INFLUENCE OF INTER-CONTINENTAL TRANSPORT ON BACKGROUND 0_3 AND PM CONCENTRATIONS IN THE UNITED STATES

Final Report – Phase 1
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Influence of Inter-Continental Transport on Background O_3 and PM Concentrations in the United States

Introduction

Numerous scientific publications have indicated that inter-continental transport of pollutants can influence background air quality in the U.S. As a result, the CRC contracted with Dr. Daniel Jaffe to investigate the spatial and seasonal patterns and long-term trends for O_3 and PM at background monitoring sites in the U.S. This project began on Sept. 1, 2004 and is expected to last 2 years.

This report consists of four parts:

1. Discussion of available emission inventories for the western U.S.
2. Draft journal article, "Increase in Surface Ozone at Rural Sites in the Western U.S." by Dan Jaffe and James Dennison for submission to *Environmental Science and Technology.* This article should be ready for submission following completion of a few additional statistical analyses.
3. Trend in $PM_{2.5}$ concentrations at 6 background parks in the western U.S.
4. Outstanding scientific questions and focus of year 2.

Part 1: Trends in NO_x and VOC Emissions in the Western U.S.

Emission inventories provide information on sources. However, due to changes in emission calculations it can be tricky to determine trends in emissions over multiple years, unless the inventories are generated in a consistent manner. In this regard, there are two emission inventories that can help us determine emission trends in the western U.S.; one inventory is from the U.S. EPA and the other is from the Western Regional Air Partnership (WRAP). The EPA data (described below) are from the EPA AIRS emission database and from a recent trends report. WRAP data are from the report "Development of WRAP Mobile Source Emission Inventories" (ENVIRON 2004) and covers 13 western states. The WRAP report gives mobile emission (on and off highway sources) for a base year (1996) and projects emissions in 2003, 2008, 2013 and 2018, based on state data provided in the 2002-2003 timeframe. The graph below shows the EPA and WRAP emission data from these sources.

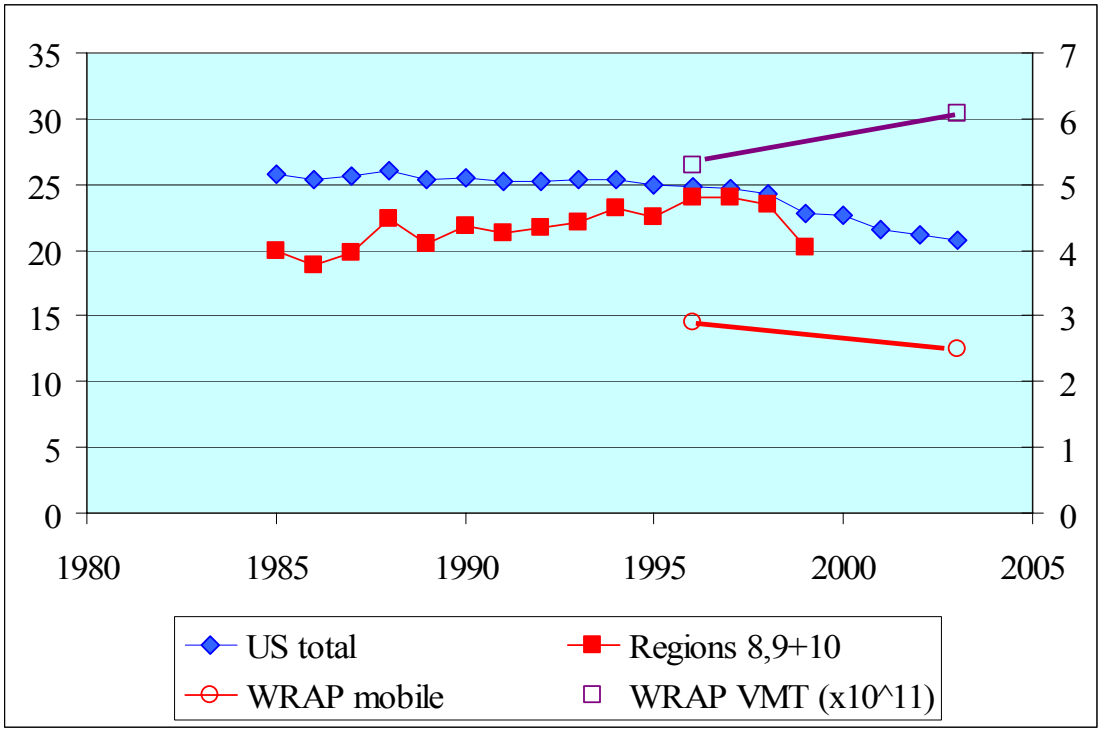

Figure 1. US total NO_x emissions in million tons (solid blue diamonds-left axis), EPA Regions 8,9, and 10 NO_x emissions in million tons (solid red squares-right axis), WRAP mobile sources in million tons for 1996 and 2003 (red circles-right axis) and WRAP annual VMT ($x10^{11}$) for 1996 and 2003 (purple squares-right axis).

As of August 2005, EPA has not released state by state emission data for years 2000 and on. I spoke with Carey Jang at EPA-OAQPS about this and he said that EPA is planning to release this data in late 2005. However in 2004 EPA presented the emission data by region, but only in graphical form. Below is a graph of the VOC and NO_x emission data by region from the EPA report, "The Ozone Report: Measuring Progress Through 2003" (April 2004).

