Ozone distribution and phytotoxic potential in mixed conifer forests of the San Bernardino Mountains, southern California

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Although peak ozone concentrations have greatly decreased in the San Bernardino Mountains, very high ozone phytotoxic potential remains.

Abstract

In the San Bernardino Mountains of southern California, ozone (O3) concentrations have been elevated since the 1950s with peaks reaching 600 ppb and summer seasonal averages >100 ppb in the 1970s. During that period increased mortality of ponderosa and Jeffrey pines occurred. Between the late 1970s and late 1990s, O3 concentrations decreased with peaks \( \leq 180 \) ppb and \( \leq 60 \) ppb seasonal averages. However, since the late 1990s concentrations have not changed. Monitoring during summers of 2002–2006 showed that O3 concentrations (2-week averages) for individual years were much higher in western sites (58–69 ppb) than eastern sites (44–50 ppb). Potential O3 phytotoxicity measured as various exposure indices was very high, reaching SUM00 \( \leq 173.5 \) ppm h, SUM60 \( \leq 112.7 \) ppm h, W126 \( \leq 98.3 \) ppm h, and AOT40 \( \leq 75 \) ppm h, representing the highest values reported for mountain areas in North America and Europe.

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1. Introduction

In the Los Angeles Basin (LA Basin) severe episodes of photochemical smog (also known as the Los Angeles type smog) have been known since the early 1950s (Turco, 1997). In the summer season, emissions of nitrogen oxides (NOx), carbon monoxide (CO), and volatile organic compounds (VOCs) from millions of cars, and to a smaller degree also from stationary air pollution sources, are trapped in a thermal inversion layer of air. High temperature and solar radiation promote complex photochemical reactions that produce various secondary air pollutants, among them highly toxic ozone (O3) (Finlayson-Pitts and Pitts, 1986). Contaminated LA Basin air masses move inland with the westerly on-shore winds and are pushed against the San Bernardino Mountains (SBM). Because the marine inversion layer typically does not exceed 915 m (Bailey, 1966) and the SBM crest is about 1700–2000 m high, these mountains effectively trap contaminated air masses (Fujioka et al., 1999). As a result, very high O3 concentrations occur in the western side of the range facing the LA Basin. In the 1970s, when the first reliable measurements of O3 started, peak concentrations could reach 600 ppb (National Academy of Sciences, 1977), and national and state air pollution standards were exceeded during most of the photochemical smog season (http://www.arb.ca.gov/html/brochure/history/htm). During that time it was also determined that the mysterious “X” disease killing thousands of sensitive ponderosa (Pinus ponderosa) and Jeffrey (Pinus jeffreyi) pines in the SBM in the 1950s was caused by high O3 concentrations in combination with frequent drought stress and severe bark beetle attacks (Miller et al., 1963; Taylor,
This was the first worldwide evidence of a large-scale decline of coniferous forests caused by ambient O₃ (Mackenzie and El-Ashty, 1989).

While the U.S. population has nearly doubled since 1950, it has tripled in the state of California and grown even more in southern California (U.S. Census Bureau, 2006). Historical and projected population changes for the six counties of the Southern California Association of Governments (SCAG) region indicate that growth was highest in those counties from which emissions may directly affect the air pollution status of the SBM. The highest population growth between 1960 and 2000 was recorded in Riverside County (5.05-fold increase), Orange County (4.04-fold increase), and San Bernardino County (3.4-fold increase), compared with only 1.58-fold growth in Los Angeles County (http://www.scag.ca.gov/livable/download/pdf/GV1950_2025.pdf). These demographic changes led to increased traffic in eastern parts of the LA Basin, resulting in modified distribution of air pollution throughout the LA Basin and in the adjacent areas.

At the same time, during this rapid expansion of the southern California population, numerous air pollution control initiatives were initiated by the California Air Resources Board (CARB) and implemented by the South Coast Air Quality Management District (SCAQMD). In 1975, the first two-way catalytic converters came into use as part of the CARB Motor Vehicle Emission Control Program. In 1984, the California Smog Check Program aimed at identifying vehicles in need of maintenance and ensuring the effectiveness of their emission control systems on a biennial basis. The 1992 Phase I California Cleaner Burning Gasoline (CBG) resulted in 220 tons reduction of reactive organic gases (ROG) released every day (6% reduction) and elimination of lead in gasoline. In the same year, CARB required addition of oxygenates to gasoline to cut CO emissions by 10%. In 1993, CARB enacted new standards for cleaner diesel fuels, resulting in a reduction of NOₓ by 70 tons/day. In 1996, California Phase II of CBG further reduced amounts of O₃ precursors by 300 tons/day. This reduction was equivalent to taking 3.5 million cars off the road. All these measures led to significant reductions of pollutant emissions resulting in substantially lowered ambient O₃ concentrations in the LA Basin and the adjacent SBM.

