

# Influence of Fires on O<sub>3</sub> Concentrations in the Western U.S.

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Because forest fires emit substantial NO<sub>x</sub> and hydrocarbons—known contributors to O<sub>3</sub> production—we hypothesize that interannual variation in western U.S. O<sub>3</sub> 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 O<sub>3</sub> mixing ratios from nine rural Clean Air Status and Trends Network (CASTNET) and National Park Service (NPS) sites. Large fire years exhibited widespread enhanced O<sub>3</sub>. The summer BA was significantly correlated with O<sub>3</sub> at all sites. For each 1 million acres burned in the western U.S. during summer, we estimate that the daytime mean O<sub>3</sub> was enhanced across the region by 2.0 ppbv. For mean and maximum fire years, O<sub>3</sub> was enhanced by an average of 3.5 and 8.8 ppbv, respectively. At most sites O<sub>3</sub> 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 O<sub>3</sub> production and destruction in a high NO<sub>x</sub> environment. BC was a slightly better predictor of O<sub>3</sub>, compared with BA. The relationship between O<sub>3</sub> 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 O<sub>3</sub> were not significantly correlated. This indicates that the presence of fire is a more important predictor for O<sub>3</sub> than is temperature.

## I. Introduction

Biomass burning generates substantial emissions of aerosols and gases, including nonmethane hydrocarbons (NMHCs) and NO<sub>x</sub> (NO + NO<sub>2</sub>). Combined with sunlight, these precursors result in significant photochemical production of O<sub>3</sub>. However, this process is complex and depends on numerous factors including emissions, temperature, the NMHC/NO<sub>x</sub> 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<sub>x</sub> tend to be greatest during the flaming stage of combustion (2).

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It has been known for some time that large scale biomass burning can result in significant O<sub>3</sub> production (3). More recently, several studies have shown that large scale fires can have far reaching influence on O<sub>3</sub> (4–11). In some cases, the smoke and O<sub>3</sub> 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 O<sub>3</sub> 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 O<sub>3</sub>. 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 O<sub>3</sub> in the western U.S. has increased approximately 4 ppbv (20). Several hypotheses were put forward to explain this trend, including changing anthropogenic NO<sub>x</sub> emissions, changing global background O<sub>3</sub> 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 O<sub>3</sub> and particulate matter (PM). In this paper we evaluate the influence of fires on O<sub>3</sub> in this region. Because O<sub>3</sub> 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 O<sub>3</sub> 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 O<sub>3</sub> at these nine rural sites across the western U.S. In a separate analysis, we have examined how fires influence PM<sub>2.5</sub> 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 O<sub>3</sub> data are used. For this reason, we combined fire and O<sub>3</sub> data for the summer months of June, July, and August. These three months are responsible for 70–93% of annual acres