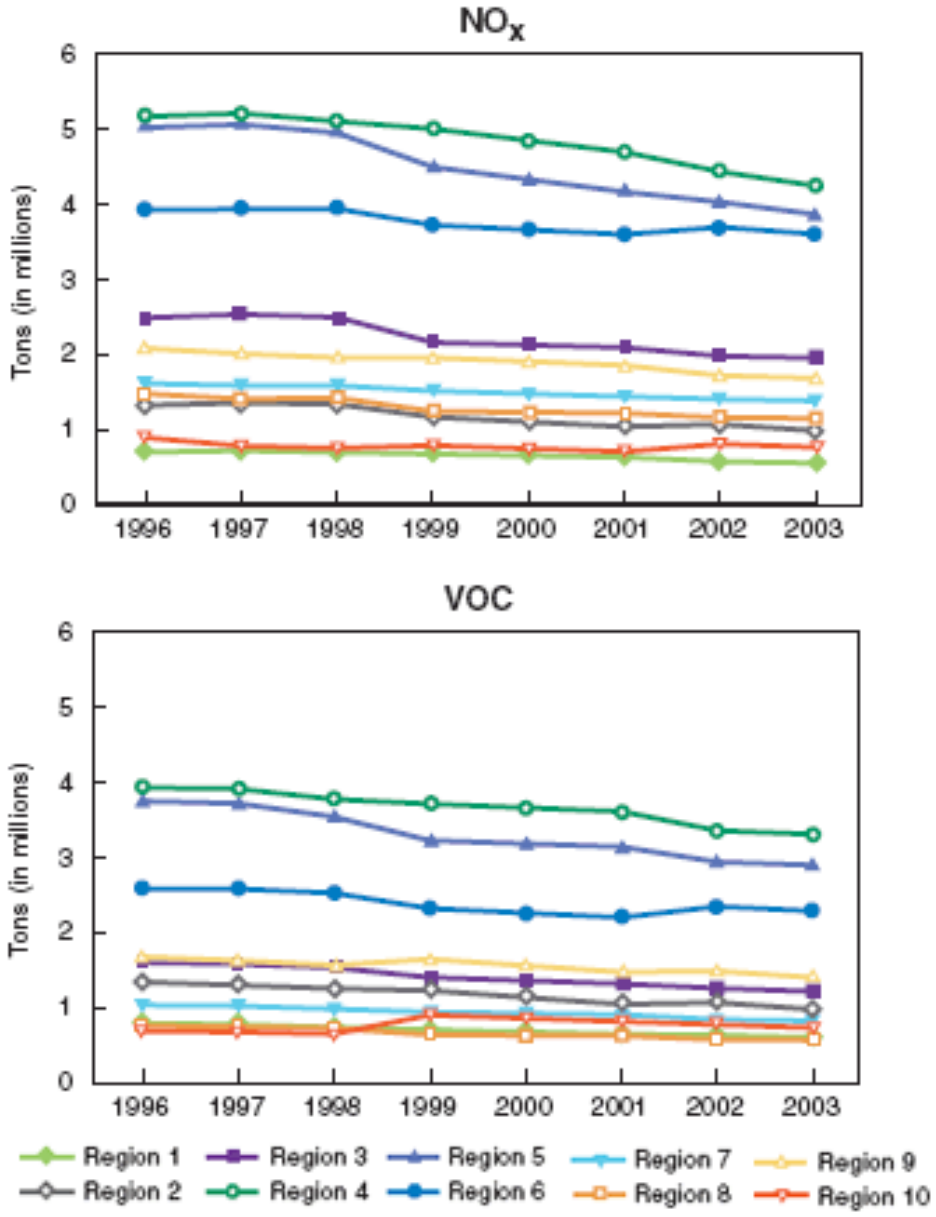

Figure 2. NO_x and VOC emissions by EPA region [US EPA 2004]. Note that the increase in Region 10 VOC emissions between 1998-1999 reflects a change in methodology, not a real change in emissions.

From Figure 2, it seems that all EPA regions have decreased emissions between 1996 and 2003. On the other hand, it is certainly true that there has been a substantial increase in population, development and vehicle miles traveled. Figure 1 shows a 15% increase in annual VMT for the 13 WRAP states between 1996 and 2003. The decrease in emissions reflects a significant decline in emission factors, both for mobile as well as stationary sources. However, it should be kept in mind

that emission inventories are complex and reflect a wide array of source types. Changes in procedures, our understanding of real-world emission factors and other problems can introduce significant uncertainties.

Finally, it is useful to see if all states in the western regions have decreased their emissions similarly. While at present, EPA has not released the complete inventory (mobile + stationary) by state to rigorously evaluate this, we can look at the mobile sources by state, based on the WRAP inventory. For the US as a whole, the EPA reports a decline in NO_x emissions of 16% between 1996 and 2003. The WRAP mobile inventory reports a decline of 14% in NO_x emissions for the same time period. Table 1 shows the state-by-state changes in mobile sources from the WRAP inventory.

State	1996	2003	% change
AZ	566.10	496.00	-12.38
CA	3181.10	2545.00	-20.00
CO	622.30	525.00	-15.64
ID	200.50	186.00	-7.23
MT	261.40	250.00	-4.36
NV	229.20	287.00	25.22
NM	246.80	211.00	-14.51
ND	247.60	239.00	-3.47
OR	725.00	681.00	-6.07
SD	181.90	160.00	-12.04
UT	355.70	331.00	-6.94
WA	913.80	729.00	-20.22
WY	196.30	214.00	9.02
Total	**7927.70**	**6854.00**	**-13.54**

Table 1. Total NO_x mobile emissions (on and off-road vehicles) from the WRAP inventory. Values are in tons/day.

Within the 13 state WRAP region, all states show a decline in emissions except for Nevada and Wyoming. In these two states, the increase is a result of significant increases in "off-road" emissions from diesel vehicles (ENVIRON 2004).

References for the emission inventories:

U.S. EPA AIRData (http://www.epa.gov/air/data/index.html)

U.S. EPA. (2004), The Ozone Report: Measuring Progress Through 2003. EPA 454/K-04-001, Research Triangle Park, NC, April 2004. (Available at: http://www.epa.gov/air/airtrends/)

ENVIRON International Corp. Development of WRAP Mobile Source Emission Inventories, Novato Calif., Feb 2004. (Available at: http://www.wrapair.org/forums/ef/inventories/mobile/040209Final_MSEI.pdf)

Part 2: Analysis of Ozone Trends in the Western U.S.

Draft journal article on increasing O_3 in the western U.S.

Increase in Surface Ozone at Rural Sites in the Western U.S.

By Dan Jaffe and James Dennison

0. Abstract
1. Introduction
2. Experimental/data sources
3. Results/Statistical analysis
   - 3.1 Analysis of trends using multiple statistical tools (de-seasonalized monthly means 10 sites and analysis using t-test adjusted for seasonality)
   - 3.2 Analysis of seasonal trends (4 sites)
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4. Interpretation/discussion
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0. Abstract

We evaluated O_3 data from 12 relatively unpolluted sites in the north and western U.S., including 2 sites in Alaska, for the period 1987-2004. At the 2 sites in Alaska, no trend was present.

At 9 out of 10 sites in the continental U.S., there is a statistically significant increase in O_3 with a mean trend of 0.35 ppbv/year (range 0-0.70 ppbv/year). At 4 of these sites, we examined the data in more detail to find that the trends are statistically significant in all seasons and are somewhat stronger at night. Temperature changes can explain only a small fraction of the surface O_3 trend. The change in O_3 at these sites has occurred both at the high and low end of the frequency distributions.

Over the same time period, anthropogenic NO_x and VOC emissions in the western U.S. peaked in the 1990s and have fallen by approximately 15% since then, based on two separate emission inventories. Thus, increasing regional NO_x and VOC emissions do not appear to explain the positive O_3 trend. We hypothesize that changes in regional photochemistry and/or increasing global background O_3 are responsible for these trends.

While most sites we examined were relatively free from nearby human influence, at two sites, Rocky Mountain National Park (RMNP) in Colorado and Lassen Volcanic National Park (LVNP) in California, there are some days with 8-hour averages in excess of the 0.08 ppmv level. These occur when regional photochemical pollution is transported to the sites. At RMNP, most of these days have occurred since 1998. While the primary cause is regional pollution, it is likely that the trend in regional or global background O_3 is contributing to the increasing frequency of days in excess of the 0.08 ppmv level.

1. Introduction

EPA inventories indicate significant declines in NO_x and VOC emissions over the recent past (EPA 2004). Nationally, VOC emissions peaked in the 1970s and have declined by 54% since then. NO_x emissions peaked later, in 1993, and have declined 18% since then. According to the EPA inventories, the declines have occurred in all EPA regions (EPA 2004). A mobile source inventory for 1996 and 2003 is available for 13 western states (AZ, CA, CO, ID, MT, NV, NM, ND, OR, SD, UT, WA and WY) from the Western Regional Air Partnership (ENVIRON 2004). This inventory indicates a decline in NO_x emissions of 14% from mobile sources, including both on and off-road vehicles. Within the 13-state region, mobile NO_x emissions have declined in all but 2 states, Nevada and Wyoming. These declines have occurred despite significant increases in population and a 15% increase in annual vehicle miles traveled (VMT) (ENVIRON 2004).

As a result of the reductions in emissions of precursors, peak O_3 concentrations have declined in many regions of the U.S. The U.S. EPA (2004) reports a decline in exceedances of the

O_3 standard in all regions of the country. The decline in the number of sites in excess of the 1-hour standard (annual second highest value no greater then 0.12 ppmv), has been larger then the decline in the number of sites in excess of the 8-hour standard, (annual fourth highest value no greater then 0.08 ppmv). While these conclusions are based on a large number of O_3 monitoring sites, these are largely located in urban/suburban areas. Much less is known about O_3 concentrations in rural/remote parts of the U.S. In the western U.S., some regions report a discrepancy between the trends in the 1-hour and 8-hour peak values. For example, the state of Colorado has reported (Colorado DPHE, 2004) that the annual second highest 1-hour concentration has declined over the past two decades, whereas the fourth highest 8-hour concentration has increased.