In the Northern Hemisphere there is a general trend of increasing background levels of O₃ due to long-range transport of its precursors (NOₓ, CO, and VOCs) to remote areas (Elvingson, 2003). This trend is influenced by long-range transport of polluted air masses: trans-Pacific from Asia to North America, trans-Atlantic from North America to Europe, and transcontinental from Europe to Asia. Rapid industrial growth without effective air pollution control and increasing number of internal combustion engine vehicles in Asia, especially in China and India, will probably be the main causes of the increasing background concentrations of tropospheric O₃ in the coming years. While it is expected that peak values of the pollutant will stay below 200 ppb, it is also predicted that the steadily increasing background O₃ concentrations in parts of Asia, North America, or Europe will cause negative changes in forests (Fowler et al., 1999).

Air pollution control measures introduced in the LA Basin resulted in reduction of O₃ concentrations in the SBM. The 1991–1993 air quality monitoring at Barton Flats (BF) showed that concentrations of O₃ rarely exceeded 200 ppb, but that the 120 ppb h national air pollution standard was still exceeded on about 20% of days (Watson et al., 1999). This significant improvement in air quality also resulted in the improvement of forest conditions in the SBM and much lower tree mortality rates (Arbaugh et al., 1998; McBride and Miller, 1999). However, measurements at the Crestline (CR) monitoring site indicated that since 1999, similarly to the Pomona site in the LA Basin, O₃ peak concentrations have generally not changed (Fig. 1).

In the early 2000s, a widespread dieback of trees in the SBM started to take place due to prolonged drought, overstocking of forests caused by long-term fire suppression, air pollution, and bark beetle infestation that eventually resulted in a death of 4.6 million trees (Christensen et al., 2007). Such enormous amounts of dead biomass caused a very serious risk to the remaining forests and to the local population. The 2003 fires in the SBM (Keeley et al., 2004) showed that a very high probability of catastrophic fires exists in southern California mountainous forests.

Long-term information on spatial and temporal O₃ distribution trends in the SBM is essential for understanding the O₃ phytotoxic potential for forests and health risks to the SBM inhabitants. Therefore, a network of passive samplers and active instruments for O₃ monitoring was established in the SBM in 2002 in order to better understand O₃ distribution and its phytotoxic potential.

2. Materials and methods

2.1. Monitoring network

Eighteen sites for air pollution and forest health monitoring were used in the SBM in 2002 (Fig. 2). These included 10 Forest Health sites previously
established in 1968–1974 study (Miller et al., 1963), such as Camp Paivika (CP), Breezy Point (BP), Mill Creek (Mill), Miller Canyon (MC1: 2002–2004; MC2: 2005–2006), Strawberry Peak (SP), Tunnel 2 (T2), Rim of the World (RW), Heaps Peak (HP), Snow Valley (SV), Green Valley (GV), Keller Peak (KP), Camp Angeles (CA), Arctic Circle (AC), Converse Flats (CF), Holcomb Valley (HV), Barton Flats (BF), Heart Bar (HB), and Onyx Summit (OS); and eight recently established sites (Arbaugh et al., 2003), including Mill Creek (Mill), Miller Canyon (MC1 [2002–2004] and MC2 [2005–2006]), Strawberry Peak (SP), Rim of the World (RW), Heaps Peak (HP), Keller Peak (KP), Arctic Circle (AC), and Converse Flats (CF). The sites were selected following ground inspection and available information on distribution of photochemical smog, soil condition, forest condition, and stand/tree health (Arbaugh et al., 2003). Air quality monitoring sites were selected in open-terrain locations (such as forest clearings, burnt areas, forest nurseries, etc.) on a western aspect, at least 100 m from local roads and 200 m from main roads. Free air movement from all directions was required, but sites exposed to continuously strong winds were avoided. Passive samplers for O₃ monitoring were placed at a distance at least two times the height of the tallest tree from forest edges, however, sparsely dispersed smaller trees or shrubs that did not directly obstruct the samplers were allowed. Passive samplers were exposed for 2-week periods during summer and fall seasons of 2002–2006. Monitoring was performed between May and October/November with the beginning and end of the monitoring campaigns depending on weather conditions. Samplers in protective caps were hung on wooden stands about 2 m above ground level. In addition, real-time monitoring of O₃ was performed at Crestline (CR) by the California Air Resources Board (CARB), at KP and OS by the USDA Forest Service, and at CF by the Clean Air Status and Trends Network (CASTNET). For a comparison with the LA Basin, results of O₃ monitoring at the San Bernardino (SB) site operated by CARB were also used.

