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Monitoring Tropospheric Ozone in California Mountains

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S u m m a r y

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In California mountains distribution of O_3 has been monitored by the USDA Forest Service scientists and managers with carefully designed networks of passive samplers and portable, battery-operated active monitors. Ozone concentrations, digital elevation model and selected meteorological parameters have been used for development of distribution maps using geostatistical software. This approach helps to understand trends of O_3 distribution in complex mountain terrain. Past results are discussed and new data from the Kings River Project in Central Sierra Nevada are presented to illustrate the USDA Forest Service monitoring approach.

Introduction

Concentrations of ambient ozone (O_3) have been increasing in remote locations of the northern hemisphere for over 100 years (BRASSEUR & al. 2001). While peak O_3 concentrations have significantly decreased mainly due to reformulation of gasoline and more efficient combustion engines (LEFOHN & al. 2001), concentrations of the pollutant in rural and remote locations (including mountain ranges) have been continuously increasing (NAJA & al. 2003). It is predicted that this trend will continue throughout the 21st century (FOWLER & al. 1999). During the 1990s, the 8-hour daytime average O_3 concentrations in 25 U.S. national parks increased nearly 8%, with parks in the western mountain ranges experiencing very high levels of the pollutant (EPA 2000). At present, phytotoxic O_3 levels are common in

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many mountain areas of North America and Europe affecting health of forest and other ecosystems (BYTNEROWICZ & al. 2004, SMIDT & HERMAN 2004). It is also believed that such elevated O_3 levels may be affecting health of residents and visitors to many mountain national parks and other frequently visited scenic areas (PROCTER & al. 2003).

From the global and regional perspectives, background concentrations of atmospheric pollutants occur in the areas where anthropogenic sources do not directly influence the atmosphere. In the northern hemisphere, however, such regions are scarce due to extensive human activities in most of the continental areas. Therefore the possible background areas are limited to the central Pacific, middle Atlantic and central Eurasia (POCHANART & al. 2003). Modern day annual average O_3 concentrations over the mid-latitudes of the northern hemisphere generally range between approximately 23 and 45 ppb, with variability being a function of geographic location, elevation and extent of anthropogenic influence (VINGARZAN 2004). Backward air mass trajectory analysis is one of the methods used for evaluation of O_3 origin and estimates of background concentrations of the pollutants (POCHANART & al. 2003). Based on such analyses it has been determined that continental background O_3 levels in Asia and North America are generally higher than in Europe (Table 1). Seasonal cycles of O_3 typically show the spring maximum - summer minimum in the remote background areas of the northern hemisphere (POCHANART & al. 2003). After the April-May maximum (optimal conditions for photochemical O_3 generation), the summer O_3 background concentrations of the pollutant significantly decrease due to surface deposition and active vegetation uptake (POCHANART & al. 2003).

Table 1. Background concentrations of ozone - annual averages (ppb).

Location	Concentration	Reference
Europe		
Finland	30	LAURILA & LATTILA 1994
Arosa (Swiss Alps)	35	POCHANART & al. 2001
North America		
Continental US, inland	25-45	ALTSHULLER & LEFOHN 1996
Continental US, coastal	25-35	Ibidem
Canada	23-34	VINGARZAN 2004
Asia		
Mondy Mtn (China)	43.5	POCHANART & al. 2003
Happo (Japan)	44.4	POCHANART & al. 2004
Mt Abu (India)	33.4	NAJA & al. 2003
Pacific		
Mauna Loa, Hawaii	37-46	VINGARZAN 2004

Annual average O_3 concentrations for 2002 in the United States based on the national Clean Air Status and Trends Network (CASTNET) monitoring results ranged from 13.6 to 53.5 ppb. The highest regional O_3 pollution (annual averages