The National Park Service (NPS) also monitors O_3 concentrations (NPS 2002; 2005). Generally, these rural/remote National Park sites have shown fewer declines in peak O_3 concentrations over time, compared with the urban/suburban sites. At many parks, especially in the western U.S., there has been a positive trend in the annual, fourth-highest 8-hour mean O_3 concentration over the past decade (NPS 2002; 2005). The goal of our study is to understand why these rural and remote sites show O_3 trends that differ from the national pattern, as reported by the EPA (EPA 2004).

Besides regional emissions, other factors can influence surface O_3. Changes in surface O_3 could be due to changes in global background O_3 (Lin et al., 2000; Jacob et al., 1999; Berntsen et al., 1999; Fiore et al., 2002), forest fires (e.g., Jaffe et al., 2004) and/or climate (e.g., Lin et al,. 2000; Fiore et al., 2005). An increase in anthropogenic nitrogen oxides and non-methane hydrocarbons (NMHCs) has caused substantial increases in global tropospheric O_3 over the past century (Volz and Kley, 1988; Marenco et al., 1994). In Asia the growth in emissions began in the latter part of the 20th century. Since 1980, NO_x emissions in East Asia have grown by approximately 4%-6% per year (Akimoto and Narita, 1994; Streets et al., 2001). The increase in NO_x emission is largest in China and appears to have continued steadily through at least 1997 (Streets et al., 2001). This increase will likely continue in the 21st century (IPCC 2001). 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).

Because tropospheric O_3 plays a key role in global atmospheric chemistry, and because of its health, vegetation and climate impacts, possible trends in tropospheric O_3 have been examined by numerous researchers. At three Japanese sites, Kagoshima, Tsukuba and Sapporo, ozonesonde data since 1969 have shown significant positive trends of 1.5-2.5%/year in the lower troposphere up to

about 1990. In the past decade the reported trend, while still generally positive, has slowed (Oltmans et al., 1998; Logan et al., 1999). A more 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, surface emissions of NO_x, changing climate and UV radiation (Fusco and Logan 2003).

Evaluation of data at Okinawa from 1989-1997 indicates an O_3 increase of 2.5%/year 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 for the period of 1984-1999, which was attributed to increased emissions from China. In Europe, background O_3 appears to have risen substantially in the past two decades and in all seasons (Simmonds et al., 2004). This is based on analysis of data from Mace Head, Ireland, which has seen an increase of about 0.5 ppbv/year in all seasons. 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 airmasses (Jaffe et al., 2003). Similarly, in Canada, a positive trend was seen at rural sites in the Province of British Columbia (Vingarzan and Taylor 2003; Vingarzan and Thompson 2004). Lin et al. (2000), examined O_3 trends using the database of EPA monitoring sites in the U. S. 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; Jacob et al., 1999; Berntsen et al., 1999; Fiore et al., 2002).

If global background O_3 is increasing, then we would expect this change to be most evident at clean sites in the western U.S. Nonetheless, sites that receive significant regional pollution, such as in the east, southeast or southwestern U.S., 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 relatively clean monitoring sites throughout western North America. This will extend our earlier work, which analyzed only one site along the west coast of the U.S. (Jaffe et al., 2003).

2. Experimental/data sources

For this analysis, we wish to examine O_3 records in remote locations, which are relatively unaffected by nearby pollution sources. We considered only sites with at least 15 years of data and sites that have no major gaps in the data record. However, we have also included two sites with only 12 years of data. Finally, we have restricted our analysis, generally, to sites in the western U.S. and Alaska which are least affected by continental U.S. sources.

Data for this analysis have come from several different sources. Surface O_3 data are collected at many National Parks in the U.S.; however, at most of these sites, the data record is relatively short. We have identified 8 National Parks with adequate data records. We have also used data from 3 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 10 sites in the continental U.S. and 2 sites in Alaska. Tables 1 and 2 give information on each site. Two sites, Rocky Mountain National Park and Lassen National Park, are adjacent to major population centers Denver and Sacramento, respectively. The Denver-Boulder-Greeley Consolidated Metropolitan Statistical Area (CMSA) has a population greater then 2.4 million and the Sacramento-Yolo MSA has a population of approximately 1.7 million, based on 1999 census data (most recent CMSA data). These sites are the only locations included in our analysis that have had 8-hour average concentrations greater then 84 ppbv (see Table 1).

At all surface sites O_3 has been measured using UV absorption and has followed consistent calibration procedures based on U.S. 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 periods were identified based on constant O_3 concentrations at either very high or very low levels for 6 or more hours in a row. For Barrow, the data were obtained as monthly means. The hourly averages have an uncertainty of less then 4%.

Detection of trends in geophysical data is complicated by a number of factors, including natural variability and changes in site or operator characteristics. 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 will use a combination of ordinary least squares (OLS) analysis, OLS on

deseasonalized monthly means, t-tests adjusted for seasonality and a multiple regression model which incorporates the trend and temperature. Data at each site were deseasonalized by subtracting out the difference between the monthly mean for all years and the annual mean. Statistical analyses were conducted using SPSS software (Chicago, IL) versions 12 and 13.

Table 1. Sites used in O_3 trends analysis.

Location	Lat.(^{o}N)/Long.(^{o}W)/elevation (meters)	Data record (mm/yy)	# days with 8-hour mean >0.08 ppmv
Lassen N.P., California	40.54/121.58/1756	10/87-8/04	6
Rocky Mtn. N.P., Colorado	40.28/105.55/2743	1/87-11/04	19
Voyageurs N.P., Minnesota	48.41/92.83/429	4/87-8/04	0
Yellowstone N.P., Wyoming	44.56/110.40/2400	4/87-8/04	0
Glacier N.P., Montana	48.51/114.00/976	4/89-10/04	0
Denali N.P., Alaska	63.73/148.96/661	7/87-11/04	0
Barrow, Alaska	71.32/156.60/11	3/73-12/03	0
Pinedale, Wyoming	42.93/109.79/2388	1/89-12/03	0
Gothic, Colorado	38.96/106.99/2926	7/89-12/03	0
Centennial, Wyoming	41.36/106.24/3178	7/89-12/03	0
Craters of the Moon, Idaho	43.46/113.56/1815	10/92-12/04	0
Canyonlands N.P., Utah	38.46/109.82/1809	8/92-12/04	0

Table 2. Additional information about each site

Location	Site type	Changes in O_3 measurements over this time frame?	Nearest population centers (City name/distance/population)
Lassen N.P., CA	NPS	No site changes	Redding, CA- 61 km -80,865 Sacramento, CA – 204 km – 407,018
Rocky Mtn. N.P., CO	NPS	Site relocated <1 km NW in 1996	Longmont, CO 35 km - 71,093 Denver, CO 87 km- 554,636
Voyageurs N.P., MN	NPS	Site relocated 32 km SE in 1996	International Falls, MN 45 km – 6,703 Duluth, MN 140 km – 98,000
Yellowstone N.P., WY	NPS	Site relocated <1km NW in 1996	Yellowstone, WY 59 km - 1,177 Jackson, WY 109 km - 8,647
Glacier N.P., MT	NPS	No site changes	Columbia Falls, MT 19 km - 3,645 Kalispell, MT 29 km - 14,223
Denali N.P., AK	NPS	No site changes	Fairbanks, AK 180 km - 30,224 Anchorage, AK 220 km – 260,283
Barrow, AK	NOAA/CMDL	No site changes	Barrow, AK 0 km - 4,581
Pinedale, WY	CASTNET	No site changes	Pinedale, WY 0 km - 1,412 Jackson, WY 98 km - 8,647
Gothic, CO	CASTNET	No site changes	Crested Butte, CO 10 km - 1,529 Gunnison, CO 51 km - 5,409
Centennial, WY	CASTNET	No site changes	Laramie, WY 42 km - 27,204 Boulder, CO 163 km - 94,673
Craters of the Moon, Idaho	NPS	No site changes	Pocatello, ID 100 km – 50,723 Twin Falls, ID 120 km – 37,619
Canyonlands N.P., Utah	NPS	No site changes	Moab, UT 40 km - 4825 Grand Junction, CO 130 km – 44,693

3. Results

3.1 Basic statistical analysis

Hourly averages were converted into monthly averages and the seasonal component was removed from the monthly means. OLS analysis was then conducted on the deseasonalized monthly means. 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 section 3.2, we show that assumption is justified.

