

Influence of Fires on O₃ Concentrations in the Western U.S.

DAN JAFFE,^{*,†} DULI CHAND,[†]
WILL HAFNER,^{†,‡}
ANTHONY WESTERLING,[‡] AND
DOMINICK SPRACKLEN[§]

University of Washington Bothell, 18115 Campus Way NE,
Bothell, Washington 98011, University of California, Merced,
and University of Leeds, England UK

Received January 9, 2008. Revised manuscript received
April 28, 2008. Accepted May 22, 2008.

Because forest fires emit substantial NO_x and hydrocarbons—known contributors to O₃ production—we hypothesize that interannual variation in western U.S. O₃ is related to the burned area. To evaluate this hypothesis we used a gridded database of western U.S. summer burned area (BA) and biomass consumed (BC) by fires between 101–125° W. The fire data were compared with daytime summer O₃ mixing ratios from nine rural Clean Air Status and Trends Network (CASTNET) and National Park Service (NPS) sites. Large fire years exhibited widespread enhanced O₃. The summer BA was significantly correlated with O₃ at all sites. For each 1 million acres burned in the western U.S. during summer, we estimate that the daytime mean O₃ was enhanced across the region by 2.0 ppbv. For mean and maximum fire years, O₃ was enhanced by an average of 3.5 and 8.8 ppbv, respectively. At most sites O₃ was significantly correlated with fires in the surrounding 5 × 5° and 10 × 10° regions, but not with fires in the nearest 1 × 1° region, reflecting the balance between O₃ production and destruction in a high NO_x environment. BC was a slightly better predictor of O₃, compared with BA. The relationship between O₃ and temperature was examined at two sites (Yellowstone and Rocky Mountain National Parks). At these two sites, high fire years were significantly warmer than low fire years; however, daytime seasonal mean temperature and O₃ were not significantly correlated. This indicates that the presence of fire is a more important predictor for O₃ than is temperature.

I. Introduction

Biomass burning generates substantial emissions of aerosols and gases, including nonmethane hydrocarbons (NMHCs) and NO_x (NO + NO₂). Combined with sunlight, these precursors result in significant photochemical production of O₃. However, this process is complex and depends on numerous factors including emissions, temperature, the NMHC/NO_x ratio and other variables (1). The emissions from a wildfire will vary a great deal depending on the ecosystem type and the stage of combustion. Emissions of NO_x tend to be greatest during the flaming stage of combustion (2).

Corresponding author e-mail: djaffe@u.washington.edu.

[†] University of Washington Bothell.

[‡] University of California.

[§] University of Leeds.

^{||} Current address: Science Applications International Corporation, 18912 North Creek Parkway, Suite 101 Bothell, WA 98011.

It has been known for some time that large scale biomass burning can result in significant O₃ production (3). More recently, several studies have shown that large scale fires can have far reaching influence on O₃ (4–11). In some cases, the smoke and O₃ from fires has been shown to have significant influence a long distance from the fires (7, 12–14).

In western North America, wildfires are a regular occurrence each year, but there is evidence that the frequency of extreme fire years may be increasing (14). This is due to several factors related to climate change: increased spring and summer temperatures, earlier spring snowmelt, and dryer conditions (15–18). At the same time forest management, especially fire suppression, has led to an accumulation of fuels and possibly contributed to the increase in large fire events (19).

It is also important to recognize that nonurban O₃ in the western U.S. has increased between the late 1980s to present (20). This is based on an analysis of ~18 years of data from nine rural/remote sites in the western U.S. At seven of the nine sites we found a statistically significant increase in surface O₃. The average increase over this time period, averaged across all nine sites, was 0.26 ppbv/year. Thus, over the 18 years of this data record, rural/background O₃ in the western U.S. has increased approximately 4 ppbv (20). Several hypotheses were put forward to explain this trend, including changing anthropogenic NO_x emissions, changing global background O₃ concentrations (21, 22), changing climate, changing soil emissions (23); and/or increasing emissions associated with fires.

Because of the increase in large fire years, we sought to evaluate how these emissions influence air quality in the western U.S., especially O₃ and particulate matter (PM). In this paper we evaluate the influence of fires on O₃ in this region. Because O₃ production is linked with temperature (e.g., <http://epa.gov/air/airtrends/2007/report/groundlevel-elozone.pdf>) we also evaluated the linkage between temperature, fires and O₃ on a daily and seasonal basis. For our analysis, we utilized a 1 × 1° database of monthly area burned described by Westerling et al. (24) which was combined with maps of ecosystem-specific fuel loadings (25). We found that fires can explain a substantial fraction of the interannual variations in mean O₃ at these nine rural sites across the western U.S. In a separate analysis, we have examined how fires influence PM_{2.5} and its chemical components (26).

Materials and Methods

Burned Area and Biomass consumed. The database of area burned in the western U.S. has been previously described in several recent papers (15, 24). The extension of this database to biomass fuel consumed and application to particulate matter (PM) concentrations has been described by Spracklen et al. (25) and Jaffe et al. (26). In short, the gridded 1 × 1° database of monthly area burned was developed based on reports from multiple government agencies, including the U.S. Forest Service, Bureau of Land Management, National Park Service (NPS), and Bureau of Indian Affairs. The database spans from 1980 through 2004 with a 1 × 1° resolution ranging from 101–125° west longitude and 31–49° north latitude (24). In each grid cell, the number of acres burned was reported for the month of the fire start date. Since much of the annual area burned came from a number of large fires which burned over extended periods, this simplification in having only the fire start date can pose a problem if monthly O₃ data are used. For this reason, we combined fire and O₃ data for the summer months of June, July, and August. These three months are responsible for 70–93% of annual acres

