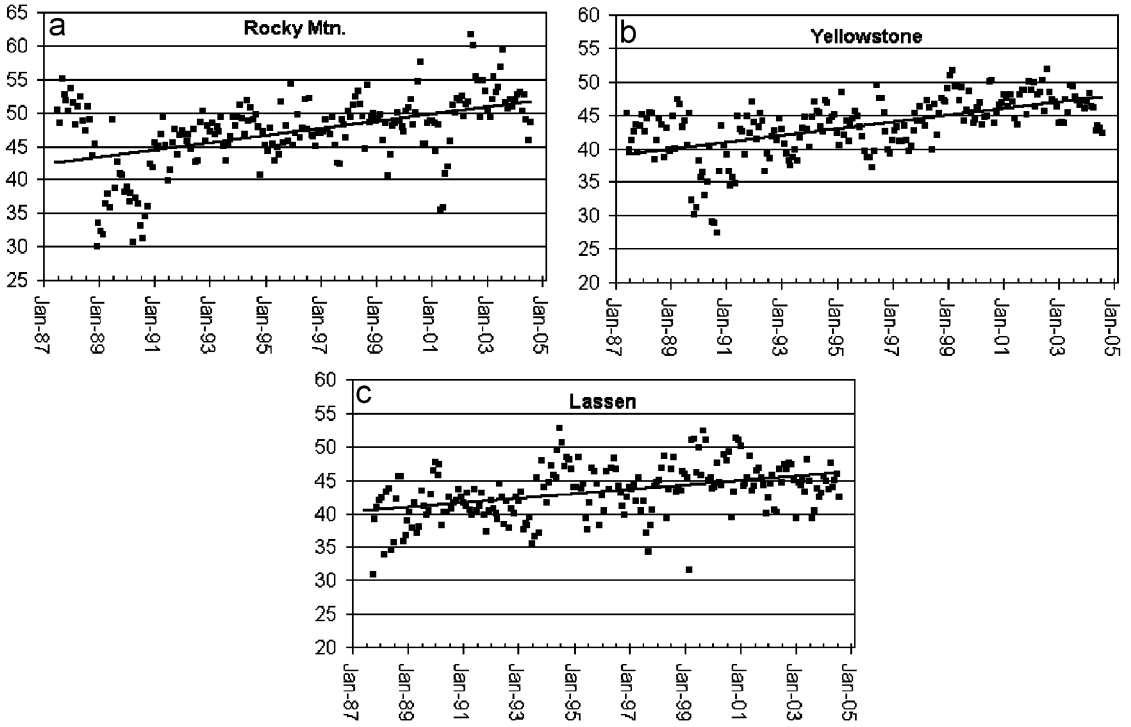

Fig. 3. (a) Deseasonalized daytime monthly means for Rocky Mountain National Park. (b) Deseasonalized daytime monthly means for Yellowstone National Park. (c) Deseasonalized daytime monthly means for Lassen Volcanic National Park.

Table 2
Trend analysis using ordinary least squares (OLS) and Theil's method on deseasonalized monthly mean O_3 concentrations, daytime data (10:00–18:00 LST)

Site	Mean	OLS trend (ppbv year^{-1})	R^2	P value	Theil's trend (ppbv year^{-1})
Rocky Mt.	47.2	**+0.51**	**0.22**	**<0.01**	**+0.48**
Yellowstone	43.6	**+0.50**	**0.32**	**<0.01**	**+0.45**
Lassen	43.3	**+0.33**	**0.17**	**<0.01**	**+0.32**
Centennial	51.1	**+0.25**	**0.13**	**<0.01**	**+0.31**
Canyonlands	48.0	**+0.28**	**0.11**	**<0.01**	**+0.26**
Craters	44.0	**+0.22**	**0.05**	**0.01**	**+0.22**
Gothic	51.0	**+0.19**	**0.10**	**<0.01**	**+0.19**
Denali	32.4	+0.08	0.02	0.06	**+0.13**
Pinedale	49.4	+0.06	0.01	0.17	+0.11
Barrow	26.0	0.00	0.00	0.19	+0.04
Glacier	32.8	0.00	0.00	0.45	−0.08

R^2 and P value refer to OLS. Values in bold are significant at $P = 0.01$ or better.