Figures 1a-d show the deseasonalized monthly means for 4 of the sites, Lassen, Rocky Mountain, Voyageurs and Yellowstone National Parks with an OLS regression line. Table 3 gives the statistical information for all 12 sites.

Figure 1a: Deseasonalized monthly means, Lassen Volcanic National Park.

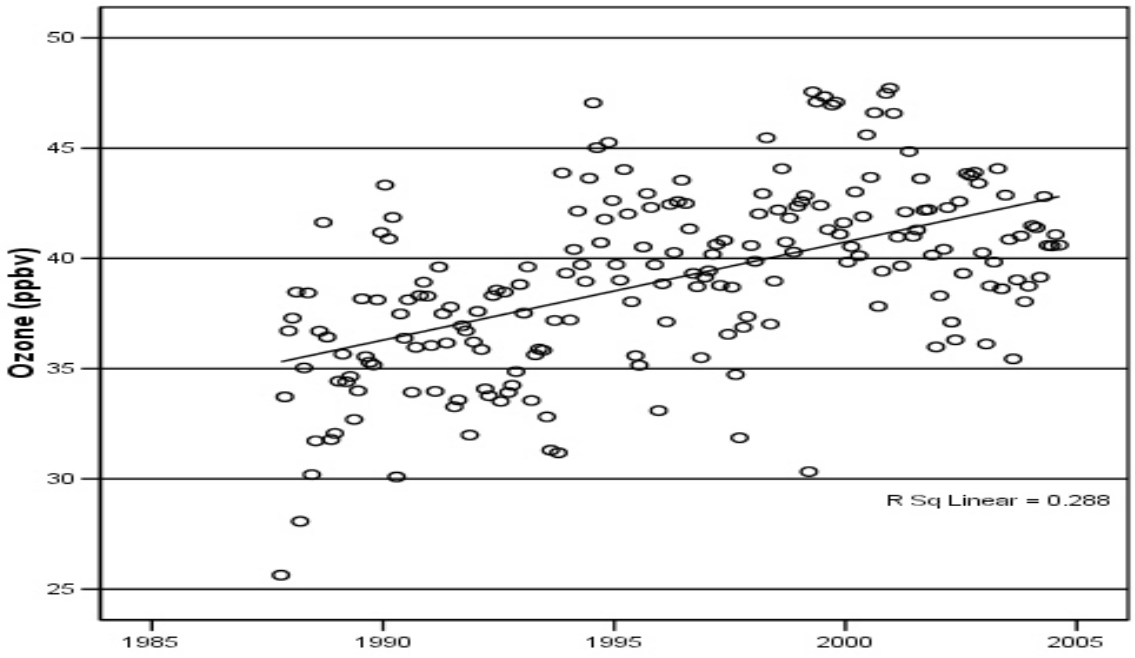


Figure 1b: Deseasonalized monthly means, Rocky Mountain National Park.

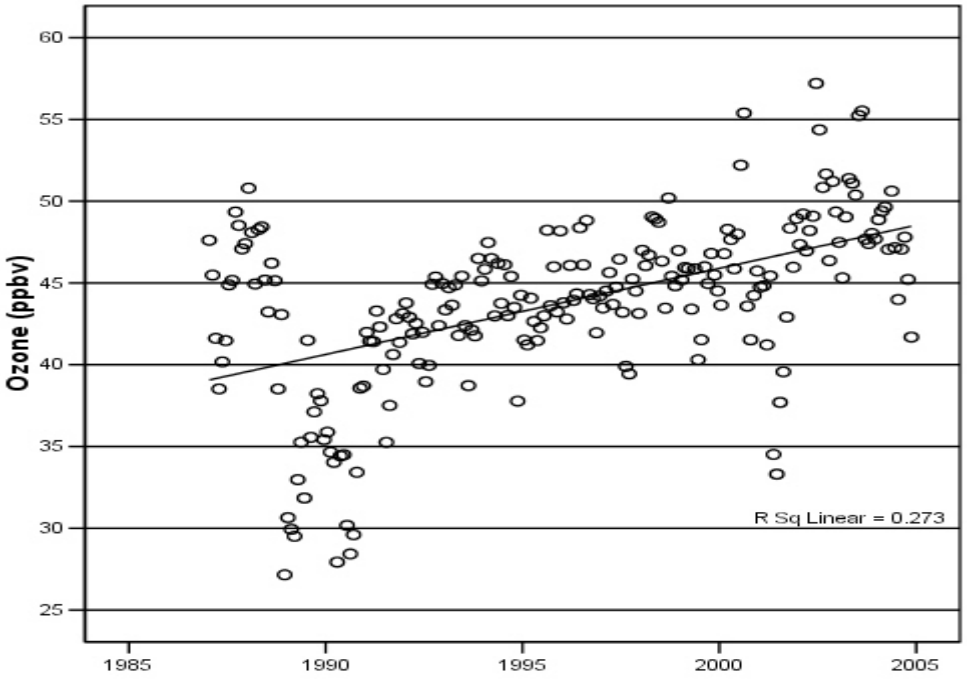


Figure 1c: Deseasonalized monthly means, Voyageurs National Park.

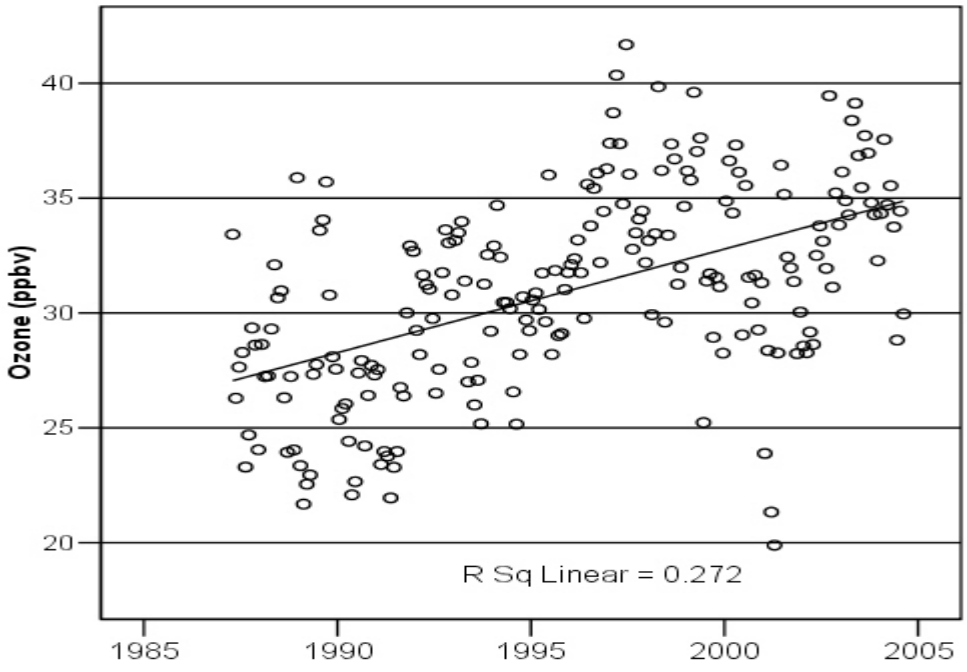


Figure 1d: Deseasonalized monthly means, Yellowstone National Park.