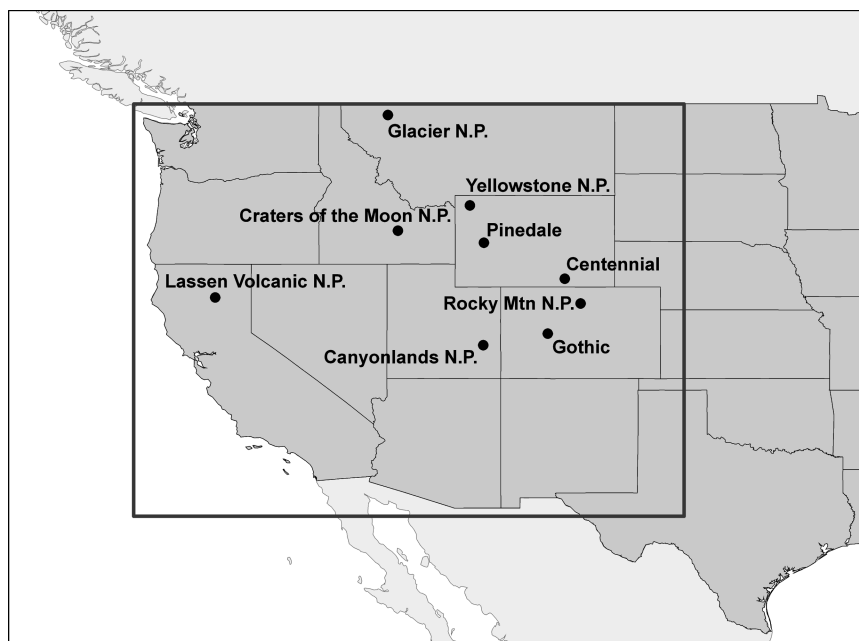


FIGURE 1. Ozone monitoring locations and fire region used in this analysis. The fire database covers the region between 101–125° W and 31–49° N (shown by a box).

TABLE 1. Sites Used in the Analysis

location	site type	lat.(°N)/long.(°W)/elevation (meters)	data record (mm/yy-mm/yy)	no. days >0.08 ppmv in data record ^a
Lassen Volcanic 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
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 N.M, 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 O₃ concentrations greater than 0.08 ppmv.

burned in the western U.S., depending on the year. The gridded database of fuel consumption was based on ecosystem-specific fuel loadings (see <http://www.fs.fed-us/pnw/fera/fccs/maps.shtml>). For detailed procedures, the reader is referred to previous publications (25, 26).

Ozone and Temperature Data. O₃ and temperature data for this analysis comes from CASTNET and NPS sites in the western U.S. (see Figure 1 for site locations and <http://www.epa.gov/castnet/> for more information about the data). The data covers the period 1988–2004. We chose sites with at least 12 years of data, yielding nine sites. These are the same nine sites used in our recent analysis of O₃ trends (20). Table 1 shows the names and locations of each site, along with the number of days with an exceedance of the 8-h 0.08 ppmv air quality standard. Only at the Rocky Mountain and Lassen National Park sites have there been any exceedances of the 8-h standard. These sites experience occasional transport of polluted air masses from adjacent metropolitan areas and could also experience transported pollutants from distant sources (8, 14).

At all sites O₃ has been measured using UV absorption and using a standard calibration procedure. While this network of sites has been maintained consistently, there have been some changes over the nearly two decades of observations. This includes a change in the inlet height at most sites in the mid-1990s and, for the Yellowstone National Park site,

a change in location (by 1.5 km). Jaffe and Ray (20) discuss these changes in more detail and show that while the inlet height had a significant impact on nighttime O₃ data, there was no discernible influence on daytime O₃ data. For this reason, the trend analysis previously reported (20) and our analysis of the influence from fires reported in this paper utilizes only the daytime data (1000–1800 local time). This is also the time frame for most O₃ exceedances.

The monthly burned areas (BA) and biomass consumed (BC) data were summed for each summer (June, July, and August). The annual summer daytime mean O₃ mixing ratios were computed by averaging the three monthly means for each site.

Results

Between Site Correlations. In our previous work we identified a significant correlation in the monthly O₃ mixing ratios between most sites even after removing the seasonal cycle (20). With the exception of Glacier National Park, all sites showed significant correlations with most of the other sites. Given the great distance between the Lassen site and the other sites, more than 1000 km, it is surprising that even the monthly mean O₃ concentrations at Lassen were significantly correlated with O₃ at the other parks in the Rocky Mountain west, although the *R* values tended to be somewhat lower. This indicates that the interannual variations in O₃ are, at

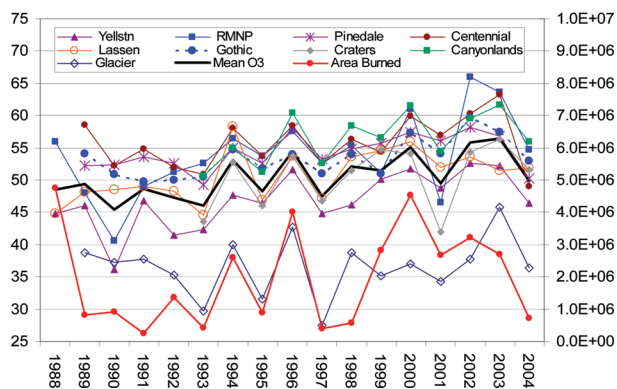


FIGURE 2. Annual summer daytime O₃ mixing ratio (ppbv, left axis) at nine sites in the western U.S. along with summer area burned for the western U.S. (acres, right axis). Also shown is the mean O₃ from all nine sites.

least in part, due to large scale factors that impact the entire western U.S. Here we focus on the intersite correlation in O₃ mixing ratios using the summer data only.