Table 3
Correlation matrix for DSMM values between sites in the western US. At each site there are between 147 and 209 months of data

		Glacier	Yellowstone	RMNP	Lassen	Centen.	Gothic	Pinedale	Craters
Yellow-stone	R	0.14							
	P value	0.05							
RMNP	R	0.10	0.56						
	P value	0.22	0.00						
Lassen	R	0.28	0.36	0.24					
	P value	0.00	0.00	0.00					
Centen.	R	0.40	0.54	0.57	0.36				
	P value	0.00	0.00	0.00	0.00				
Gothic	R	0.30	0.44	0.51	0.33	0.62			
	P value	0.00	0.00	0.00	0.00	0.00			
Pinedale	R	0.33	0.35	0.22	0.35	0.47	0.50		
	P value	0.00	0.00	0.00	0.00	0.00	0.00		
Craters	R	0.40	0.48	0.50	0.35	0.44	0.41	0.33	
	P value	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Canyon-land	R	0.53	0.50	0.55	0.30	0.57	0.63	0.44	0.51
	P value	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

significant trend of 0.5 ppbv year^{-1}, which was present in both the continental and marine air masses arriving to the Lassen monitoring site.

At both Rocky Mountain and Yellowstone National Parks (Figs. 3a and b), there was a period of high O_3 mixing ratios, followed by lower O_3 mixing ratios in 1988–1990. We have no good explanation for this pattern. Close examination of the hourly averages does not reveal any obvious discrepancy, nor does this pattern appear at other NPS sites (e.g. Lassen, Fig. 3c). We believe it reflects large scale variations in background O_3 that are seen in common at these two parks. Comparing the DSMM values for the two parks, we find a positive correlation with an R^2 of 0.31, statistically significant, with a P value <0.01. Table 3 shows a correlation matrix comparing the DSMM values at all nine sites in the western US. We find that the DSMM values at many parks are significantly correlated. As a test of this method, we also compared the values from Denali National Park to sites in the western US and found almost no correlation. Since this analysis uses the deseasonalized data, this result reflects large-scale interannual variations that are seen across many sites.

We conducted additional analyses on data from the three sites that have the longest data records and strongest trend: Rocky Mountain, Yellowstone and Lassen National Parks.

Table 4
Daytime O_3 mixing ratio for the first and second half of each data record, based on deseasonalized monthly means

Site	Mean (ppbv)	P value
Rocky Mt.—1st half	44.9	<.01
Rocky Mt.—2nd half	49.4	
Yellowstone—1st half	41.3	<.01
Yellowstone—2nd half	45.7	
Lassen—1st half	41.8	<.01
Lassen—2nd half	44.6	

Following the recommendations of Hess et al. (2001), we examined these data sets using a t-test adjusted for seasonality. In this approach, we compared the DSMM for the first and second halves of the data record. The results for three sites are shown in Table 4.

The t-tests, adjusted for seasonality, support the trend analyses shown in Table 2 previously.

3.2. Analysis of seasonal trends

The trend in O_3 by season was evaluated for Rocky Mountain, Yellowstone and Lassen National Parks. For each site, daytime hourly data were averaged into a single seasonal mean mixing ratio. Winter included the months of December, January and February, and other seasons were defined accordingly. Data from December were included with the January and February data from the next year. The results are shown in Table 5.

Most of the trends shown in Table 5 are statistically significant at a P value of 0.05 or better and the slopes do not exhibit any obvious pattern with respect to season. Because there are fewer data points, some of the trends have lower P values; however, overall the positive trend appears to be present in all seasons.

3.3. Influence of temperature on trend analysis

O_3 production is known to be a strong function of temperature due to a variety of factors (increased reaction rates, increased solar insolation), increased natural VOC emissions, reduced wind speeds, etc. (Lin et al., 2001; NRC, 1991). It is possible that increasing temperature may have increased O_3 production regionally. To investigate whether temperature changes can explain the O_3 trend, we examined the relationship between O_3 and temperature.