2.2. Equipment and chemical analyses

Real-time concentrations were monitored with UV absorption instruments: 2B Technologies Model 202 at KP and OS sites and Thermo Environmental Model 49 C at the CF, CR, and SB sites. The 2B Technologies’ monitors were calibrated before each season by the manufacturer, while the Thermo Environmental instruments were calibrated once a month according to the CASTNET and CARB protocols.

Ogawa samplers (Ogawa & Co., USA, Inc., Pompano Beach, Florida) were used to measure 2-week O₃ concentrations (Koutrakis et al., 1993). In each sampler, two replicate cellulose filters saturated with nitrite (NO₂⁻) were used. Nitrite on the cellulose filters is oxidized by ambient O₃ to nitrate (NO₃⁻). Nitrate was extracted from passive sampler filters with ultra pure deionized water, and its concentration was determined by ion chromatography ( Dionex, Model DX 600). A rate of NO₃⁻ formation for each sample was calculated. These rates were compared to the real-time O₃ concentration obtained by UV absorption instruments at the collocated sites. Based on these comparisons, empirical coefficients (averages of all individual comparisons from the collocated sites and exposure periods) were derived for every year of the study. These coefficients were used for calculation of 2-week long average O₃ concentrations.

2.3. Geostatistical analysis

Pollutant distribution maps were developed with the Geostatistical Analyst, extension of ArcGIS software (Environmental Systems Research Institute, Redlands, CA). The Geostatistical Analyst uses values measured at sample points at different locations in the landscape and converts them (through interpolation and extrapolation) into a continuous surface. Using a set of pollutant concentration measurements for the study area, a spatial model of O₃ concentration was constructed using the inverted distance weighted (IDW) method (Johnston et al., 2001).
of hours when concentrations of O₃ exceeded 100 ppb. The SUM00 index is an exposure dose resulting from multiplying all hourly concentrations by time (h). Indices SUM60, SUM70, SUM80, SUM100 and SUM120 were derived by multiplying number of hours when O₃ concentrations stayed above >60 ppb, >70 ppb, >80 ppb, >100 ppb and >120 ppb, respectively, by those concentrations. The W126 is a sigmoidally weighted index (Lefohn and Runeckless, 1987) in which higher concentrations has a greater weighing. Concentrations. The W126 is a sigmoidally weighted index (Lefohn and Runeckless, 1987) in which higher concentrations has a greater weighing. All these O₃ exposure indices were calculated for 24 h for 4 month periods. Among the calculated indices, N100, SUM00, SUM60 and W126 are most commonly used in the United States (Musselman et al., 2006). The SUM00 index has been successfully used for predicting O₃ phytotoxic effects on ponderosa and Jeffrey pines in the California mountains (Arbaugh et al., 1998). The SUM60 and W126 have been suggested as the most acceptable vegetation exposure indices by the U.S. Environmental Protection Agency (U.S. EPA, 1996). The N100 index combined with the W126 or SUM60 indices has been used as a surrogate for peak hourly concentrations that may affect vegetation sensitivity to O₃ (Musselman et al., 2006).

In addition, for a comparison with the European studies, AOT40 exposure index was also calculated. It is a cumulative dose of values >40 ppb for the standardized daylight hours (0800–2000 PST) during the 6 month growing season (April 1 to September 30) (Fuhrer, 1996). A critical level of O₃ (dose above which O₃ damage on trees could develop) at AOT40 values of 10,000 ppb h (10 ppm h) has been proposed (Bull, 1996).