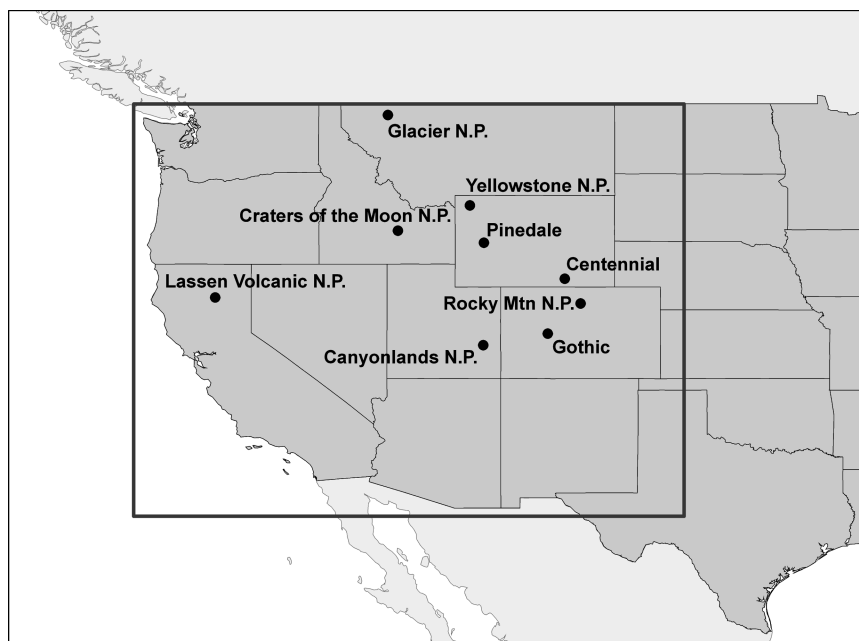


FIGURE 1. Ozone monitoring locations and fire region used in this analysis. The fire database covers the region between 101–125° W and 31–49° N (shown by a box).

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 <sup>a</sup>
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

<sup>a</sup> This column gives the number of days in the data record with 8 h daily maximum O<sub>3</sub> 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.** O<sub>3</sub> 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 O<sub>3</sub> 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).

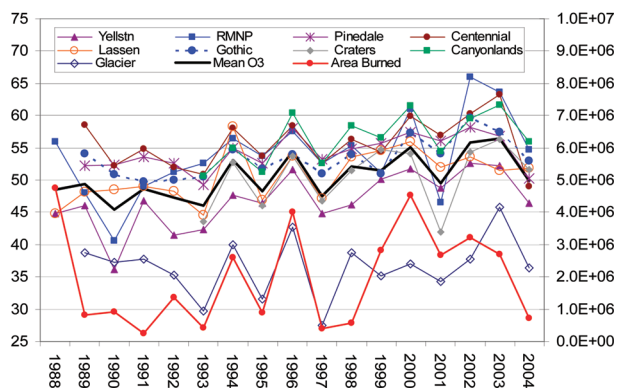
At all sites O<sub>3</sub> has been measured using UV absorption and using a standard calibration procedure. While this network of sites has been maintained consistently, there have been some changes over the nearly two decades of observations. This includes a change in the inlet height at most sites 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 O<sub>3</sub> data, there was no discernible influence on daytime O<sub>3</sub> 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 O<sub>3</sub> 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 O<sub>3</sub> 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 O<sub>3</sub> 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 O<sub>3</sub> concentrations at Lassen were significantly correlated with O<sub>3</sub> 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 O<sub>3</sub> are, at



**FIGURE 2.** Annual summer daytime O<sub>3</sub> 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 O<sub>3</sub> 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 O<sub>3</sub> mixing ratios using the summer data only.

Figure 2 shows the summer mean O<sub>3</sub> 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 O<sub>3</sub>. For example, mean, daytime O<sub>3</sub> 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).

O<sub>3</sub> mixing ratios at Glacier National Park are consistently lower than all other sites by 15–20 ppbv. In addition, PM<sub>2.5</sub> 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 O<sub>3</sub> and PM<sub>2.5</sub> monitoring site (27). Emissions from this facility include particulate fluorides, PAHs, NO<sub>x</sub> and other compounds. Thus, it is likely that O<sub>3</sub> 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 O<sub>3</sub> 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 O<sub>3</sub> and Burned Area and/or Biomass Consumed.** Summer O<sub>3</sub> 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, O<sub>3</sub> 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<sub>x</sub> emissions and reduced photochemistry from the smoke probably reduced O<sub>3</sub> 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 O<sub>3</sub> mixing ratios locally, whereas fires further afield result in significant O<sub>3</sub> 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 O<sub>3</sub> from these nine sites are significantly correlated with burned area for the western U.S. The regression equations for the relationship between mean O<sub>3</sub> 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 O<sub>3</sub> 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 O<sub>3</sub> of 3.5 and 8.8 ppbv, respectively, across the entire western U.S.