Table 5
Trend in O_3 concentrations (daytime data) by season for three parks

	Slope (ppbv year^{-1})	R^2	P value
Rocky Mt.			
Winter	+0.62	0.32	0.01
Spring	+0.59	0.32	0.02
Summer	+0.50	0.20	0.07
Fall	+0.32	0.20	0.06
Yellowstone			
Winter	+0.56	0.53	0.01
Spring	+0.38	0.19	0.08
Summer	+0.49	0.39	<0.01
Fall	+0.56	0.63	<0.01
Lassen			
Winter	+0.21	0.19	0.08
Spring	+0.33	0.41	0.01
Summer	+0.43	0.31	0.02
Fall	+0.28	0.17	0.12

For this analysis, we have used a linear function, which expresses the O_3 concentration as a function of several variables:

$$\text{Observed } O_3 = \text{seasonal factor} + \text{temperature factor} + \text{trend} + \text{residual} \quad (1)$$

For the deseasonalized data, the seasonal factor can be removed, so this becomes:

$$\text{Deseasonalized } O_3 = \text{temperature factor} + \text{trend} + \text{residual}. \quad (2)$$

To quantify each factor, we first calculate the departure from the monthly mean temperature. The monthly mean temperature departure is then used in a linear regression model, along with time, as a predictor on the deseasonalized monthly mean O_3 concentrations:

$$\delta O_3 = A_1 * \Delta\text{temp} + A_2 * \text{time} + \text{residual}, \quad (3)$$

where δO_3 refers to the deseasonalized monthly mean O_3 concentration and Δtemp refers to the departure from the monthly mean temperature. Note that the difference between the monthly mean departure and the deseasonalized monthly mean values is simply the annual average. Either value could be used in the regression model as the final results are identical.

We did this analysis separately for the warm season (May–September) and cold season months. Not surprisingly, we found that temperature is not a useful predictor for O_3 concentrations during the

Table 6
Two-variable regression model (temperature and time) as predictors for the deseasonalized daytime monthly mean O_3 for the months of May–September

Site	Temperature coefficient-A_1 (ppbv $^\circ C^{-1}$)	Trend coefficient-A_2 (ppbv year^{-1})	R^2
Rocky Mt.	1.3 (<0.01)	0.46 (<0.01)	0.26
Yellowstone	0.27 (0.20)	0.45 (<0.01)	0.28
Lassen	0.74 (<0.01)	0.36 (<0.01)	0.27

All regressions are statistically significant ($P<0.01$). For the temperature and trend coefficients, the P value for each coefficient is given in parentheses.

colder months. Table 6 shows the results for May–September. For comparison, Table 2 showed the trend analysis without including temperature.

For Rocky Mountain and Lassen, inclusion of temperature improved the model fit (R^2), compared to the model without temperature, whereas for Yellowstone, temperature is a rather poor predictor of the O_3 concentration. These results show that for summer months with above average temperature, O_3 will also be above average, with a coefficient ranging from 0.27 to 1.3 ppbv $^\circ C^{-1}$. However, inclusion of temperature in the regression model does not significantly change the interpretation or magnitude of the trend component. For example, for Rocky Mountain N.P. the May–September trend using this model is 0.46 ppbv year^{-1}, compared to a trend of 0.50 ppbv year^{-1} for the whole year or 0.51 ppbv year^{-1} for the summer only when temperature is not considered.

For the cold season (October–April), no clear pattern emerges. Temperature is uncorrelated with O_3 at some sites, and inversely correlated at others, but only weakly. Overall, we do not feel that inclusion of temperature in the regression model is justified for the winter months.

3.4. Evaluation of free tropospheric trend

The broad distribution of increasing O_3 suggests a large scale phenomenon. For this reason we examined whether an O_3 increase could be identified from any free tropospheric data sets in the region. The National Oceanic and Atmospheric Administration (NOAA) makes regular ozonesonde measurements at two sites in the western US: Boulder, Colorado (since 1979) and Trinidad Head, California (since 1997) (Newchurch et al., 2003). However, the shortness of the Trinidad Head record prohibits a trend analysis. Therefore, we have examined only the Boulder data for trends. Between 1979 and 2004, there have been more than 970 ozonesonde launches, but these have not been evenly spaced. In some years there were only nine ozonesondes launched, while in other years there were as many as 56. Generally, there were fewer launches in the early part of the data record, with a significant increase in the number of launches starting in 1985. It should also be noted that ozonesondes are subject to interferences (especially SO_2) and launch procedures have been changed (e.g., ECC cathode solution). Both of these issues make trend determination from ozonesondes more problematic than from continuous surface measurements.