Figure 2 shows the summer mean O₃ mixing ratios for these sites for the years 1988–2004 and Table 2 shows the between site correlations. Figure 2 also gives the burned area (acres) for each summer for the entire western U.S. From Figure 2 it is apparent that there are significant interannual variations in summer O₃. For example, mean, daytime O₃ was elevated during the summers of 1994, 1996, 2000, 2002, and 2003, and these years also had burned areas of at least 2 million acres. Not surprisingly, the summer mean concentrations are significantly correlated between most sites (see Table 2). The Craters of the Moon site has the fewest significant correlations, most likely due to its relatively short record (12 years).

O₃ mixing ratios at Glacier National Park are consistently lower than all other sites by 15–20 ppbv. In addition, PM_{2.5} concentrations at this site are significantly greater than most other sites in the Rocky Mountain region (26). Both of these are likely due to significant emissions from an aluminum smelter located ~20 km from the O₃ and PM_{2.5} monitoring site (27). Emissions from this facility include particulate fluorides, PAHs, NO_x and other compounds. Thus, it is likely that O₃ is lowered due to reaction with NO or heterogeneous reactions on the surface of particulate emissions. So while the Glacier National Park site shows a similar pattern as other O₃ monitoring sites in the west, and the variations are significantly correlated with other sites, it is clear that this data shows substantial local influence.

Relationship Between O₃ and Burned Area and/or Biomass Consumed. Summer O₃ data starts in 1987 for two sites: Rocky Mountain and Yellowstone National Parks. One additional site, Lassen National Park, has summer data starting in 1988. Starting with the summer of 1989, seven of the nine sites have data. 1988 was also the year of the large

Yellowstone fires, which burned primarily in July through September. In this year, 36% of Yellowstone National Park burned, approximately 0.8 million acres. In all, 4.76 million acres burned throughout the western U.S. in 1988. However, O₃ mixing ratios at these three sites (Yellowstone, Rocky Mountain, and Lassen) were not significantly elevated in 1988. The fact that the fires surrounded the Yellowstone monitoring location suggests that a combination of high NO_x emissions and reduced photochemistry from the smoke probably reduced O₃ concentrations locally. In a later section of this paper, we show more rigorously that fires adjacent to a monitoring location (within 1° or approximately 100 km) do not result in enhanced O₃ mixing ratios locally, whereas fires further afield result in significant O₃ enhancements. So for all further analyses we use data from 1989–2004, since these years have at least seven sites operating in all years.

Figure 2 shows that the interannual variations in summer O₃ from these nine sites are significantly correlated with burned area for the western U.S. The regression equations for the relationship between mean O₃ at the nine sites and fire are shown below using data from 1989–2004:

$$O_3(\text{ppbv}) = 1.96 \times 10^{-6} \times \text{burned area}(\text{acres}) + 47.1 \quad R^2 = 0.60(1)$$

$$O_3(\text{ppbv}) = 2.38 \times 10^{-10} \times \text{biomass consumed}(\text{kg}) + 47.7 \quad R^2 = 0.64(2)$$

The intercepts in the equations above, 47.1 and 47.7 ppbv, respectively, are a measure of the mean daytime O₃ concentration in the western U.S. in the absence of fires. For the average and maximum fire years, burned areas of 1.8 and 4.5 million acres, respectively, these correspond to an average enhancement in summer O₃ of 3.5 and 8.8 ppbv, respectively, across the entire western U.S.

We also examined the relationship between O₃ and fires at individual sites. This was done by looking at the correlation between O₃ at each site with burned area and biomass consumed at multiple scales. For this, we used fire data in 1 × 1°, 5 × 5°, and 10 × 10° boxes around each monitoring site. Since the burned area and biomass consumed data for each site at the 1 × 1°, 5 × 5°, and 10 × 10° scales have nonGaussian distributions, the correlations were calculated using the natural log of burned area and biomass consumed. Table 3 shows the correlation coefficients for each site with fire data at multiple scales. Table A1, in the Supporting Information, provides the data from each site and for each summer between 1989 and 2004.

Figure 3 shows an example of the relationship between the burned area for the Pinedale, Wyoming site. Figure 3a shows the relationship between Pinedale O₃ and natural log of burned area in the 10 × 10° region around the site and Figure 3b shows the relationship with burned area for the entire western U.S.

The correlations in Table 3 show that the relationships are slightly better when using biomass consumed, compared

TABLE 2. R Values for between Site Correlation in Summer Mean O₃^a

	Yellow-stone	Rocky Mtn	Pinedale	Centen.	Lassen	Gothic	Glacier	Craters of the Moon
Yellowstone		0.75*	0.77*	0.72*	0.62*	0.70*	0.42*	0.70*
RMNP	0.75*		0.55*	0.58*	0.46*	0.76*	0.36	0.74*
Pinedale	0.77*	0.55*		0.81*	0.71*	0.69*	0.53*	0.56
Centennial	0.72*	0.58*	0.81*		0.53*	0.81*	0.68*	0.55
Lassen	0.62*	0.46	0.71*	0.53*		0.59*	0.55*	0.67*
Gothic	0.70*	0.76*	0.69*	0.81*	0.59*		0.54*	0.57
Glacier	0.42	0.36	0.53*	0.68*	0.55*	0.54*		0.75*
Craters of the Moon	0.70*	0.74*	0.56	0.55	0.67*	0.57	0.75*	
Canyon	0.85*	0.70*	0.78*	0.76*	0.66*	0.77*	0.82*	0.82*

^a Values that are significant at *P* < 0.05 or better are marked with an asterisk.