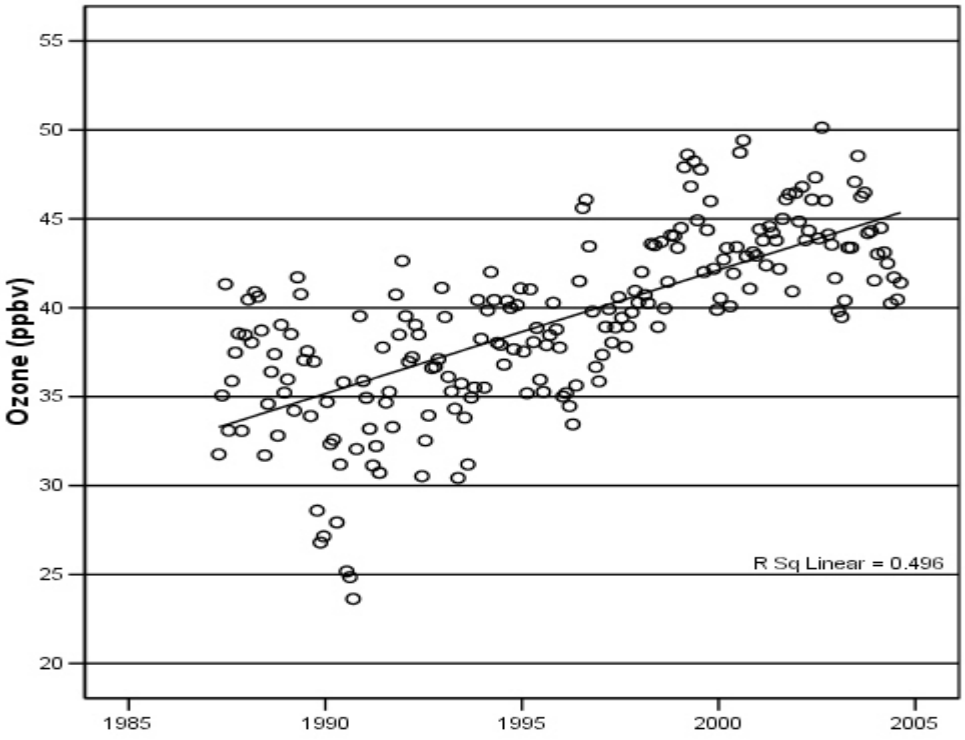


Table 3. Trend analysis on deseasonalized monthly mean O_3 concentrations.

Site	Slope (ppbv/year)	R^2	P value
Lassen	0.45	0.29	<0.01
Rocky Mtn.	0.53	0.27	<0.01
Voyageurs	0.45	0.27	<0.01
Yellowstone	0.70	0.50	<0.01
Glacier	0.00	0.01	0.68
Denali	0.07	0.01	0.10
Barrow	0.00	0.00	0.19
Pinedale	0.14	0.05	<0.01
Gothic	0.23	0.12	<0.01
Centennial	0.48	0.41	<0.01
Craters of the Moon	0.19	0.04	0.02
Canyonlands	0.26	0.11	<0.01

At the two sites in Alaska, no significant trend was identified. Of the 10 sites in the continental U.S., 9 have a statistically significant positive trend ($P<0.02$). For these 10 sites, the trends range from 0.0-0.70 ppbv/year, with a mean trend of 0.35 ppbv/year. For the 18 year period between 1987-2004, this corresponds to an average O_3 increase of 6 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 significant trend of 0.5 ppbv/year, which was present in both the continental and marine airmasses arriving at the Lassen monitoring site.

Following the recommendations of Hess et al. (2001), we also examined the data record using a t-test adjusted for seasonality. In this approach, we compared the deseasonalized monthly means for the first and second halves of the data record. This analysis was done for the 9 sites with statistically significant trends listed in Table 3. The results from 4 stations are shown in Table 4.

Table 4: Mean O_3 mixing ratio for the first and second half of each data record, based on deseasonalized monthly means. All differences are significant (P<0.01). Also shown are the 10, 50 and 90th percentile for each dataset based on hourly averages.

Site	Mean value (ppbv)	10/50/90th Percentile (ppbv)
Lassen-1st half	37.1	24/36/51
Lassen-2nd half	41.0	28/40/45
Rocky Mtn. -1st half	41.2	27/41/54
Rocky Mtn. -2nd half	46.3	32/46/59
Voyageurs-1st half	28.6	15/27/42
Voyageurs-2nd half	33.3	19/32/47
Yellowstone-1st half	36.0	21/35/48
Yellowstone-2nd half	42.6	32/42/54

In all cases, the t-tests adjusted for seasonality support the trend analyses previously shown in Table 3. The O_3 changes, shown in Table 4 (4-6 ppbv), are about half of the overall change in O_3 mixing ratios from the beginning of the data record (1987) to the end (2004). At Yellowstone Park, the O_3 changes are much stronger at the low end of the ozone distributions; however, the other parks do not show this effect.

To better understand the cause of this long-term trend, we evaluated the data from these 4 sites in greater detail: Lassen, Rocky Mtn., Voyageurs and Yellowstone National Parks.

3.2 Analysis of seasonal trends (4 sites)

Seasonal trends were evaluated for 4 parks (Lassen, Rocky Mtn., Voyageurs and Yellowstone) and reported in Table 5. Hourly data were averaged into a single seasonal mean value. Winter included the months of December, January and February, and other seasons were defined accordingly. Data from December was included with the January and February data from the next year.

Table 5. Trend in O_3 concentrations by season for 4 parks.

Lassen	**Slope (ppbv/year)**	**R^2**	**P value**
Winter	0.29	0.30	0.02
Spring	0.49	0.54	<0.01
Summer	0.54	0.45	<0.01
Fall	0.59	0.51	<0.01
Rocky Mtn.			
Winter	0.56	0.36	0.01
Spring	0.65	0.41	<0.01
Summer	0.60	0.29	0.02
Fall	0.36	0.28	0.02
Voyageurs			
Winter	0.46	0.39	<0.01
Spring	0.48	0.26	0.03
Summer	0.52	0.50	<0.01
Fall	0.43	0.54	<0.01
Yellowstone			
Winter	0.59	0.59	<0.01
Spring	0.60	0.41	<0.01
Summer	0.88	0.66	<0.01
Fall	0.78	0.82	<0.01

All of the trends shown in Table 5 are statistically significant at 95% confidence and most are significant at the 99% confidence level. The slopes do not exhibit any obvious pattern.