Because of the small number of sondes in earlier years, we evaluated the trends only from 1985 to 2004. This includes 897 ozonesondes, for an average of 45 sondes year^{-1} (none launched between December 1989 and June 1991). Fig. 4 shows the DSMM O_3 mixing ratios averaged between 3 and 8 km asl. No significant trend is observed. The mean O_3 mixing ratio is 56.6 ppbv, with a standard deviation of 5.1. We also examined possible trends in different regions of the troposphere and by season and were unable to identify any significant trends.

Examination of Fig. 4 suggests significant variations in the DSMM values. These month-to-month variations limit our ability to detect trends (Weatherhead et al., 1998). While it is possible that these variations are an inherent property of the free troposphere, we feel it is more likely that with only four samples per month, significant month-to-month variability is introduced due to undersampling. To test this hypothesis, we compared 10 years of data from the ozonesonde measurement site near Boulder, Colorado with two continuous surface monitoring sites which are part of the EPA/State of Colorado air monitoring network. The two continuous monitoring sites, South Boulder and Rocky Flats North, are approximately 3 and 7 km from the ozonesonde launch site. All three sites are located approximately 8–12 km south of Boulder,

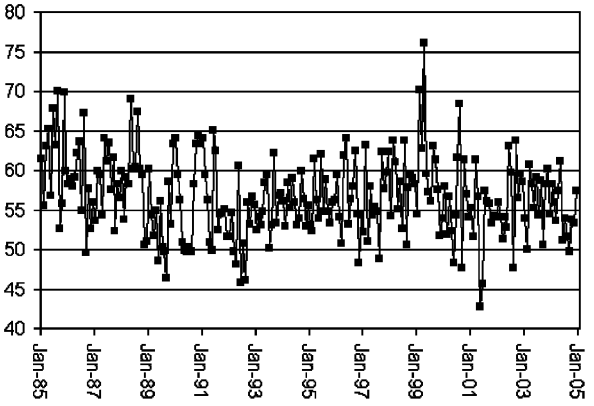

Fig. 4. Deseasonalized monthly means for 3–8 km from the Boulder ozonesonde data. The R^2 for the linear fit is 0.02. No significant trend is present in these data.

Table 7
Comparison of deseasonalized O_3 monthly means and standard deviation from ozonesondes and continuous surface observations (daytime data only), June 1994–December 2004

Data set	Mean (ppbv)	σ (DSMM, ppbv)
Rocky flats, continuous monitor, daytime only	43.7	4.1
S. Boulder, continuous monitor, daytime only	40.0	5.6
Boulder ozonesonde, lowest surface layer	42.4	7.7

Colorado. Table 7 compares 10 years of data from these three sites. Because the ozonesondes are only launched routinely during the daytime, we used only the daytime data to calculate the DSMM values from the continuous surface data. For the ozonesonde data, we used the surface O_3 mixing ratios reported in the 2–3 min prior to launch (B. Johnson, personal communication, 2005). We also used the sonde data from the lowest 250 meter atmospheric layer. Both gave a very similar result.

The 10-year mean daytime O_3 mixing ratio observed at the three measurements are within a few ppbv of each other. This suggests that the air masses sampled at the three locations are, on average, similar. However, the standard deviations for the ozonesonde DSMM values are greater compared to the continuous measurements by 88% and 38%. The larger variance results in a longer time to detect trends. Based on Weatherhead et al. (1998), detection of a 1% year^{-1} trend with an autocorrelation of 0.3 would require 13, 16 or 20 years of observations from the two surface sites and the ozonesonde, respectively. Detection of a 0.5% year^{-1} trend would require 20, 25 or 31 years of observations, respectively, at these sites. Thus it appears that sampling the O_3 distribution four times per month increases the time required to detect these trends by 25–50%, compared to continuous sampling. Nonetheless, the Boulder ozonesonde record does extend for ~20 years, so if a significant trend at the 1% year^{-1} level were present in the data record, it should be detectable. At the surface sites, the trends we have identified (Table 2) range from 0.4 to 1.1% year^{-1}. Since no trend was identified in the ozonesonde data, we conclude that the trend we have detected at the seven surface sites does not extend to the free troposphere or is not yet detectable using the ozonesonde data.