TABLE 3. Correlation Coefficient (*R*) between Burned Area or Biomass Consumed at Various Scales and Summer Mean O₃ at Nine Sites^a

	Yellow-stone	Rocky Mountain	Pinedale	Centen.	Lassen	Gothic	Glacier	Craters of the Moon	Canyon-lands
all western U.S. BA	0.714 ^b	0.544 ^b	0.840 ^b	0.668 ^b	0.730 ^b	0.667 ^b	0.459	0.544	0.724 ^b
10 × 10° BA	0.600 ^b	0.644 ^b	0.857 ^b	0.822 ^b	0.669 ^b	0.880 ^b	0.707 ^b	0.535	0.651 ^b
5 × 5° BA	0.619 ^b	0.416	0.632 ^b	0.496	0.674 ^b	0.875 ^b	0.712*	0.494	0.609*
all western U.S. BC	0.657 ^b	0.673 ^b	0.783 ^b	0.741 ^b	0.639 ^b	0.855 ^b	0.503 ^b	0.554 ^b	0.760 ^b
10 × 10° BC	0.586 ^b	0.607 ^b	0.831 ^b	0.846 ^b	0.580 ^b	0.924 ^b	0.722 ^b	0.622 ^b	0.734 ^b
5 × 5° BC	0.652 ^b	0.436	0.682 ^b	0.576 ^b	0.621 ^b	0.938 ^b	0.709 ^b	0.630 ^b	0.645 ^b
1 × 1° BC or BA	0.373	0.296	0.567 ^b	0.714 ^b	-0.214	0.704 ^b	0.443	0.305	-0.179

^a Significant correlations ($P < 0.05$) are marked with an asterisk. For the 1, 5, and 10° regions, the natural log of BA or BC was used in the regression. ^b BA refers to burned area; BC refers to biomass consumed.

TABLE 4. Average Daytime O₃ and Temperature for the Three Highest and Three Lowest Fires Years Based on Area Burned in 10 × 10° Region around Each Site

site	high fire years	low fire years	O ₃ (ppbv) high/low years	temperature (°C) high/low years
Yellowstone N.P.	2000, 2003, 2006	2004, 1993, 1997	51.7/44.6	18.7/14.7
Rocky Mtn. N.P.	2002, 2000, 2003	1997, 1991, 1992	63.5/50.9	18.0/15.7

Only data from 1989–2004 is considered. Temperature and O₃ results show the mean of all daytime data (1000–1800 local time) for each site.

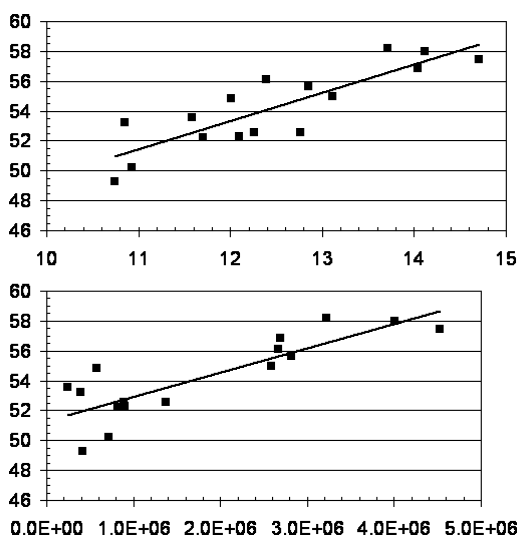


FIGURE 3. a,b: Scatterplot of summer mean O₃ (ppbv) at Pinedale, Wyoming vs natural log of 10 × 10° burned area (3a: top) and burned area (acres) for entire western U.S. (3b: bottom). For 3a, the regression equation is $y = 1.90x + 30.5$ ($R^2 = 0.734$). For 3b, the regression equation is $y = 1.62 \times 10^{-6}x + 51.3$ ($R^2 = 0.708$).

with burned area, both in terms of the number of significant correlations and the magnitude of the R^2 value. For the 10 × 10° region, all sites are significantly correlated with biomass consumed, and all but Craters of the Moon are correlated with burned area. This scale appears to give the best correlation between fires and O₃. Most sites also show statistically significant correlation with fire at the 5 × 5° scale and with fire data from the entire western U.S. At the 1 × 1° scale, only three out of the nine sites show a significant correlation. We interpret this result to imply that fires that are near the monitoring location (within approximately 100 km) result in only minor enhancement in O₃, due to the combined effects of NO_x titration and reduced solar flux. It should be noted that at the 1 × 1° scale, there is no difference between the correlation coefficients using BC or BA, since the relationship is fixed by the mix of ecosystem types in the 1 × 1° grid box.

Role of Temperature. While fires clearly result in enhanced O₃ due to precursor emissions, we would also like to evaluate the role that climate variations play. This is relevant since fires are enhanced during hot, dry summers (24). Thus, conditions that lead to enhanced fires also result in increased O₃ production. In our previous work (20), we examined the correlation between seasonal mean temperatures and O₃ mixing ratios. During the warm months (May–September) and only at some sites, temperature was found to be positively correlated with O₃ mixing ratios,

To examine the role that temperature variations play on O₃, we evaluated daily 8 h daytime (1000–1800 local time) temperature and O₃ mixing ratios measured at two sites, Yellowstone (YNP) and Rocky Mountain (RMNP) National Parks, for the three highest and three lowest fire years. Table 4 compares data on temperature and O₃ for the high and low fire years. As described previously, high fire years have significantly greater O₃ mixing ratios.