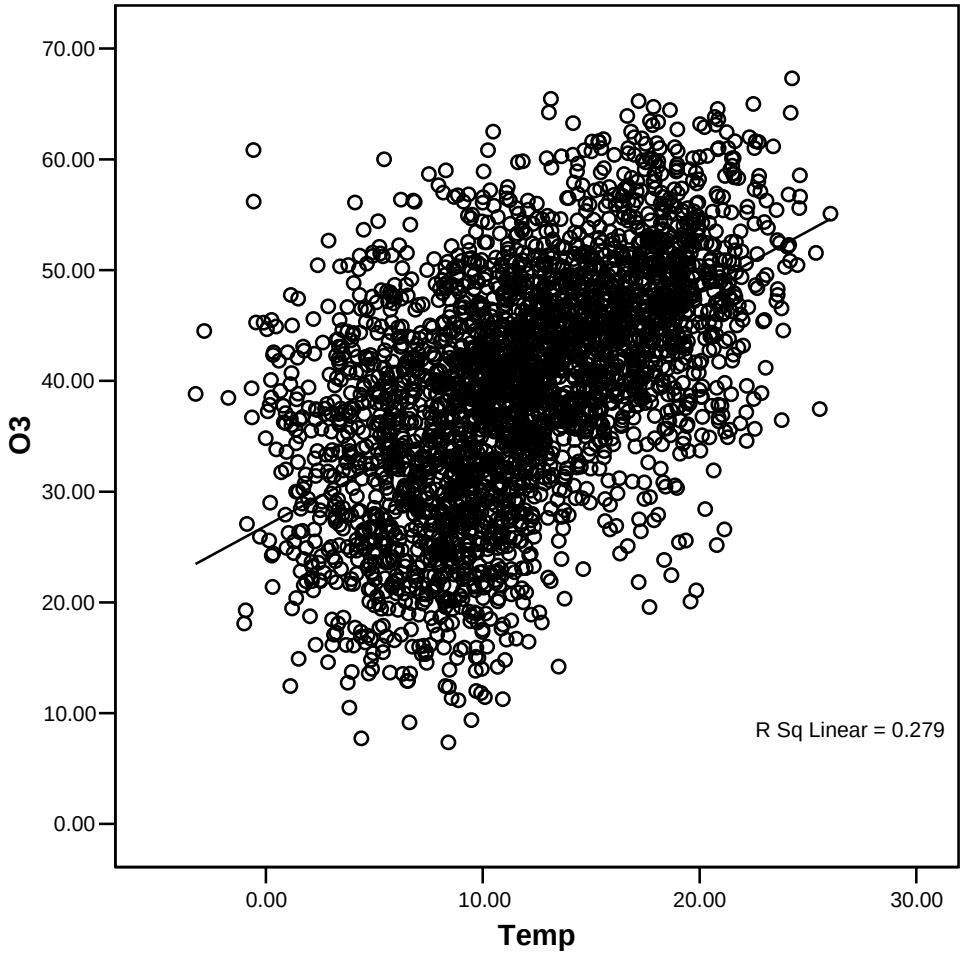
3.3 Influence of temperature on trend analysis (4 sites)

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.) (NRC 1991; Lin et al., 2001). It is possible, that due to increasing temperature, O_3

production has been enhanced regionally. To investigate whether temperature changes could explain some or all of the O_3 increase we have seen, we have examined temperature data at each site over the same time period as the O_3 data.

Using 12 hour mean summer data, we can examine the relationship between O_3 concentrations and temperature. Figure 2 below shows this relationship for Yellowstone.

Figure 2. Plot of 12 hour mean O_3 mixing ratios (ppbv) vs temperatures (^oC) for summer data at Yellowstone N.P. (1987-2004 data). The equation for the linear regression line is O_3 = Temperature(^oC) * 1.064 + 26.91 and the R^2 value is 0.28.



The table below shows the linear regression fit for similar data at each park.

Table 6. O_3 vs Temperature relationship using 12-hour mean data at each Park (summer data only). All correlations are statistically significant (P<0.01).

Site	Slope (ppbv/^{o}C)	Intercept (ppbv)	R^2
Lassen	1.21	24.72	0.32
Rocky Mtn.	1.45	28.05	0.27
Voyageurs	1.36	5.60	0.29
Yellowstone	1.06	26.91	0.28

This indicates that for each 1^{o}C increase in 12-hour mean temperature, we can expect a 1 ppbv increase in 12-hour mean O_3. During the winter months, there is no clear relationship between temperature and O_3. We have also examined these relationships using 8-hour day/night means and 8-hour daily maximums and have found the correlations and slopes to be similar.

Inclusion of temperature into regression model

Because of the role that temperature plays, some researchers have chosen to apply a meteorological adjustment to the observed O_3 concentrations (see for example U.S. EPA 2004). In this approach, the observed O_3 values are adjusted up or down by an amount which depends on the observed temperature. Occasionally, additional meteorological variables are used as well, although temperature has generally been found to be the most important. In our analysis, we will use the observations to quantify the influence of temperature on the actual O_3 concentrations using a multiple regression model. This is functionally the same as the meteorological adjustment, but we prefer this direct method as it provides a better accounting of the factors responsible for the observed O_3 concentrations, without changing the values. Our method is essentially identical to the "meteorological adjustment" approach.

To do this, we start with a linear expression for O_3 concentration as a function of several factors:

Observed O_3 = seasonal factor + temperature factor + trend + residual

To quantify each component in this expression, we first calculate the departure from the monthly mean temperatures. 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:

$$\delta O_3 = A_1 * \Delta temp + A_2 * time + residual$$

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, and the final results are identical.

We did this 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 colder months. Table 7 shows the results for the warm season months. For comparison, Table 3 shows the trend analysis without including temperature.

Table 7. Two variable regression model (temperature and year) as predictors for the deseasonalized monthly mean O_3 for the months of May-September. The correlations are statistically significant (P<0.01). The P values for the independent variables (temperature and time) are given in parentheses.

Site	Temperature coefficient-A_1 (ppbv/^{o}C)	Trend coefficient-A_2 (ppbv/year)	R^2
Lassen	0.61 (0.02)	0.41 (<0.01)	0.34
Rocky Mtn.	1.1 (<0.01)	0.48 (<0.01)	0.33
Voyageurs	1.0 (<0.01)	0.55 (<0.01)	0.51
Yellowstone	0.31 (0.20)	0.76 (<0.01)	0.54

In all cases, inclusion of temperature improved the model fit, compared to the model without temperature. These results show that for summer months with above average temperature, O_3 will also be above average, with a coefficient ranging from 0.31 to 1.1 ppbv/^{o}C. However, inclusion of temperature in the regression model does not significantly change the interpretation or magnitude of

the trend component. For example for Yellowstone, the May-September trend using the multiple variable regression model is 0.76 ppbv/year, compared to a trend of 0.70 ppbv/year for the whole year or 0.88 ppbv/year for the summer only. The R^2 is improved in the multiple regression model which includes temperature as a predictor, compared to the model without temperature.

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 Day/night trends (4 sites)

Whether the observed O_3 trend is stronger in the daytime vs nighttime data can give us important clues as to the cause of the trend. A stronger trend during the day would suggest a regional photochemical source, whereas a stronger trend at night would suggest another cause. Table 8 below shows the trend for each site, separated into a day and night component.

Table 8. Ozone trends calculated on day/night deseasonalized monthly means. All trends are statistically significant (P<0.01).

Site	Slope (ppbv/year)	R^2
Lassen-day	0.33	0.17
Lassen-night	0.50	0.32
Yellowstone-day	0.50	0.32
Yellowstone-night	0.88	0.54
Voyageurs-day	0.37	0.19
Voyageurs-night	0.52	0.33
Rocky Mtn. –day	0.51	0.23
Rocky Mtn. –night	0.61	0.34

Day and night are defined as 10 am – 6 pm and 10 pm-6 am, local standard time, respectively. While the trends are statistically significant in both datasets, the nighttime trends are greater and statistically more robust. This result is consistent at all 4 of the sites considered.