4. Discussion

In summary, this analysis shows that surface O_3 in the western US has undergone a significant increase over the past 2 decades. This increase was statistically significant at seven out of nine rural/remote monitoring sites in the continental US. At two sites in Alaska, no clear pattern was found. For the nine continental US sites, we found an average O_3 increase of 0.26 ppbv year^{-1}, using both OLS and Theil's method. This corresponds to an increase of approximately 5 ppbv over the 18 years of observations (1987–2004). Based on a detailed analysis at three sites, we have found that the increase is present in all seasons.

In contrast, Oltmans et al. (2006) report finding no trend at Yellowstone, Olympic and Glacier National Parks, although a statistical analysis was not presented. At Glacier, our results are similar, but at Yellowstone N.P. we find a significant positive trend using both OLS and Theil's method. We did not analyze the Olympic National Park data record, since the monitor is located in the city of Port Angeles and the data show the usual characteristics of an urban polluted environment. We have no explanation for the difference between our results and the results of Oltmans et al (2006) at Yellowstone N.P.

Because past work has shown that temperature is an important predictor for high O_3 mixing ratios, we have incorporated temperature into a multiple regression model. This model has an improved fit compared to a simple regression model. However, the trends calculated from the multiple regression

are similar to those calculated without incorporating temperature. This indicates that temperature changes are not the dominant cause for these long-term O_3 trends.

Recent EPA and NPS reports (US EPA, 2004; NPS, 2002, 2006a, b) have also identified positive trends in the annual 4th highest 8-h average at several National Parks in the western US. In the EPA report (US EPA, 2004), most of this trend was attributed to high O_3 concentrations seen during the warm dry summers of 2002 and 2003. In contrast, we find that the O_3 trend is statistically significant in all seasons and even if the trend analysis ends with 2001 data. Thus we believe that the O_3 trend is a broader phenomenon, not explained solely by temperature trends. Understanding the cause of these trends is important to understanding future changes.

We propose several possible explanations for these O_3 trends:

(1) *Increasing regional emissions*. O_3 production depends mainly on NO_x and NMHC concentrations, but in a complex and non-linear way. If regional NO_x and NMHC concentrations increase, we would expect O_3 production to increase. In many regions of the western US, population and vehicle miles have increased significantly over this time frame. Despite this, according to the US EPA, emissions of NO_x and NMHCs have declined in nearly all parts of the US, including the western US (US EPA, 2003). However, the downward trend in mobile source emissions has been challenged by Parrish (2006). For the period 1990–2000, the EPA inventory reports a mobile source reduction in US NO_x emissions of 12%, whereas Parrish estimates an increase of 23%. This discrepancy is large and prevents a definitive conclusion concerning the cause of the O_3 trends in the western US. In addition, soil emissions of NO_x may also be important in the western US, and these could be increasing due to climate change (Jaeglé et al., 2005).

(2) *Changes in the regional distribution of emissions*. Even if NO_x emissions were constant or declining, it is still possible for O_3 production to increase due to the non-linear nature of O_3 production (Liu et al., 1987). An increase in O_3 could occur if, for example, NO_x emissions shifted from regions of high emission density to regions of lower emission density. This hypothesis would be consistent with an increase in population in rural and suburban communities in the western US.

(3) *Increasing biomass burning in the western US*. Biomass burning is an important source of O_3 precursors. In the western US there is evidence that fires have increased in severity over the past 50 years and that the length of the fire season has increased (Westerling et al., 2006). Fires could also play an important role in the interannual variations in O_3 concentrations, as seen in Fig. 3. In addition, biomass burning in distant regions, such as Siberia, can also influence background O_3 in the western US (Jaffe et al., 2004). Biomass burning influences on O_3 will be most important during summer.