To assess the relationship between warm years and O₃ we evaluated the correlation between seasonal daytime temperature and O₃ at both YNP and RMNP. We found that these correlations are much weaker, and not statistically significant, in contrast to the correlations between O₃ and burned area (or biomass consumed). For YNP, the correlation between daytime seasonal mean O₃ and temperature yields an R^2 of 0.224 compared to an R^2 of 0.351 for the correlation of O₃ with the natural log of burned area in the 10 × 10° region. For RMNP, the comparable R^2 values are 0.138 and 0.414. We conclude from this that while high fire years have above average temperatures and O₃ levels, warm years alone do not lead to high O₃ mixing ratios.

We also examined daily temperature and O₃ variations at YNP and RMNP. Daily (8 h) temperature and O₃ mixing ratios using the data from all years is weakly correlated at both sites ($R^2 = 0.16, 0.09$ at RMNP and YNP, respectively). At RMNP, the correlation is somewhat stronger if only data in the high fire years is considered ($R^2 = 0.24$), but this is not true at YNP. Overall, it seems that daily variations in local temperature are a relatively small factor in explaining daily O₃ variations at these sites. While both sites are impacted by local emissions, especially vehicle traffic in summer, local photochemical production does not appear to be a dominant source for O₃. Instead, transport from other regions is likely to play a significant role in explaining O₃ mixing ratios.

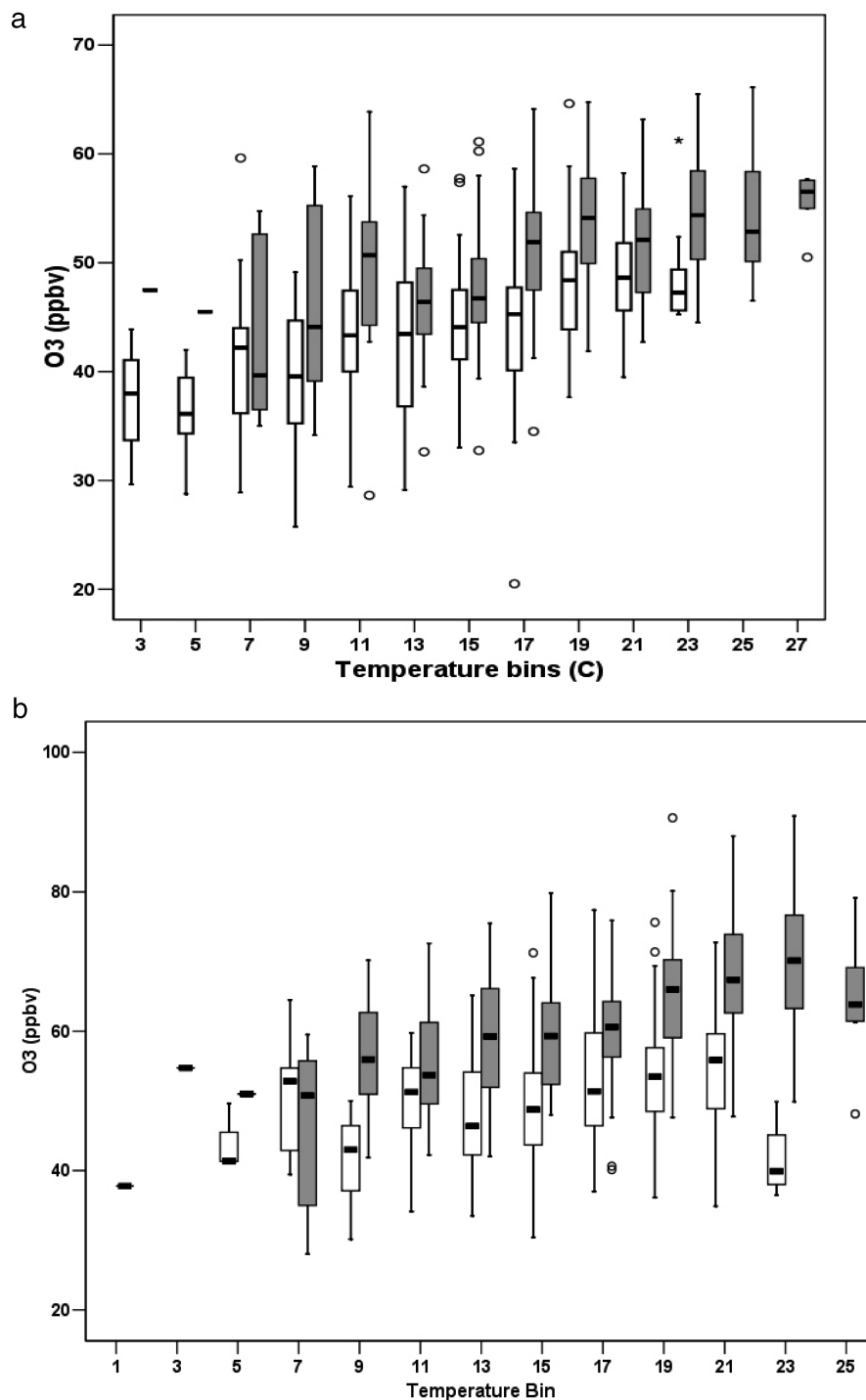


FIGURE 4. a. Comparison of daily daytime (1000–1800 local time) O₃ and temperature data from Yellowstone N.P. The data are sorted by average daytime temperature in 2 °C increments. Gray boxes show data for the high fire years and white boxes show the low fire years (see Table 4). Both boxes correspond to the identical 2 °C range. The center of the temperature range is shown on the x-axis. The boxes show the 25th, 50th, and 75th percentiles, the bars show the range, and outliers are shown by a single marker (outliers are defined as greater than 1.5 times the inner quartile range). Most bins contain between 10 and 60 data points. 4b: Same as in Figure 4a, but for Rocky Mountain N.P.