We also examined the relationship between O<sub>3</sub> and fires at individual sites. This was done by looking at the correlation between O<sub>3</sub> 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 O<sub>3</sub> 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 O<sub>3</sub><sup>a</sup>

	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*

<sup>a</sup> 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 O<sub>3</sub> at Nine Sites<sup>a</sup>**

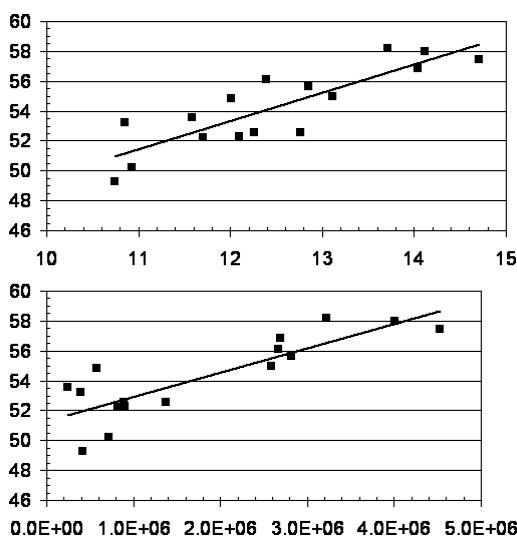
	Yellow-stone	Rocky Mountain	Pinedale	Centen.	Lassen	Gothic	Glacier	Craters of the Moon	Canyon-lands
all western U.S. BA	0.714 <sup>b</sup>	0.544 <sup>b</sup>	0.840 <sup>b</sup>	0.668 <sup>b</sup>	0.730 <sup>b</sup>	0.667 <sup>b</sup>	0.459	0.544	0.724 <sup>b</sup>
10 × 10° BA	0.600 <sup>b</sup>	0.644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

<sup>a</sup> 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. <sup>b</sup> BA refers to burned area; BC refers to biomass consumed.

**TABLE 4. Average Daytime O<sub>3</sub> 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 <sub>3</sub> (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 O<sub>3</sub> results show the mean of all daytime data (1000–1800 local time) for each site.



**FIGURE 3. a,b: Scatterplot of summer mean O<sub>3</sub> (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  $y = 1.62 \times 10^{-6}x + 51.3$  ( $R^2 = 0.708$ ).**