~50 ppb) was in the western states, especially in California, Nevada, Arizona, Utah, Montana and Colorado (CASTNET 2003). Very high values found in the West Coast locations probably indicate effects of large urban agglomerations (Los Angeles) or intensive emissions from the urban/agricultural interface (California Central Valley). However, the trans-Pacific transport of polluted air masses from Asia also significantly contributes to these high values (HUDMAN & al. 2004). Although most of the CASTNET monitoring sites in the western US are located in the mountains, this coarsely spaced continental network does not allow for understanding O_3 distribution on a smaller scale of individual mountain ranges. In complex topography of the mountainous terrain and high variability of climatic conditions high variability of O_3 concentrations do not allow for adequate predictions of O_3 distribution patterns based on sparsely located active monitors (VAN OOY & CARROLL 1995). In order to fill this gap in our understanding of O_3 distribution, much denser monitoring networks have to be implemented. In this regard passive samplers, the inexpensive and easy to install devices (KRUPA & LEGGE 2000) come very handy. Monitoring of O_3 with passive samplers in remote locations of the Ukrainian Carpathian Mountains started in 1995 (BLUM & al. 1997). During 1997 - 1999 summer seasons such monitoring efforts expanded into entire Carpathian Mountains and resulted in development of the geostatistical maps of O_3 distribution for this Central European range (BYTNEROWICZ & al. 2002). In late 1990s similar monitoring activities were also taking place in Yosemite National Park in the Sierra Nevada and Smoky National Park in the Appalachian Mountains (RAY 2001). Passive sampler networks have also been established in the San Bernardino Mountains of southern California (ALONSO & al. 2002) and the Tatra Mountains in central Europe (BYTNEROWICZ & al. 2004). In 1999 summer a network of about 90 passive samplers was established throughout the Sierra Nevada in California. As a result of that effort, spatial and temporal patterns of O_3 distribution were characterized for most of the Sierra Nevada range (ARBAUGHT & BYTNEROWICZ 2003). Northern parts of the Sierra Nevada near Lassen National Park had the lowest concentrations of the pollutant, while the western slopes of the southern parts of the range had the highest levels as a result of a short-distance transport of O_3 from the highly polluted California Central Valley. Eastern slopes of the Sierra Nevada were generally cleaner than the western slopes, however, during the SW wind events, transport of the polluted air masses from the California Central Valley resulted in elevated levels of the pollutant in eastern Sierras as well (FRĄCZEK & al. 2003).

The U. S. Forest Service scientists and managers continue such efforts in the California Mountains. In this article our approach to O_3 monitoring is presented and discussed by using an example of the Kings River Project in central Sierra Nevada.

Material and Methods

Ogawa passive samplers (Pompano Beach, FL) are based on an oxidative reaction of O_3 with nitrite resulting in nitrate formation (KOUTRAKIS & al. 1993). Calibration of the sampler performed in continuously stirred tank reactor (CSTR) chambers in Riverside, California, showed that

O_3 concentrations determined with passive samplers and the UV absorption monitors are highly correlated (R^2=0.995). This linear relationship held up to a dose of 52,500 ppb O_3 x h (Fig. 1). This means that, for instance, at 100 ppb O_3 average concentrations the samplers can reliably work for up to 525 hours. The samplers have high precision of measurements - on the average the relative standard deviation (standard deviation/mean value) was 4.8%, with a range of 1.2-22.0%.

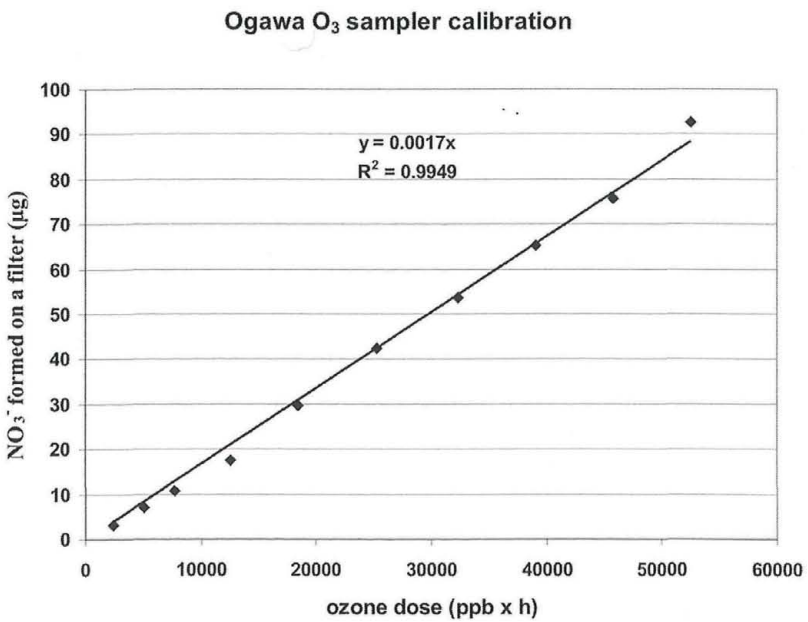


Fig. 1. Relationship between O_3 dose measured with UV absorption active monitor and amount of nitrate formed on the Ogawa passive sampler collection filter.