### 3. Results

#### 3.1. Spatial and temporal distribution of 2-week average O₃ concentrations

Ranges and means of O₃ concentrations were generally similar during the 2002–2006 monitoring seasons (Table 1). Maps developed with the Geostatistical Analysts (Fig. 3a–j) present O₃ distribution trends during 5 years of monitoring for the entire seasons and for periods of the highest pollution. These trends are similar in all monitoring years. Consistently, the highest O₃ concentrations were recorded in the western part of the network, especially at the CP, RW, and HP sites. In 2003, high levels of O₃ were also detected along the Bear Creek drainage at KP and AC, as well as at HB in the east end of the Santa Ana River drainage. Consistently, during all 5 years of monitoring, the lowest O₃ concentrations were found north of Big Bear Lake at HV. Occasionally elevated O₃ levels were also recorded in the eastern side of the network at OS as those observed in 2006 (Fig. 3j).

#### 3.2. Trends in real-time O₃ concentrations

Summary of hourly O₃ concentration changes at the CR and CF sites during 2005 is shown in Fig. 4 as monthly maximum, mean, and minimum values. Both sites showed clear seasonal differences in mean monthly concentrations: very low in January and February, gradually increasing from March until July, and then decreasing to very low values in November and December. Maximum concentrations for both sites had very similar trends: low values in January and February, a sharp increase in March and April leading to 150 ppb at CR and 159 ppb at CF in May, a decline in June, another increase to the highest annual values of 170 ppb at CF in July and 182 ppb at CR in August, and then a sharp decline of concentrations until November and December. The CR minimum values (which occurred at nighttime) were at 0 ppb during most of the year with an exception of June and July; while at CF, minimum nighttime values were generally higher, at about 20 ppb (with an exception of 0 ppb in November).

### 3.4. Ozone exposure indices in selected sites


Only the CR and SB sites had O₃ data allowing for calculation of all exposure indices. The N100 index was clearly decreasing at CR and CF in time. At KP the index was higher in 2006 than in 2005, while at OS both 2005 and 2006 values were the same. The SB site did not show any clear trends in the temporal distribution of the N100 index (Fig. 6a). The SUM00 index at CR was the highest in 2002 and since 2004 there was a steady decrease of the index, similar to the CF and KP sites. There were no clear trends for the SB and OS site changes (Fig. 6c). Changes in the W126 index were similar to those described above for the SUM60 index (Fig. 6d).

### 3.4.2. Comparison of U.S. indices in 2005

For the SUM00 and SUM60 indices, values for CR, KP, and CF were the highest, while those for SB and OS were much lower. For the SUM70 through W126 indices, values at CR were consistently the highest, followed by CF and KP. For the SUM80 through W126 indices, SB had higher values than KP and OS (Fig. 7).
CR had highest AOT40 values during the entire evaluation period, which were much higher than those for the urban SB. For 2005 and 2006, when data from all the sites were available, CF values were lower than those at CR, while the KP values were similar to those at SB, and the OS values were the lowest (Table 2).

4. Discussion

4.1. Historical trends

Only limited historical information is available on the O3 pollution status of the SBM. Lee et al. (2003) reconstructed hourly O3 data for the CR site since 1963. Mean concentrations of O3 for the June–September periods obtained from that paper for 1963–2000 and for 2001–2006 from CARB (2006) are shown in Fig. 8. While mean O3 concentrations in 1970s could exceed 100 ppb, they gradually declined reaching a plateau oscillating around 60–70 ppb that began around 1995 and continues until today. This decline was much less pronounced than the sharply decreasing maximum hourly O3 concentrations at CR between 1974 and 1999 (Fig. 1). This phenomenon of a sharp decrease of maximum O3 concentrations and less pronounced decline of annual or summer average O3 concentrations is quite typical for the Northern Hemisphere, especially in remote mountainous areas (Brasseur et al., 2001). In the SBM a pronounced decrease of maximum O3 levels was caused by the effective air pollution control measures implemented in southern California in the late 1970s. Similar measures were later introduced in the
eastern United States and Europe, resulting in this trend of lowered O₃ peak values in the Northern Hemisphere. However, it is also predicted that O₃ emissions’ precursors from the rapidly increasing fleet of motor vehicles, especially in Asia, will elevate local mid-level O₃ concentrations and consequently the Northern Hemisphere O₃ background concentrations (Fowler et al., 1999).