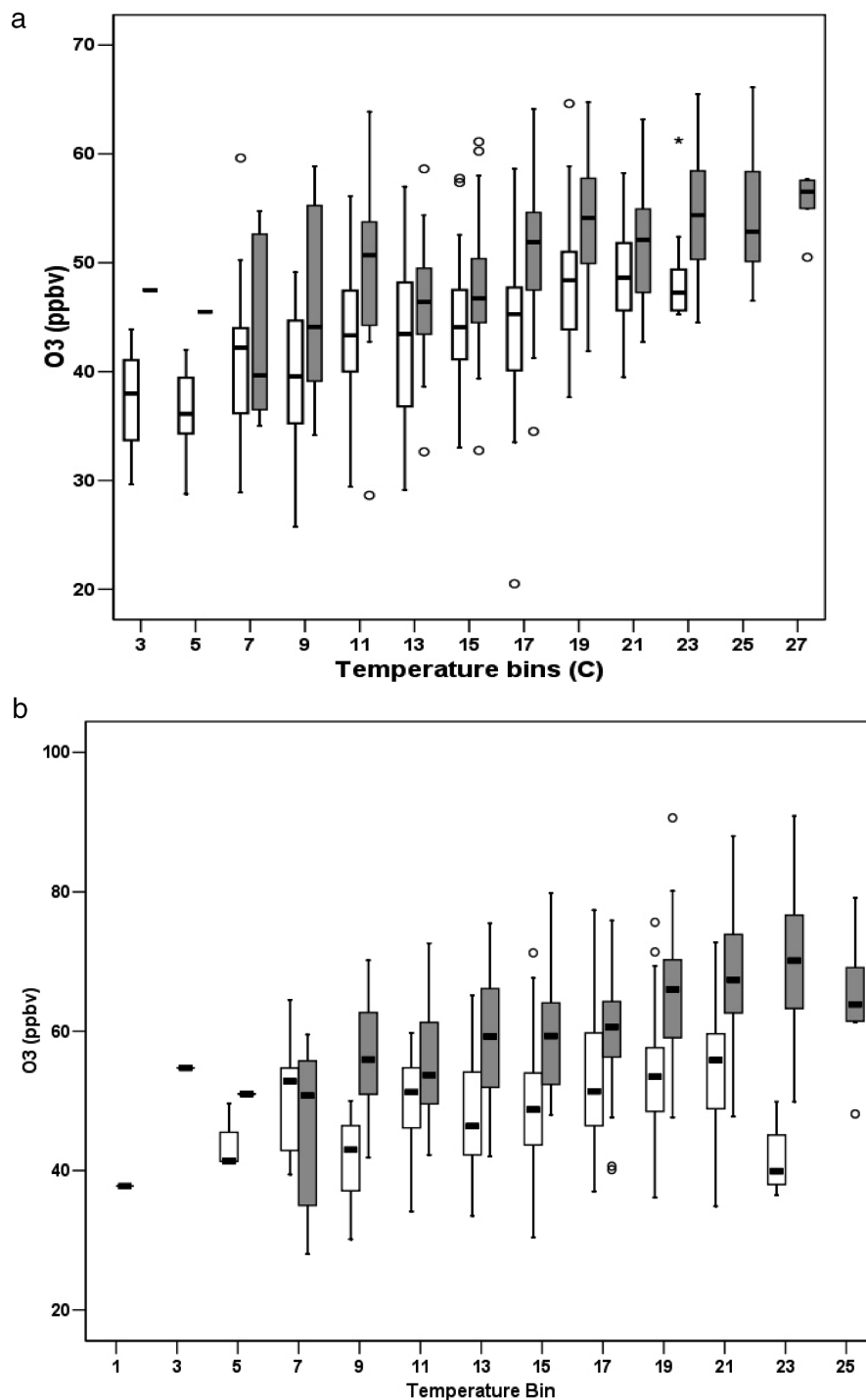
with burned area, both in terms of the number of significant correlations and the magnitude of the  $R^2$  value. For the 10 × 10° region, all sites are significantly correlated with biomass consumed, and all but Craters of the Moon are correlated with burned area. This scale appears to give the best correlation between fires and O<sub>3</sub>. 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 O<sub>3</sub>, due to the combined effects of NO<sub>x</sub> 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 O<sub>3</sub> 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 O<sub>3</sub> production. In our previous work (20), we examined the correlation between seasonal mean temperatures and O<sub>3</sub> mixing ratios. During the warm months (May–September) and only at some sites, temperature was found to be positively correlated with O<sub>3</sub> mixing ratios,

To examine the role that temperature variations play on O<sub>3</sub>, we evaluated daily 8 h daytime (1000–1800 local time) temperature and O<sub>3</sub> 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 O<sub>3</sub> for the high and low fire years. As described previously, high fire years have significantly greater O<sub>3</sub> mixing ratios.

To assess the relationship between warm years and O<sub>3</sub> we evaluated the correlation between seasonal daytime temperature and O<sub>3</sub> at both YNP and RMNP. We found that these correlations are much weaker, and not statistically significant, in contrast to the correlations between O<sub>3</sub> and burned area (or biomass consumed). For YNP, the correlation between daytime seasonal mean O<sub>3</sub> and temperature yields an  $R^2$  of 0.224 compared to an  $R^2$  of 0.351 for the correlation of O<sub>3</sub> 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 O<sub>3</sub> levels, warm years alone do not lead to high O<sub>3</sub> mixing ratios.

We also examined daily temperature and O<sub>3</sub> variations at YNP and RMNP. Daily (8 h) temperature and O<sub>3</sub> 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 O<sub>3</sub> 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 O<sub>3</sub>. Instead, transport from other regions is likely to play a significant role in explaining O<sub>3</sub> mixing ratios.