Because nighttime tends to be the period of minimum O_3 concentrations, this result is consistent with the results reported by Lin et al. (2000) who found the strongest increase in O_3 concentrations at the low end of the distribution. The low nighttime concentrations can be caused by dry deposition, especially if a shallow nocturnal boundary layer is present. In more polluted areas, low nighttime concentrations can also be caused by reaction with NO (nitric oxide); however, this does not apply at these clean sites.

4. Interpretation/discussion

In summary, this analysis shows that surface O_3 in the western U.S. has undergone a significant increase over the past 2 decades. This increase was present at 9 of 10 rural/remote sites in the continental U.S. At two sites in Alaska, no trend was found. For the 10 continental U.S. sites, we found an average O_3 trend of 0.35 ppbv/year. This implies that surface O_3 has increased by more then 6 ppbv over the 18 years of observations (1987-2004). Based on a detailed analysis at 4 of these sites, we have found that the increase is statistically significant in all seasons, and if the data are segregated by day or night. However, the trend is somewhat stronger in the nighttime data.

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 and so confirms that temperature is an important predictor of elevated O_3 mixing ratios. The trends calculated from the multiple regression model are similar to those calculated without incorporating temperature. This indicates that temperature changes do not explain these long-term O_3 trends.

Recent EPA and NPS reports (U.S. EPA 2004; NPS 2002) have also identified positive trend in the annual 4^{th} highest concentration at several National Parks in the western U.S. In the report by the U.S. EPA (2004) most of the trend peak O_3 was attributed to high 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 also even if the trend analysis ends with 2001 data. Thus, we find that the O_3 trend is a broader phenomena not explained solely by annual temperature variations or trends. Understanding the causes of these trends is important to understanding future changes.

We consider three possible explanations for these O_3 trends:

1) Increasing NO_x and/or VOC emissions in the vicinity of these monitoring sites.

Increasing anthropogenic emissions of NO_x and VOCs could be responsible for the O_3 increase seen at these sites, however, this would be counter to both the EPA and WRAP emission inventories. As mentioned previously, anthropogenic NO_x and VOC emissions have decreased in all regions. Also, despite significant growth in VMT, mobile source emissions declined in all western states between 1996 and 2003, except for Nevada and Wyoming, due to reductions in the emission factors. However, emission inventories have significant uncertainties and it is possible that emissions are still increasing. To date, there has been little evaluation of the trend in emissions in the western U.S.

2) Changes in photochemistry, climate and/or biomass burning.

While the anthropogenic emission of O_3 precursors has most likely declined, other factors play an important role in the photochemistry. For example even if emissions have declined, the geographic distribution of these emissions is not constant. Because O_3 production is a non-linear function of NO_x concentrations (Liu et al., 1987; Lin et al., 1988; NRC 1991), it is still possible that net O_3 production could have increased over the recent past, even if total emissions have declined. Other factors, such as temperature and/or natural emissions, can also change O_3 production. Increasing temperatures in the western U.S. (Easterling et al., 1997) can influence O_3 production, through isoprene (Fiore et al., 2005) or through changes in biomass burning (Jaffe et al., 2004).

3) Increasing global background O_3

Long-term trends in background O_3 have been identified on several continents of the Northern Hemisphere (e.g., Lin et al., 2000; Chan et al., 2003; Jaffe et al,. 2003; Simmonds et al., 2004). A change in O_3 over all seasons and in both day and night data is consistent with a large-scale or hemispheric phenomenon. In particular, rapid growth in emissions from Asia is important for O_3 concentrations over the western U.S. (Jaffe et al., 1999; Jacob et al., 1999; Fiore et al., 2002; Jaffe et al., 2003; Vingarzan and Thomson. 2004). Thus it is possible that changes in global background O_3 are responsible for the trends seen in the western U.S.

Finally, it is important to consider how changes in regional O_3 influence urban air quality and exceedances of the air quality standards. While an increase in the background O_3 of 6 ppbv is only a small part of the 85 ppbv standard, it could play an important role for locations that are already close to this level 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-hour maximum concentrations in excess of 0.08 ppmv; 17 of these days have occurred since 1998, while only 2 occurred between 1987-1997. For summer days at RMNP, 4% have daily 8-hour 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-hour maximum shows a significant trend with a slope of 0.55 ppbv/year. This is similar to the results in Table 4, which shows increasing O_3 at both high and low concentrations and is consistent with an increase in global background O_3. Thus, a relatively small change in background O_3 may increase the number of sites out of attainment with the 8-hour O_3 standard and this could be a contributing factor to the recent increase in exceedances at RMNP.

5. References

Akimoto, H. and H. Narita, Distribution of SO_2, NO_x, and CO_2 Emissions from Fuel Combustion and Industrial Activities in Asia with 1^ox1^o Resolution, *Atmos. Environ. 28*: 213-225, 1994.

Berntsen, T. K., S. Karlsdottir, and D. A. Jaffe, Influence of Asian emissions on the composition of air reaching the Northwestern United States, *Geophys. Res. Letts. 26*: 2171-2174, 1999.

Chan, C.Y., Chan, L.Y. and 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.

Colorado Department of Public Health and Environment (CDPHE). Colorado Air Quality Data Report 2003. Air Pollution Control Division, APCD-TS-B1, Denver Colorado, Nov. 2004.

Easterling, D.R., Horton, B., Jones, P.D., Peterson, T.C., Karl, T.R., Parker, D.E., Salinger, M.J., Razuvayev, V., Plummer, N., Jamason, P., Folland, C.K. Maximum and minimum temperature trends for the globe. *Science 277*: 364-367, 1997.

ENVIRON International Corp., Development of WRAP Mobile Source Emission Inventories, Novato, Calif., Feb. 2004.

Fiore, A. M., L. W. Horowitz, D. W. Purves, H. Levy II, M. J. Evans, Y. Wang, Q. Li, R. M. Yantosca (2005), Evaluating the contribution of changes in isoprene emissions to surface ozone trends over the eastern United States, *J. Geophys. Res. 110*: D12303, doi:10.1029/2004JD005485.

Fiore, A.M., D.J. Jacob, I. Bey, R.M. Yantosca, B.D. Field, A.C. Fusco, and J.G. Wilkinson, Background ozone over the United States in summer: origin, trend, and contribution to pollution episodes, *J. Geophys. Res. 107*(15): 10.1029/2001JD000982, 2002.

Fusco, A. C., and J. A. Logan, Analysis of 1970–1995 trends in tropospheric ozone at Northern Hemisphere midlatitudes with the GEOS-CHEM model, *J. Geophys. Res.108* (D15): 4449, doi:10.1029/2002JD002742, 2003.

Hess, A., H. Iyer, and W. Malm, Linear trend analysis: A comparison of methods, *Atmos. Environ. 35*: 5211-5222, 2001.

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

Jacob, D. J., J. A. Logan, and P. P. Murti, Effect of rising Asian emission on surface ozone in the United States, *Geophys. Res. Letts*., *26*: 2175-2178, 1999.

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. and Uno, I. Transport of Asian Air Pollution to North America. *Geophys.Res.Letts*. 26:711-714, 1999.

Jaffe, D., McKendry, I., Anderson, T., and Price, H. Six 'new' episodes of trans-Pacific transport of air pollutants. *Atmos. Envir. 37*: 391-404, 2003.

Jaffe, D.A., Parrish, D., Goldstein, A., Price, H., and Harris, J. Increasing background ozone during spring on the west coast of North America. *Geophys.Res Letts*. *30:* No. 12, 1613, doi: 10.1029/2003GL017024, 2003.