(4) *Increasing global background O_3*. Long-term trends in background O_3 have been identified on several continents of the Northern Hemisphere (e.g. Chan et al., 2003; Jaffe et al., 2003; Lin et al., 2000; Simmonds et al., 2004). A change in O_3 over all seasons is consistent with a large-scale or hemispheric phenomenon. In particular, rapid growth in emissions within Asia is important for background O_3 concentrations over the western US (Fiore et al., 2002; Jacob et al., 1999; Jaffe et al., 1999, 2003). Also, the magnitude of the O_3 increase we report here is approximately consistent with the O_3 change that we would expect due to Asian emissions (Berntsen et al., 1999; Jacob et al., 1999). However, this explanation is in contrast to the Boulder ozonesonde results. On the other hand, Ziemke et al. (2005) have reported a significant increase in tropospheric O_3 in the North Pacific over the past 25 years from TOMS and SBUV data. Thus we leave open the possibility that the ozonesonde data set, due to the small number of sonde launches, is not yet able to detect a statistically significant trend.

At this point, it is not certain which of these explanations is correct, so each must be considered as a hypothesis for future investigations. To better understand the cause of this O_3 increase, a better understanding of NO_x and NMHC sources is needed. A more accurate emission inventory, and carefully updated emissions over time, would help clarify the importance of development and increasing VMT in the western US. This should include emissions from increasing oil and gas exploration in the western US. This would address uncertainties

associated with points 1 and 2 above. A better understanding of the emissions from fires in the western US would help clarify the importance of these sources on O_3 (point 3 above). Finally, long-term observations of nitrogen species in intercontinental inflow to the US, especially PAN (Berntsen et al., 1999; Kotchenruther et al., 2001; Hudman et al., 2004) would help clarify the importance of global and Asian emission sources on O_3 in the US (e.g. point 4 above). Detailed regional and global modeling studies would also aid in our understanding of the long-term changes in O_3 in the western US.

Finally, it is important to consider how changes in background O_3 influence urban air quality and exceedances of the air quality standards. While an increase in background O_3 of 5 ppbv is only a small part of the air quality standard, it could play an important role for locations that are already close to the standard due to local or regional pollution. Thus it is conceivable that changes in background O_3 may offset local reductions in O_3 precursors, as suggested by Jacob et al. (1999). For example, for Rocky Mountain National Park over the course of this data period, there have been 19 days with a daily 8-h maximum in excess of the 0.08 ppmv standard. Seventeen of these days have occurred since 1998, while only two occurred between 1987 and 1997. For summer days at RMNP, 4% have daily 8-h maximums of 77 ppbv or greater, while only 1% of these days have values of 85 ppbv or greater. A regression analysis of the 95th percentile of the RMNP summer daily 8-h maximum shows a significant trend with a slope of 0.55 ppbv $year^{-1}$. Thus, a relatively small change in background O_3 may increase the frequency of days that exceed the air quality standard.

Acknowledgements

This report was sponsored by the Coordinating Research Council (CRC) under Project A-54. The data used were collected by the National Park Service, NOAA and the EPA. We acknowledge the efforts of the many individuals who made these observations.

References

Akimoto, H., Narita, H., 1994. Distribution of SO_2, NO_x, and CO_2 emissions from fuel combustion and industrial activities in Asia with $1^\circ \times 1^\circ$ resolution. Atmospheric Environment 28, 213–225.

Berntsen, T.K., Karlsdottir, S., Jaffe, D.A., 1999. Influence of Asian emissions on the composition of air reaching the Northwestern United States. Geophysical Research Letters 26, 2171–2174.

Chan, C.Y., Chan, L.Y., Harris, J.M., 2003. Urban and background ozone trend in 1984–1999 at subtropical Hong Kong, South China. Ozone-Science and Engineering 25, 513–522.

Conover, W.J., 1980. Practical Nonparametric Statistics, second ed. Wiley, New York.

Fiore, A.M., Jacob, D.J., Bey, I., Yantosca, R.M., Field, B.D., Fusco, A.C., Wilkinson, J.G., 2002. Background ozone over the United States in summer: origin, trend, and contribution to pollution episodes. Journal of Geophysical Research 107 (D15).

Fusco, A.C., Logan, J.A., 2003. Analysis of 1970–1995 trends in tropospheric ozone at Northern Hemisphere midlatitudes with the GEOS-CHEM model. Journal of Geophysical Research 108 (D15), 4449.