4.2. Spatial distribution

Beginning in 1992, the reformulation of gasoline aimed at reducing O₃ concentrations in LA Basin urban areas delayed O₃ formation in the photochemical smog plume. This resulted in greater reduction of O₃ concentrations in the western LA Basin compared to its eastern part and the SBM. Consequently, a much less pronounced O₃ west-to-east gradient currently exists in the SBM compared to the 1970s (Miller et al., 1989). Such changes were already seen in the 2001 study — the summer average concentrations on the western end of the SBM gradient were at ~70 ppb, while those on the eastern end of the gradient were at ~50 ppb (compared with the 1974–1978 values of 115 ppb and 30 ppb, respectively) (Alonso et al., 2003). The reported trends in the distribution of O₃ revealed during this study indicate meteorological
stability of the region during the 2001–2006 seasons. In summer, with the LA Basin’s well-defined Mediterranean climate, the daytime westerly winds from the Pacific Ocean steadily move the polluted urban air masses from the LA Basin towards the SBM and around them through the Cajon and San Gorgonio Passes into the Mojave Desert (Fujioka et al., 1999). Although not as pronounced as in the 1970s, this movement of air masses results in the clearly defined and strong west-to-east O₃ air pollution gradient caused by the increased distance from the main pollution source area, the LA Basin. While concentrations of the pollutant are very high in the west end of the gradient (seasonal averages as high as 68 ppb, 2-week averages up to 88 ppb), they were very low at its east end (seasonal averages and 2-week averages as low as 44 ppb). Ozone concentrations at the high end of the gradient were comparable with 67 ppb determined during the 2003 summer season in the nearby Joshua Tree National Park (NP), which is the most polluted national park in the United States. These values were higher than 60 ppb measured during that period at the second most polluted national park, Sequoia and Kings Canyon NP (CASTNET, 2007). These comparisons confirm that although the present O₃ levels are much lower than the historic ones, parts of the SBM still experience the highest exposures to ambient O₃ in the United States.

As the urban sprawl continues and moves outside of the LA Basin into the Coachella Valley, traffic intensifies in the eastern part of the LA Basin and beyond the SBM along Interstate Freeway 10 in the Banning/Palm Springs/Indio areas. Consequently, elevated O₃ concentrations are found in western parts

Fig. 5. Diurnal distribution of O₃ concentrations during the June–September 2005 period in four mountain locations (CF, CR, KP, and OS) and the eastern part of the LA Basin (SB).

Fig. 6. Ozone exposure indices for four mountain locations (CR, CF, KP and OS) and the eastern part of the LA Basin (SB) between 2002 and 2006: (a) N100, (b) SUM00, (c) SUM60, and (d) W126.
of the Mojave Desert in the Coachella Valley and Joshua Tree NP (Allen et al., in press) further reducing the SBM west-to-east gradient.

4.3. Seasonal trends

Ozone monitoring at the CR and CF stations with UV absorption monitors allowed for determining seasonal trends of O₃ concentrations (Fig. 4). In winter months (January, February, and December 2006), mean O₃ concentrations were very low at the CR site (23 ppb) and much higher at the CV site (38 ppb). In 1991–1993 winters, O₃ concentration at Barton Flats (BF) near the CF site was also 38 ppb (Watson et al., 1999). Low O₃ values at the CR site in winter could be caused by its titration by the local traffic-generated NO. The CF site is much further away from the automobile traffic, and therefore O₃ concentrations are less affected by this potential effect. In March, mean O₃ concentrations were similar at both sites (32–26 ppb) and started increasing to 60–62 ppb in May. For the CF site the spring season mean was at 48 ppb, which was lower than the BF site value of 53 ppb during the 1991–1993 study (Watson et al., 1999). Low O₃ values at the CR site in winter could be caused by its titration by the local traffic-generated NO. The CF site is much further away from the automobile traffic, and therefore O₃ concentrations are less affected by this potential effect. In March, mean O₃ concentrations were similar at both sites (32–26 ppb) and started increasing to 60–62 ppb in May. For the CF site the spring season mean was at 48 ppb, which was lower than the BF site value of 53 ppb during the 1991–1993 study (Watson et al., 1999). In May, O₃ peak values of 150 ppb at CF and 159 ppb at CR could have negative effects on sensitive plants in their physiologically active stage. The summertime concentrations at both sites were the highest for the year, reaching 80 ppb mean at the CF site in July. However, the highest peak value was determined at the CR site in August (182 ppb). These values definitely have a phytotoxic potential, although plants at that point could be already drought-stressed. Therefore, the effective O₃ flux to plants and the resulting phytotoxicity may be substantially reduced (Grulke et al., in press). In the 1991–1993 study, the peak O₃ values at BF were still exceeding 200 ppb, while the mean summer was 65 ppb (Watson et al., 1999), which is lower than 68 ppb at CF in 2005 summer. A sharp decline of O₃ concentrations was seen in the fall. The mean value for fall at the CF site (46 ppb) was slightly lower than the 50 ppb determined by Watson et al. (1999) at BF in the early 1990s. Results of this study and their comparison with the earlier study in the area (Watson et al., 1999) indicate that since the 1990s, the O₃ status in the central part of the SBM (where CF and BF are located) has not significantly changed.