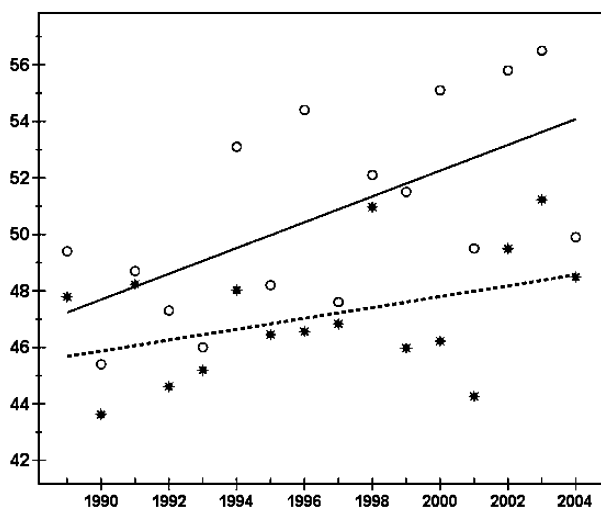


**FIGURE 4.** a. Comparison of daily daytime (1000–1800 local time) O<sub>3</sub> and temperature data from Yellowstone N.P. The data are sorted by average daytime temperature in 2 °C increments. Gray boxes show data for the high fire years and white boxes show the low fire years (see Table 4). Both 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 O<sub>3</sub>-temperature relationship further, Figure 4 shows box plots of the daytime O<sub>3</sub> distribution sorted by daily temperature, in 2 °C bins, for the high and low fire years for two sites. For nearly all temperature bins, O<sub>3</sub> is greater during the high fire years. For example, in the 19 °C bin for YNP (Figure 4), high fire years have mean daytime O<sub>3</sub> 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 O<sub>3</sub> mixing ratios are much higher at the same temperature

indicates that local temperature is not the dominant factor in explaining the enhanced O<sub>3</sub>. Instead, enhanced emissions from the fires and/or regional accumulation of photochemically generated O<sub>3</sub> are likely the primary causes for enhanced O<sub>3</sub> during high fire years.

Further analysis of this daily O<sub>3</sub>-temperature relationship suggests some differences between YNP and RMNP. For YNP the O<sub>3</sub>-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 O<sub>3</sub> (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 O<sub>3</sub>, compared to burned area or biomass consumed.

## Discussion and Summary

We previously reported a significant positive trend in O<sub>3</sub> 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 O<sub>3</sub>. In Table 3 we show that fire area burned or biomass consumed are significantly correlated with interannual variations in O<sub>3</sub>, 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 O<sub>3</sub> may also be important. The question arises as to whether an increase in fire extent is responsible for the positive trend in O<sub>3</sub> in the western U.S.

Figure 5 shows summer mean O<sub>3</sub> mixing ratios averaged at the nine sites for 1989–2004, along with an estimated O<sub>3</sub> concentration in the absence of fires for each year. This was done by using the O<sub>3</sub>-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 O<sub>3</sub> reported

by Jaffe and Ray (20). However, fires cannot explain the trend in O<sub>3</sub> reported for other seasons (20).

As mentioned previously, summer average O<sub>3</sub> 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 O<sub>3</sub> was not found (20). Additionally, summertime PM<sub>2.5</sub> at Glacier N.P. is 1–2.5  $\mu$ g/m<sup>3</sup> higher than any other sites in the region. The presence of significantly lower O<sub>3</sub> and higher PM<sub>2.5</sub> 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 O<sub>3</sub> and PM monitor (27). Thus, we believe the Glacier N.P. site is not representative of regional atmospheric conditions, for both O<sub>3</sub> and PM.

Based on our analysis of nine rural sites, fires play a significant role on O<sub>3</sub> in the western U.S. The next logical step in this analysis would be to evaluate how fires influence exceedances of the 8-h O<sub>3</sub> 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 O<sub>3</sub> concentrations thus increasing the likelihood of an exceedance of the 8-h standards.

Our analysis of the relationship between temperature and O<sub>3</sub> 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 O<sub>3</sub> were not significantly correlated. This indicates that the presence of fire is a more important predictor for O<sub>3</sub>, 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 O<sub>3</sub> 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.; Surtipito, 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<sub>x</sub> 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<sub>2.5</sub> 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) Sitoh, 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.