Hess, A., Iyer, H., Malm, W., 2001. Linear trend analysis: a comparison of methods. Atmospheric Environment 35, 5211–5222.

Hoaglin, D.C., Mosteller, F., Tukey, J.W., 1983. Understanding Robust and Exploratory Data Analysis. Wiley, New York, pp. 160–163.

Hudman, R.C., et al., 2004. Ozone production in transpacific Asian pollution plumes and implications for ozone air quality in California. Journal of Geophysical Research 109, D23S10.

IPCC, 2001. Climate change 2001: the scientific basis. In: Houghton, J. T., Ding, Y., Griggs, D.J., Noguer, M., van der Linden, P. J., Xiaosu, D. (Eds.), Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change (IPCC). Cambridge University Press, Cambridge, UK, pp. 944.

Irie, H., Sudo, K., Akimoto, H., Richter, A., Burrows, J.P., Wagner, T., Wenig, M., Beirle, S., Kondo, Y., Sinyakov, V.P., Goutail, F., 2005. Evaluation of long-term tropospheric NO_2 data obtained by GOME over East Asia in 1996–2002. Geophysical Research Letters 32 (11), L11810.

Jacob, D.J., Logan, J.A., Murti, P.P., 1999. Effect of rising Asian emission on surface ozone in the United States. Geophysical Research Letters 26, 2175–2178.

Jaeglé, L., Steinberger, L., Martin, R.V., Chance, K., 2005. Global partitioning of NO_x sources using satellite observations: Relative roles of fossil fuel combustion, biomass burning and soil emissions. Faraday Discussions 130, 407–423.

Jaffe, D.A., Anderson, T., Covert, D., Kotchenruther, R., Trost, B., Danielson, J., Simpson, W., Berntsen, T., Karlsdottir, S., Blake, D., Harris, J., Carmichael, G., Uno, I., 1999. Transport of Asian air pollution to North America. Geophysical Research Letters 26, 711–714.

Jaffe, D.A., Parrish, D., Goldstein, A., Price, H., Harris, J., 2003. Increasing background ozone during spring on the west coast of North America. Geophysical Research Letters 30 (12), 1613.

Jaffe, D., Bertschi, I., Jaeglé, L., Novelli, P., Reid, J.S., Tanimoto, H., Vingarzan, R., Westphal, D.L., 2004. Long-range transport of Siberian biomass burning emissions and impact on surface ozone in western North America. Geophysical Research Letters 31, L16106.

Johnson, B.J., Oltmans, S.J., Vömel, H., Smit, H.G.J., Deshler, T., Kröger, C., 2002. Electrochemical concentration cell

(ECC) ozonesonde pump efficiency measurements and tests on the sensitivity to ozone of buffered and unbuffered ECC sensor cathode solutions. Journal of Geophysical Research 107 (D19), 4393.

Kotchenruther, R.A., Jaffe, D.A., Jaeglé, L., 2001. Ozone photochemistry and the role of PAN in the springtime northeastern Pacific troposphere: Results from the PHOBEA campaign, J. Geophysical Research 106, 28,731–28,741.

Lee, S.-H., Akimoto, H., Nakane, H., Kurnosenko, S., Kinjo, Y., 1998. Lower tropospheric ozone trend observed in 1989–1997 at Okinawa, Japan. Geophysical Research Letters 25, 1637–1640.

Lin, C., Jacob, D.J., Munger, W., Fiore, A., 2000. Increasing background ozone in surface air over the United States. Geophysical Research Letters 27, 3465–3468.

Lin, C., Jacob, D.J., Fiore, A.M., 2001. Trends in exceedances of the ozone air quality standard in the continental United States, 1980–1998. Atmospheric Environment 35, 3217–3228.

Liu, S.C., Trainer, M., Fehsenfeld, F.C., Parrish, D.D., Williams, E.J., Fahey, D.W., Hubler, G., Murphy, P.C., 1987. Ozone production in the rural troposphere and the implications for regional and global ozone distributions. Journal of Geophysical Research 92, 4191–4207.