4.4. Diurnal variation

Among the locations with real-time UV absorption O₃ monitors, OS, the most distant site from the LA Basin mountain location, was characterized by a relatively flat diurnal distribution of the pollutant (Fig. 5). Such distribution is typical for remote mountain sites with a weak urban air pollution signal and similar to those recorded on the Mammoth Mountain in the eastern Sierra Nevada (Bytnerowicz et al., 2001) or Tioga Pass in Yosemite NP (Burley and Ray, in press). Other SBM locations (CF, CR, and KP) had more variable distribution of diurnal concentrations, with the lowest values early in the morning and a clear afternoon maximum occurring a few hours after the peak value at the urban SB site. Similar distribution pattern was also seen at BF in SBM in the 1991–1993

Table 2
AOT40 values for selected sites (ppb h)

<table>
<thead>
<tr>
<th>Year</th>
<th>SB</th>
<th>CR</th>
<th>KP</th>
<th>CF</th>
<th>OS</th>
</tr>
</thead>
<tbody>
<tr>
<td>2002</td>
<td>37,529</td>
<td>74,999</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2003</td>
<td>44,418</td>
<td>67,856</td>
<td>–</td>
<td>44,957</td>
<td>–</td>
</tr>
<tr>
<td>2004</td>
<td>44,000</td>
<td>65,492</td>
<td>–</td>
<td>60,167</td>
<td>–</td>
</tr>
<tr>
<td>2005</td>
<td>42,834</td>
<td>67,455</td>
<td>42,383</td>
<td>58,801</td>
<td>24,666</td>
</tr>
<tr>
<td>2006</td>
<td>40,106</td>
<td>57,582</td>
<td>37,124</td>
<td>51,440</td>
<td>23,848</td>
</tr>
</tbody>
</table>

* Measurements started on June 17, 2003.
4.5. Comparison with other mountain ranges and areas

The annual $O_3$ mean concentration at the CF site in the SBM in 2005 was 49.4 ppb, compared to 47.2 ppb at the Lookout site of the Sequoia NP, the most $O_3$ polluted mountainous national park in the United States (CASTNET, 2005). Among the CASTNET sites, only western Joshua Tree NP site had higher annual $O_3$ average of 52.4 ppb (CASTNET, 2005). The biweekly and summer $O_3$ mean concentrations recorded in 2001–2006 in the western SBM were similar to the levels determined in the most exposed sites in the SW Sierra Nevada (Fračzek et al., 2003), including western locations in Sequoia NP (Bytnerowicz et al., 1999), or in the Sierra National Forest (Hunsaker et al., 2007). These values were higher than those determined in the western Yosemite NP (Burley and Ray, in press) and in the Lake Tahoe Basin (Gertler et al., 2006). The maximum hourly concentrations at the SBM exceeding 180 ppb were much higher than those of 120 ppb measured at Sequoia NP (Bytnerowicz et al., 2002b) and 115 ppb at Fence Meadow of the Sierra National Forest (Bytnerowicz, 2005), or <80 ppb in Yosemite NP (Burley and Ray, in press). Consequently, based on all these comparisons, the western SBM can still be considered as the mountain area in the United States most polluted by ambient $O_3$. In Europe, comparable ambient $O_3$ concentrations have been determined in the Po Valley area in northern Italy (Matyssek et al., 2007), and in some national parks in Spain (Sanz et al., 2007). Similar to the SBM, all these locations are characterized by the Mediterranean climate and a vicinity of the photochemical smog source areas.