To compare the O₃-temperature relationship further, Figure 4 shows box plots of the daytime O₃ distribution sorted by daily temperature, in 2 °C bins, for the high and low fire years for two sites. For nearly all temperature bins, O₃ is greater during the high fire years. For example, in the 19 °C bin for YNP (Figure 4), high fire years have mean daytime O₃ mixing ratios that are 5.8 ppbv greater than low fire years. While the high fire years show a distribution that is shifted toward higher temperatures (see Table 4), the fact that O₃ mixing ratios are much higher at the same temperature

indicates that local temperature is not the dominant factor in explaining the enhanced O₃. Instead, enhanced emissions from the fires and/or regional accumulation of photochemically generated O₃ are likely the primary causes for enhanced O₃ during high fire years.

Further analysis of this daily O₃-temperature relationship suggests some differences between YNP and RMNP. For YNP the O₃-temperature slope is not significantly different between high and low fire years, 0.55 and 0.63 ppbv/°C, respectively, whereas the intercepts are significantly different,

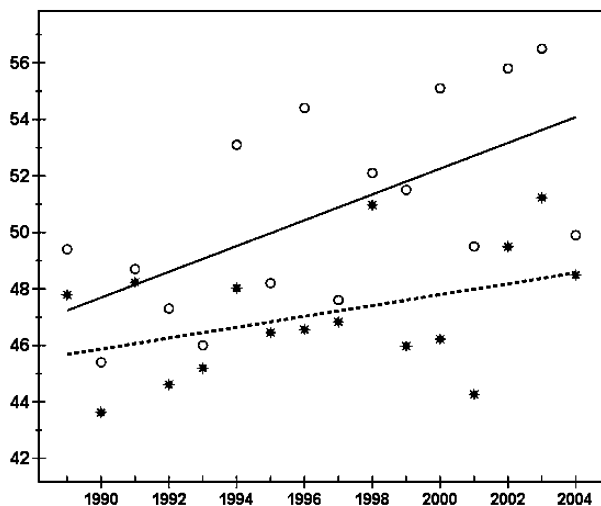


FIGURE 5. Summer O₃ (ppbv) averaged across all sites. The open circles and linear fit (solid line) show the original data. The stars with linear fit (dashed line) show the data modified to remove the influence of fires (see text for details). The solid line has an R^2 value of 0.38 and is statistically significant at $P < 0.05$, whereas the dashed line has an R^2 of 0.17 and is not statistically significant.

41.5 vs 35.1 ppbv, respectively. For RMNP, the slopes are rather different in high and low fire years, 1.15 and 0.622 ppbv/ $^{\circ}$ C, respectively, whereas the intercepts are similar at 42.9 and 41.0 ppbv, respectively. This suggests a difference in the photochemical environment at these two locations; however, a detailed analysis of this is beyond the scope of the present analysis. In summary, our analysis of the data from YNP and RMNP show that temperature is a much weaker predictor of enhanced O₃, compared to burned area or biomass consumed.

Discussion and Summary

We previously reported a significant positive trend in O₃ mixing ratios at seven out of nine of these sites for the period 1989–2004 (20). Only the Pinedale and Glacier N.P. sites failed to show a significant trend in O₃. In Table 3 we show that fire area burned or biomass consumed are significantly correlated with interannual variations in O₃, explaining between 46 and 84% of the interannual variability. While fires are clearly one important factor to explain the interannual variability, other factors, such as large scale variations in background O₃ may also be important. The question arises as to whether an increase in fire extent is responsible for the positive trend in O₃ in the western U.S.

Figure 5 shows summer mean O₃ mixing ratios averaged at the nine sites for 1989–2004, along with an estimated O₃ concentration in the absence of fires for each year. This was done by using the O₃-burned area relationship shown in equation 1 and the annual burned areas. A linear trend line is also shown for each data set. The linear trend for the original data has an R^2 value of 0.38 and is statistically significant at $P < 0.05$. The trend after removing the influence from fires (shown in the figure by the stars and the dashed line) has an R^2 of 0.17 and is not statistically significant. For the original data, the annual mean summer concentration is 50.6 with a standard deviation of 3.5 ppbv. For the data with fire influence removed, the summer mean is 47.1 with a standard deviation of 2.2 ppbv. Removing the fire influence significantly reduces the interannual variability and the positive trend.

Thus we conclude that the increase in fires has largely been responsible for the increase in summertime O₃ reported

by Jaffe and Ray (20). However, fires cannot explain the trend in O₃ reported for other seasons (20).

As mentioned previously, summer average O₃ mixing ratios at Glacier N.P. are 15–20 ppbv lower than other sites in the western U.S. Glacier was also one of only two sites where a trend in O₃ was not found (20). Additionally, summertime PM_{2.5} at Glacier N.P. is 1–2.5 μ g/m³ higher than any other sites in the region. The presence of significantly lower O₃ and higher PM_{2.5} are consistent with the presence of a nearby aluminum smelter, as described in a previous report by the NPS (26). The atmospheric influence of this smelter is known to extend for some 10 s of km downwind, a region which includes the location of the park O₃ and PM monitor (27). Thus, we believe the Glacier N.P. site is not representative of regional atmospheric conditions, for both O₃ and PM.