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*Supplementary on-line materials for the paper:*

**Influence of Fires on O<sub>3</sub> Concentrations in the Western U.S.**

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Submitted to Environmental Science and Technology, January 2008

**Table A1:**

**Summer burned area (BA) for the years 1989-2004 in a 10<sup>0</sup>x10<sup>0</sup> box around each site.**

**Area burned (acres)**

Year	Western U.S.	Yellow -stone	Rocky Moun-tain	Pine-dale	Centen-nial	Lassen	Gothic	Glacier	Craters of the Moon	Canyon-lands
1989	8.21E5	7.70E4	1.27E5	1.22E5	1.31E5	1.60E5	1.41E5	3.19E5	4.31E5	1.81E5
1990	9.04E5	1.65E5	3.08E4	1.80E5	2.35E4	5.21E5	5.44E4	1.40E5	2.53E5	1.97E5
1991	2.41E5	1.05E5	1.65E4	1.07E5	4.31E4	3.00E4	9.19E3	8.40E4	1.66E5	6.29E4
1992	1.37E6	3.42E5	4.36E3	3.48E5	7.61E3	3.59E5	8.71E3	7.12E5	9.04E5	3.87E5
1993	4.13E5	3.21E4	4.16E4	4.64E4	3.40E4	6.35E4	4.53E4	5.64E3	3.09E4	1.70E5
1994	2.59E6	4.22E5	1.20E5	4.97E5	1.26E5	6.19E5	1.34E5	9.30E5	1.32E6	5.96E5
1995	8.92E5	1.66E5	2.13E4	2.11E5	2.53E4	9.69E4	3.77E4	3.77E4	4.44E5	4.53E5
1996	4.00E6	9.60E5	2.31E5	1.35E6	2.68E5	1.69E6	2.76E5	1.05E6	2.31E6	1.40E6
1997	3.91E5	2.36E4	2.12E4	5.16E4	2.05E4	1.87E5	2.28E4	3.09E4	9.58E4	6.42E4
1998	5.78E5	1.42E5	2.62E4	1.64E5	2.19E4	1.73E5	2.08E4	9.89E4	2.84E5	2.15E5
1999	2.82E6	3.57E5	2.63E4	3.81E5	2.80E4	1.34E6	4.20E4	2.44E5	1.99E6	4.08E5
2000	4.53E6	2.30E6	4.43E5	2.42E6	6.75E5	8.13E5	5.00E5	2.06E6	3.24E6	1.24E6
2001	2.67E6	3.06E5	1.10E5	2.39E5	1.52E5	8.48E5	1.04E5	2.97E5	1.09E6	2.05E5
2002	3.22E6	5.22E5	1.12E6	8.98E5	1.22E6	1.30E6	1.10E6	2.65E5	8.01E5	9.94E5
2003	2.69E6	1.44E6	3.67E5	1.26E6	7.97E5	2.32E5	3.23E5	9.92E5	1.04E6	4.14E5
2004	7.19E5	3.76E4	5.73E4	5.54E4	5.93E4	2.11E5	1.84E5	4.05E4	6.74E4	2.36E5

\*All data is for summer daytime, defined by June-August, 1000-1800 local standard time. For individual sites, area burned and biomass consumed are for the 10<sup>0</sup>x10<sup>0</sup> region surrounding each site.

**Table A2: Summer biomass consumed (BC) by wildfires for the years 1989-2004 in a 10°x10° box around each site.**

Biomass consumed (kg)