Jaffe, D., I. Bertschi, L. Jaeglé, P. Novelli, J. S. Reid, H. Tanimoto, R. Vingarzan, and D. L. Westphal. Long-range transport of Siberian biomass burning emissions and impact on surface ozone in western North America, *Geophys. Res. Lett*. *31*: L16106, doi:10.1029/2004GL020093, 2004.

Johnson, B. J., S. J. Oltmans, H. Vömel, H. G. J. Smit, T. Deshler, and C. Kröger (2002), Electrochemical concentration cell (ECC) ozonesonde pump efficiency measurements and tests on the sensitivity to ozone of buffered and unbuffered ECC sensor cathode solutions, *J. Geophys. Res. 107*(D19): 4393, doi:10.1029/2001JD000557.

Lee, S-H., H. Akimoto, H. Nakane, S. Kurnosenko, and Y. Kinjo, Lower tropospheric ozone trend observed in 1989-1997 at Okinawa, Japan, *Geophys. Res. Lett. 25*: 1637-1640, 1998.

Lin, X., M. Trainer, and S. C. Liu, On the nonlinearity of the tropospheric ozone production, *J. Geophys. Res. 93:*15,879-15,888, 1988.

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

Lin, C., D. J. Jacob, W. Munger, and A. Fiore, Increasing background ozone in surface air over the United States, *Geophys. Res. Lett. 27*: 3465-3468, 2000.

Liu, S. C., M. Trainer, F. C. Fehsenfeld, D. D. Parrish, E. J. Williams, D. W. Fahey, G. Hubler, and P. C. Murphy, Ozone production in the rural troposphere and the implications for regional and global ozone distributions, *J. Geophys. Res. 92:* 4191-4207, 1987.

Logan, J.A. et al. Trends in the vertical distribution of ozone: A comparison of two analyses of ozonesonde data. *J.Geophys.Res.104*:26, 373-26,399, 1999.

Marenco, A., H. Gouget, P. Nedelec, and J. P. Pages, Evidence of a long-term increase in tropospheric ozone from Pic du Midi data series, *J. Geophys. Res. 99*:15,617-16,632, 1994.

National Park Service (2002), Air Quality in the National Parks, 2nd Edition. NPS Air Quality Division, Denver, Colorado.

National Park Service, Annual Data Summary 2004. Report #NPS D-1644.

National Park Service (2005), Denver, CO.

National Research Council (NRC) (1991), Rethinking the Ozone Problem in Urban and Regional Air Pollution, Nat. Acad. Press, Washington D.C.

Newchurch, M. J., M. A. Ayoub, S. Oltmans, B. Johnson, and F. J. Schmidlin (2003), Vertical distribution of ozone at four sites in the United States, *J. Geophys. Res. 108(D1)*: 4031, doi:10.1029/2002JD002059.

Oltmans S.J. et al. Trends of ozone in the Troposphere. *Geophys.Res.Letts. 25*:139-142, 1998.

Simmonds P.G., Derwent R.G., Manning A.L. and Spain G. Significant growth in surface ozone at Mace Head, Ireland, 1987-2003. *Atmos.Env. 28:* 4769-4778, 2004.

Streets D.G., Tsai N.Y., Akimoto H., and Oka K. Trends in emissions of acidifying species in Asia, 1985-1997. *Water, Air, Soil Poll. 130*:187-192, Part 2, 2001.

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

U.S. EPA. (2004), The Ozone Report: Measuring Progress Through 2003. EPA 454/K-04-001, Research Triangle Park, NC, April 2004.

Vingarzan, R. and Taylor, B. Trend analysis of ground level ozone in the greater Vancouver/Fraser Valley area of British Columbia. *Atmos. Envir. 37*:2159-2171, 2003.

Vingarzan R and Thomson B. Temporal variation in daily concentrations of ozone and acid-related substances at Saturna Island, British Columbia *J. Air and Waste Mgt. Assn. 54*:459-472, 2004.

Volz, A., and D. Kley, Evaluation of the Montsouris series of ozone measurements made in the nineteenth century, *Nature 332*: 240-242, 1988.

Weatherhead, E. C., G. C. Reinsel, G. C. Tiao, X. L. Meng, D. Choi, W. K. Cheang, T. Keller, J. DeLuisi, D. J. Wuebbles, J. B. Kerr, A. J. Miller, S. J. Oltmans, and J. E. Frederick, Factors affecting the detection of trends: Statistical considerations and applications to environmental data, *J. Geophys. Res. 103*:17,149, 1998.

Part 3: Trend in $PM_{2.5}$ concentrations at 6 background Parks in the western U.S.

We have obtained fine particulate data from the IMPROVE program website for 6 National Parks (http://vista.cira.colostate.edu/IMPROVE/). These data have been QC'd and analyzed by OLS to evaluate trends by season. This analysis is similar to one that we conducted previously on data from Crater Lake National Park (Jaffe et al., 2005). The results are given in the Table below.

Table 1. Analysis of IMPROVE aerosol data from 6 sites (slopes in ug/m^3/year). Values in bold are statistically significant at a 95% confidence or better.

Site Name	Season	Slope	R2	N (years)	Sig @ 95%?
Rocky Mountain NP	**Winter**	**-0.07**	**0.58**	**16**	**Yes**
	Spring	0.00	0.00	16	No
	Summer	0.01	0.00	16	No
	Fall	-0.03	0.22	16	No
Yellowstone NP	**Winter**	**-0.09**	**0.79**	**16**	**Yes**
	Spring	**-0.07**	**0.28**	**16**	**Yes**
	Summer	-0.14	0.21	16	No
	Fall	**-0.09**	**0.31**	**16**	**Yes**
Voyagers NP	Winter	-0.05	0.07	10	No
	Spring	**-0.14**	**0.57**	**10**	**Yes**
	Summer	-0.11	0.18	10	No
	Fall	-0.05	0.12	9	No
Lassen Volcanic NP	**Winter**	**-0.07**	**0.67**	**16**	**Yes**
	Spring	0.00	0.00	16	No
	Summer	0.12	0.15	16	No
	Fall	0.09	0.05	16	No
Denali NP	**Winter**	**-0.10**	**0.68**	**16**	**Yes**
	Spring	-0.03	0.09	16	No
	Summer	0.02	0.01	16	No
	Fall	**-0.07**	**0.41**	**16**	**Yes**
Glacier NP	**Winter**	**-0.15**	**0.37**	**16**	**Yes**
	Spring	-0.07	0.15	16	No
	Summer	0.06	0.08	16	No
	Fall	0.00	0.00	16	No

At all sites, there is a tendency for falling concentrations with the most obvious and statistically robust changes occurring during winter, spring and/or fall. This likely reflects the

dominance of domestic sources for $PM_{2.5}$ and the decreasing emissions, both primary particulates as well as precursors. We are currently evaluating the changes in chemical speciation so that we can focus in more clearly on these declining $PM_{2.5}$ concentrations.

Jaffe, D., Tamura, S., and Harris, J. Seasonal cycle, composition and sources of background fine particles along the west coast of the U.S., *Atmos. Env. 39*:297-306, 2005.

Part 4: Outstanding scientific questions and focus of year 2.

During year 2, we will continue this study and address the following key questions:

1) Can we find other ozone data that will help us understand the influence of background O_3 on regional air quality?
2) How do O_3 and PM concentrations vary from year-to-year as a result of variability in biomass burning?
3) What is the primary cause (or causes) for the increasing frequency of O_3 exceedances at RMNP?
4) How do changing global background concentrations influence regional and urban air quality?
5) Can variations in airflow patterns (e.g., trajectories) help explain variations in O_3 and $PM_{2.5}$ concentrations, including year-to-year variations?