Based on our analysis of nine rural sites, fires play a significant role on O₃ in the western U.S. The next logical step in this analysis would be to evaluate how fires influence exceedances of the 8-h O₃ standard in both rural and urban areas of the western U.S. For example, at Rocky Mountain N.P. the largest number of exceedances of the 8-h 0.08 ppmv standard occurred in 2002 and 2003, with six and seven days each year, respectively. These were also two of the top three years with the greatest area burned in the 10 $^{\circ}$ x10 $^{\circ}$ region around RMNP. Our analysis shows that fires play a significant role in elevating background O₃ concentrations thus increasing the likelihood of an exceedance of the 8-h standards.

Our analysis of the relationship between temperature and O₃ at YNP and RMNP indicates a complex interplay of factors. At these two sites, high fire years were significantly warmer than low fire years, however daytime seasonal mean temperature and O₃ were not significantly correlated. This indicates that the presence of fire is a more important predictor for O₃, than is temperature.

Increases in temperature that are likely in coming decades (IPCC, ref 28) may further increase wildfires with consequent impact on summertime ozone concentrations. Spracklen et al. (manuscript in preparation) predict that under the IPCC A1B scenario for well-mixed greenhouse gases, wildfire area burned in the western U.S. will increase by ~40% over current (1995–2004) levels by 2050. This corresponds to an additional 1 million acres burned during June through August each year. Our analysis suggests that such an increase in wildfires would result in summer O₃ being further enhanced by ~2 ppbv across the western U.S. Increased surface ozone may damage forest health (29) potentially reducing ecosystem carbon uptake (30) with implications for feedbacks between wildfire and climate (31).

Supporting Information Available

Tables A1, A2, and A3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) McKeen, S. A.; Wotawa, G.; Parrish, D. D.; Holloway, J. S.; Buhr, M. P.; Hübler, G.; Fehsenfeld, F. C.; Meagher, J. F. Ozone production from Canadian wildfires during June and July of 1995. *J. Geophys. Res.* **2002**, *107*, (D14), 4192, doi: 10.129/2001JD000697.
- (2) Andreae, M. O.; Merlet, P. Emission of trace gases and aerosols from biomass burning. *Global Biogeochem. Cycles* **2001**, *15*, 955–966.
- (3) Fishman, J.; Watson, C. E.; Larsen, J. C.; Logan, J. A. Distribution of tropospheric ozone determined from satellite data. *J. Geophys. Res.* **1990**, *95* (D4), 3599–3617.
- (4) Fujiwara, M.; Kita, K.; Kawakami, S.; Ogawa, T.; Komala, N.; Saraspriya, S.; Suropto, A. Tropospheric ozone enhancements during the Indonesian forest fire events in 1994 and in 1997 as revealed by ground-based observations. *Geophys. Res. Lett.* **1999**, *26* (16), 2417–2420.