Year	Western U.S	Yellstn	RMNP	Pine-dale	Centen .	Lassen	Gothic	Glacier	Craters	Canyon-lands
1989	5.29E9	4.45E8	8.87E8	5.79E8	9.39E8	9.01E8	9.39E8	3.23E9	3.54E9	6.79E8
1990	7.19E9	1.25E9	1.03E8	1.27E9	1.43E8	5.22E9	1.96E8	1.38E9	1.53E9	1.12E9
1991	1.33E9	7.78E8	1.48E8	7.73E8	4.96E8	8.38E7	5.26E7	7.30E8	8.01E8	1.20E8
1992	1.08E10	1.42E9	2.00E7	1.42E9	5.55E7	4.90E9	5.40E7	4.88E9	5.12E9	1.49E9
1993	7.29E8	6.71E7	1.10E8	1.12E8	7.13E7	2.09E8	1.21E8	1.38E7	5.76E7	3.03E8
1994	1.86E10	2.79E9	8.41E8	2.74E9	9.17E8	4.81E9	7.84E8	9.44E9	1.01E10	1.52E9
1995	1.79E9	2.96E8	6.99E7	4.82E8	1.19E8	2.77E8	1.50E8	1.00E8	5.25E8	9.95E8
1996	1.96E10	5.80E9	7.35E8	6.64E9	1.20E9	1.01E10	8.17E8	6.70E9	8.24E9	5.15E9
1997	1.25E9	7.91E7	1.37E8	1.54E8	1.37E8	5.92E8	1.45E8	1.33E8	2.36E8	1.79E8
1998	1.94E9	4.45E8	9.01E7	5.22E8	1.33E8	5.37E8	9.62E7	5.27E8	7.51E8	3.91E8
1999	8.32E9	1.22E9	1.01E8	1.28E9	1.23E8	5.55E9	2.11E8	1.19E9	2.46E9	1.14E9
2000	3.60E10	2.15E10	2.47E9	2.20E10	4.95E9	2.17E9	2.73E9	2.74E10	2.89E10	4.02E9
2001	1.74E10	2.76E9	1.09E9	1.63E9	1.75E9	3.52E9	8.14E8	3.15E9	3.78E9	6.93E8
2002	3.49E10	4.15E9	8.41E9	6.22E9	9.47E9	2.15E10	8.08E9	2.03E9	4.01E9	6.52E9
2003	2.66E10	1.69E10	3.13E9	1.47E10	8.16E9	2.61E9	2.23E9	1.17E10	1.18E10	2.22E9
2004	6.02E9	3.16E8	2.82E8	3.48E8	3.66E8	3.24E9	6.65E8	2.26E8	2.99E8	7.43E8

\*All data is for summer daytime, defined by June-August, 1000-1800 local standard time. For individual sites, area burned and biomass consumed are for the 10°x10° region surrounding each site.

**Table A3: Summer mean O<sub>3</sub> mixing ratio at each site for the years 1989-2004.**Summer average O<sub>3</sub> mixing ratio (ppbv)

<b>Year</b>	<b>9 site average</b>	<b>Yellstn</b>	<b>RMNP</b>	<b>Pine-dale</b>	<b>Centen.</b>	<b>Lassen</b>	<b>Gothic</b>	<b>Glacier</b>	<b>Craters</b>	<b>Canyon-lands</b>
1989	49.4	46.0	48.1	52.2	58.6	48.2	54.1	38.8	No data	No data
1990	45.4	36.2	40.5	52.3	52.3	48.5	50.9	37.3	No data	No data
1991	48.7	46.8	49.0	53.6	54.8	49.0	49.8	37.8	No data	No data
1992	47.3	41.5	51.3	52.6	52.0	48.3	50.0	35.3	No data	No data
1993	46.0	42.3	52.7	49.3	50.9	44.6	50.5	29.7	43.6	50.6
1994	53.1	47.6	56.5	55.0	58.0	58.3	54.7	39.9	52.8	55.0
1995	48.2	46.4	53.7	52.6	53.8	46.9	51.7	31.5	46.1	51.2
1996	54.4	51.6	57.5	58.0	58.4	53.7	53.9	42.7	53.7	60.4
1997	47.6	44.9	52.6	53.3	52.6	47.1	50.9	27.4	46.8	52.7
1998	52.1	46.2	55.4	54.9	56.3	53.5	53.9	38.8	51.5	58.4
1999	51.5	50.2	51.1	55.7	54.3	54.6	50.9	35.1	54.6	56.6
2000	55.1	51.8	61.1	57.5	59.8	56.0	57.4	37.0	54.1	61.5
2001	49.5	48.8	46.5	56.1	57.0	52.0	54.0	34.2	41.9	54.5
2002	55.8	52.6	65.9	58.2	60.3	53.6	59.7	37.8	54.3	59.6
2003	56.5	52.2	63.6	56.8	63.2	51.5	57.5	45.8	56.4	61.6
2004	49.9	46.4	54.7	50.2	49.1	51.8	53.0	36.4	51.6	55.9