4.6. Phytotoxic potential

While in 2005 the SUM00 index values at CR, CF, and KP were almost the same, the other indices (including W126) showed highest exposure at the CR site. That was due to a greater proportion of high concentrations at CR compared to the other sites as shown by the N100 index. Ozone exposure indices calculated for the SB site were always lower than those at CR and CF, but higher than the exposure indices at the remote OS site (except SUM00). Most of the $O_3$ exposure indices at KP were higher than at SB, but the SUM100 and SUM120 values were lower due to a much smaller number of concentrations $>$100 ppb (N100 index). The W126 values at CR, CF and KP sites were high (78–94 ppm h), considering that they were calculated only for 4 months (June 1 to September 30). Edwards et al. (2004), reported that in forest sites in West Virginia, Virginia, and Kentucky, the 7-month (April 1 to October 31) values were mainly <70 ppm h, with the exception of 128 ppm h in 1998 at the Virginia location. Values comparable with the SBM were calculated for Joshua Tree NP in 1995 and 1996 (143 ppm h and 133 ppm h, respectively), which is understandable considering that $O_3$ concentrations measured in western SBM locations were similar to...
those determined in Joshua Tree NP. The AOT40 values calculated for SMB (Table 2) reached 75 ppm h at the CR site in 2002. Other values at that site, as well as at the CF and KP were always >37 ppm h. These values are greater than the values reported for the European forested sites—the highest AOT40 values recorded in Sicily in 2003 were ~50 ppm h and in the Po Valley in Northern Italy close to 45 ppm h (Matyssek et al., 2007). Theoretically, damage to trees could develop at AOT40 values >10 ppm h (Bull, 1996).

In general, our study showed that although the peak O₃ concentrations have significantly decreased over 40–50 years of studies, all of the calculated O₃ exposure indices were still very high. Such high doses of exposure point to a strong potential for negative physiological and biochemical effects on forests (Bytnerowicz and Gruelke, 1993), including damage to sensitive species and individuals and predisposition of trees to drought stress and bark beetle attacks (McBride and Miller, 1999). Various O₃ exposure indices calculated for this study, used both in the United States and in Europe, show that forests in the western part of the SBM are in a zone of a very high phytotoxic potential. This potential decreases eastward, but the AOT40 value >20 ppm h and the W126 value of ~40 ppm h measured in the eastern OS site are still considered as potentially phytotoxic. Obviously, in the semi-arid conditions of the mixed conifer forest of the SBM, these values can overestimate O₃ phytotoxic potential, because trees commonly start shutting their stomata in midsummer, taking up O₃ at reduced rates due to the water deficit (Gruelke et al., in press). Clearly, there is a need for better, biologically based indices of the potential O₃ phytotoxicity in order to estimate its risk to vegetation. Such indices should include a measure of an effective O₃ flux to plants (driven by stomatal conductance) as well as metabolic potential of plants to detoxify oxygen free radicals resulting from O₃ uptake and their ability to repair the O₃-caused damage (Musselman et al., 2006; Matyssek et al., 2007).

5. Conclusions

1. Although O₃ concentrations in the SBM, especially its peak values, have significantly decreased compared to the 1960s and 1970s, they are still the highest out of all the mountainous regions in the United States.

2. Although much less pronounced than in the 1970s, a strong west-to-east gradient of decreasing O₃ concentrations still characterizes the SBM.

3. During the 2001–2006 period, both passive sampler data and data from real-time monitors showed relative stability of the O₃ levels and patterns of its distribution.

4. The SBM are characterized by O₃ concentrations low in winter and high in summer, as well as low at night and higher ones in the afternoon. However, O₃ concentrations typically remain >40 ppb even at night during summer months. Such distribution of O₃ levels is typical for the Mediterranean mountain ranges influenced by large photochemical smog source areas (such as the LA Basin).

5. Potential for phytotoxic O₃ effects, expressed by various O₃ exposure indices, is the highest among the studied mountain areas in North America and Europe.

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