- (5) Wotawa, G.; Trainer, M. The influence of Canadian forest fires on pollutant concentrations in the United States. *Science* **2000**, *288* (5464), 324–328.
- (6) Thompson, A. M.; Witte, J. C.; Hudson, R. D.; Guo, H.; Herman, J. R.; Fujiwara, M. Tropical tropospheric ozone and biomass burning. *Science* **2001**, *291* (5511), 2128–2132.
- (7) Jaffe, D. A.; Parrish, D.; Goldstein, A.; Price, H.; Harris, J. Increasing background ozone during spring on the west coast of North America. *Geophys. Res. Lett.* **2003**, *30*, 12 2128–1613, doi: 10.1029/2003GL017024.
- (8) Bertschi, I. T.; Jaffe, D. A. Long-range transport of ozone, carbon monoxide and aerosols to the NE Pacific troposphere during the summer of 2003: Observations of smoke plumes from Asian boreal fires. *J. Geophys. Res.* **2005**, *110*, D05303, doi: 10.1029/2004JD005135.
- (9) Pfister, G. G.; Emmons, L. K.; Hess, P. G.; Honrath, R.; Lamarque, J.-F.; Mart, Martín, M. V.; Owen, R. C.; Avery, M. A.; Browell, E. V.; Holloway, J. S.; Nedelec, P.; Purvis, R.; Ryerson, T. B.; Sachse, G. W.; Schlager, H. Ozone production from the 2004 North American boreal fires. *J. Geophys. Res.* **2006**, *111*, D24S07, doi: 10.1029/2006JD007695.
- (10) Lapina, K.; Honrath, R. E.; Owen, R. C.; Mart, Martín, M. V.; Pfister, G. Evidence of significant large-scale impacts of boreal fires on ozone levels in the midlatitude Northern Hemisphere free troposphere. *Geophys. Res. Lett.* **2006**, *33*, L10815, doi: 10.1029/2006GL025878.
- (11) Martín, M. V.; Honrath, R. E.; Owen, R. C.; Pfister, G.; Fialho, P.; Barata, F. Significant enhancements of nitrogen oxides, black carbon, and ozone in the North Atlantic lower free troposphere resulting from North American boreal wildfires. *J. Geophys. Res.* **2006**, *111* (D23), D23S60.
- (12) DeBell, L. J.; Talbot, R. W.; Dibb, J. E. A major regional air pollution event in the northeastern United States caused by extensive forest fires in Quebec, Canada. *J. Geophys. Res.* **2004**, *109*, D19305, doi: 10.1029/2004JD004840.
- (13) Colarco, P. R.; Schoeberl, M. R.; Doddridge, B. G.; Marufu, L. T.; Torres, O.; Welton, E. J. Transport of smoke from Canadian forest fires to the surface near Washington, Injection D.C.: height, entrainment, and optical properties. *J. Geophys. Res.* **2004**, *109*, D06203, doi: 10.1029/2003JD004248.
- (14) Jaffe, D.; Bertschi, I.; Jaeglé, L.; Novelli, P.; Reid, J. S.; Tanimoto, H.; Vingarzan, R.; Westphal, D. L. Long-range transport of Siberian biomass burning emissions and impact on surface ozone in western North America. *Geophys. Res. Lett.* **2004**, *31*, L16106, doi: 10.1029/2004GL020093.
- (15) Westerling, A. L.; Hidalgo, H. G.; Cayan, D. R.; Swetnam, T. W. Warming and earlier spring increase Western U.S. forest wildfire activity. *Science* **2006**, *313*, 5789, 940–943.
- (16) Cook, E. R.; Woodhouse, C. A.; Eakin, C. M.; Meko, D. M.; Stahle, D. W. Long-term aridity changes in the Western United States. *Science* **2004**, *306* (5698), 1015–1018.
- (17) Flannigan, M. D.; Gillett, N. P.; Weaver, A. J.; Zwiers, F. W. Detecting the effect of climate change on Canadian forest fires. *Geophys. Res. Lett.* **2004**, *31*, L18211, doi: 10.1029/2004GL020876.
- (18) Flannigan, M. D.; Logan, K. A.; Amiro, B. D.; Skinner, W. R.; Stocks, B. J. Future area burned in Canada. *Climate Change* **2005**, *72*, 1–16, doi: 10.1007/s10584-005-5935-y.
- (19) Donovan, G. H.; Brown, T. C. Be careful what you wish for: The legacy of Smokey Bear. *Front. Ecol. Environ.* **2007**, *5* (2), 73–79.
- (20) Jaffe, D. A.; Ray, J. Increase in Ozone at Rural Sites in the Western U. S. *Atmos. Environ.* **2007**, *41* (26), 5452–5463.
- (21) Jaffe, D. A.; Anderson, T.; Covert, D.; Trost, B.; Danielson, J.; Simpson, W.; Blake, D.; Harris, J.; Streets, D. Observations of ozone and related species in the Northeast Pacific during the PHOBEA Campaigns: 1. Ground based observations at Cheeka Peak. *J. Geophys. Res.* **2001**, *106* (D7), 7449–7461.
- (22) Parrish, D. D.; Dunlea, E. J.; Atlas, E. L.; Schaufli, S.; Donnelly, S.; Stroud, V.; Goldstein, A. H.; Millet, D. B.; Mckay, M.; Jaffe, D. A.; Price, H. U.; Hess, P. G.; Flocke, F.; Roberts, J. M. Changes in the photochemical environment of the temperate North Pacific troposphere in response to increased Asian emissions. *J. Geophys. Res.* **2004**, *109*, D23S18, doi: 10.1029/2004JD004978.
- (23) Jaeglé, L.; Steinberger, L.; Martin, R. V.; Chance, K. Global partitioning of NO_x sources using satellite observations: Relative roles of fossil fuel combustion, biomass burning and soil emissions. *Faraday Discuss.* **2005**, *130*, 407–423, doi: 10.1039/b502128f.
- (24) Westerling, A. L.; Gershunov, A.; Brown, T. J.; Cayan, D. R.; Dettinger, M. D. Climate and fire in the western United States. *Bull. Am. Meteorol. Soc.* **2003**, *84* (5), 595–604.
- (25) Spracklen, D. V.; Logan, J. A.; Mickley, L. J.; Park, R. J.; Yevich, R.; Westerling, A. L.; Jaffe, D. Fires drive interannual variability of organic carbon aerosol in the Western U.S. in summer: Implications for trends. *Geophys. Res. Lett.* **2007**, *34*, L16816, doi: 10.1029/2007GL030037.
- (26) Jaffe, D. A.; Hafner, W.; Chand, D.; Westerling, A.; Spracklen, D. V. Inter-annual variations in Wildfire PM_{2.5} due to wildfires in the Western U.S. *Environ. Sci. Technol.* **2008**, *42*, 2812–2818.
- (27) National Park Service (NPS), Assessment of Air Quality and Air Pollutant Impacts in National Parks of the Rocky Mountains and Northern Great Plains, Chapter 6: Glacier National Park, 1998, Available at <http://www2.nature.nps.gov/air/Pubs/pdf/reviews/rm/RMtoc.pdf> and <http://www2.nature.nps.gov/air/Pubs/pdf/reviews/rm/RM6glac.pdf>.
- (28) IPCC, 2007. *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*; Solomon, D., Qin, M., Manning, Z., Chen, M., Marquis, K.B., Averyt, M., Tignor, H.L., Miller, Eds.; Cambridge University Press: Cambridge, United Kingdom and New York, NY, 2007.
- (29) Ashmore, M. R. Assessing the future global impacts of ozone on vegetation. *Plant Cell Environ.* **2005**, *28* (8), 949–964.
- (30) Sitch, S.; Cox, P. M.; Collins, W. J.; Huntingford, C. Indirect radiative forcing of climate change through ozone effects on the land-carbon sink. *Nature* **2007**, *448*, 791–794.
- (31) Randerson, J. T.; Liu, H.; Flanner, M. G.; Chambers, S. D.; Jin, Y.; Hess, P. G.; Pfister, G.; Mack, M. C.; Treseder, K. K.; Welp, L. R.; Chapin, F. S.; Harden, J. W.; Goulden, M. L.; Lyons, E.; Neff, J. C.; Schuur, E. A. G.; Zender, C. S. The impact of boreal forest fire on climate warming. *Science* **2006**, *314*, 1130.

ES800084K