Logan, J.A., et al., 1999. Trends in the vertical distribution of ozone: a comparison of two analyses of ozonesonde data. Journal of Geophysical Research 104, 26,373–26,399.

Naja, M., Akimoto, H., 2004. Contribution of regional pollution and long-range transport to the Asia-Pacific region: analysis of long-term ozonesonde data over Japan. Journal of Geophysical Research 109, D21306.

National Park Service, 2002. Air Quality in the National Parks, second ed. NPS Air Quality Division, Denver, CO.

National Park Service, 2006a. 2005 Annual data Summary, Air Resources Division, available at 〈http://www2.nature.nps.gov/air/Monitoring/network.cfm〉.

National Park Service, 2006b. 2005 Government Performance and Results Act Report, Air Resources Division, available at 〈http://www2.nature.nps.gov/air/who/npsPerfMeasures.cfm〉.

National Research Council (NRC), 1991. Rethinking the Ozone Problem in Urban and Regional Air Pollution. National Academy Press, Washington, DC.

Newchurch, M.J., Ayoub, M.A., Oltmans, S., Johnson, B., Schmidlin, F.J., 2003. Vertical distribution of ozone at four sites in the United States. Journal of Geophysical Research 108 (D1), 4031.

Oltmans, S.J., et al., 1998. Trends of ozone in the troposphere. Geophysical Research Letters 25, 139–142.

Oltmans, S.J., et al., 2006. Long-term changes in tropospheric ozone. Atmospheric Environment 40 (17), 3156–3173.

Parrish, D.D., 2006. Critical evaluation of US on-road vehicle emission inventories. Atmospheric Environment 40, 2288–2300.

Parrish, D.D., Dunlea, E., Atlas, E., Schauffler, S., Donnelly, S., Stroud, V., Goldstein, A., Millet, D., McKay, M., Jaffe, D., Price, H., Hess, P., Flocke, F., Roberts, J., 2004. Changes in the photochemical environment of the temperate North Pacific troposphere in response to increased Asian emissions. Journal of Geophysical Research 109, D23S18.

Richter, A., Burrows, J.P., Nüß, H., Granier, C., Neimeier, U., 2005. Increase in tropospheric nitrogen dioxide over China observed from space. Nature 427, 129–132.

Simmonds, P.G., Derwent, R.G., Manning, A.L., Spain, G., 2004. Significant growth in surface ozone at Mace Head, Ireland, 1987–2003. Atmospheric Environment 28, 4769–4778.

Streets, D.G., Tsai, N.Y., Akimoto, H., Oka, K., 2001. Trends in emissions of acidifying species in Asia, 1985–1997. Water, Air, and Soil Pollution 130 (Part 2), 187–192.

US EPA, 2003. Latest Findings on National Air Quality: 2002 Status and Trends Report. 454/K-03-001. EPA-OAQPS, Research Triangle Park, NC.

US EPA, 2004. The Ozone Report: Measuring Progress through 2003. EPA 454/K-04-001, Research Triangle Park, NC.

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

Vingarzan, R., Taylor, B., 2003. Trend analysis of ground level ozone in the greater Vancouver/Fraser Valley area of British Columbia. Atmospheric Environment 37, 2159–2171.

Weatherhead, E.C., Reinsel, G.C., Tiao, G.C., Meng, X.L., Choi, D., Cheang, W.K., Keller, T., DeLuisi, J., Wuebbles, D.J., Kerr, J.B., Miller, A.J., Oltmans, S.J., Frederick, J.E., 1998. Factors affecting the detection of trends: statistical considerations and applications to environmental data. Journal of Geophysical Research 103 (D14), 17,149–17,161.

Westerling, A.L., Hidalgo, H.G., Cayan, D.R., Swetnam, T.W., 2006. Warming and earlier spring increase western US forest wildfire activity. Science 313 (5789), 940–943.

Wheelwright, S.C., Makridakis, S., 1985. Forecasting Methods for Management. Wiley, New York.

Ziemke, J.R., Chandra, S., Bhartia, P.K., 2005. A 25-year data record of atmospheric ozone in the Pacific from total ozone mapping spectrometer (TOMS) cloud slicing: implications for ozone trends in the stratosphere and troposphere. Journal of Geophysical Research 110, D15105.