Portable 2B Technologies (Boulder, CO) UV absorption monitors were used for real-time monitoring of O_3 concentrations in remote mountain locations (BOGNAR & BIRKS 1996). These monitors were calibrated against the certified transfer standard UV absorption instruments in the beginning and end of the monitoring campaigns (Dasibi Model 1003 AH). Comparison of passive sampler results with three collocated 2B Technologies O_3 monitors allowed for developing calculation factors specific to this study.

Field monitoring of O_3 was performed in the Kings Rivers Project, central Sierra Nevada (Fig. 2). Passive samplers were placed in eighteen sites and changed every two weeks. Active monitors were placed in three locations (Shaver Lake, Fence Meadow, and Wishon Reservoir).

Geostatistical Analyst, an extension to ArcGIS™ 8 (Environmental Systems Research Institute, Redlands, California) was utilized in this study similarly as in other studies performed by the author and his colleagues in the Californian and Central European mountains. Geostatistical methods of ordinary kriging and ordinary cokriging were used to generate models of ambient O_3 distribution and the standard error of prediction maps based on ambient measurements on the established networks of sampling points (FRĄCZEK & al. 2003).

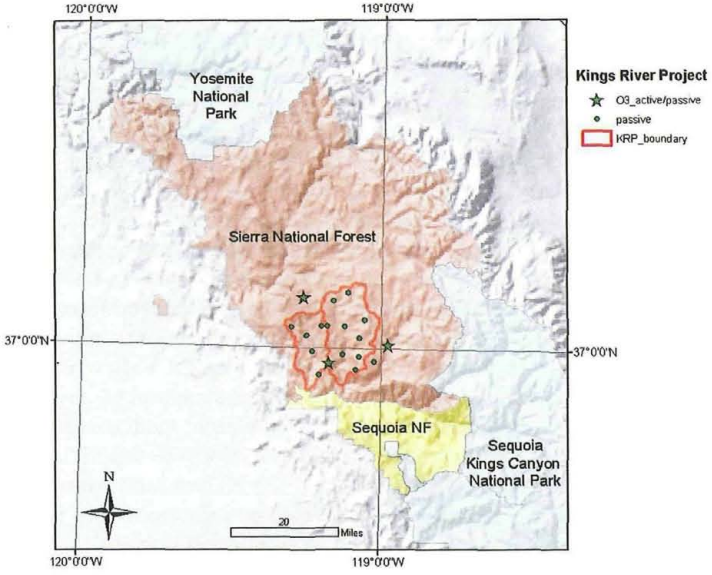


Fig. 2. Ozone monitoring network in the Kings River Project area, central Sierra Nevada.

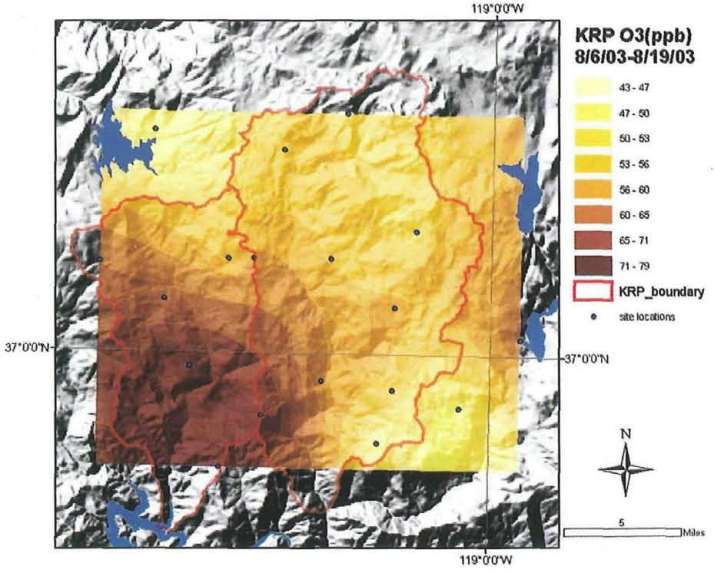


Fig. 3. Distribution of ambient O_3 concentrations in the Kings River Project area during the August 6-19, 2003 period based on passive sampler monitoring data.

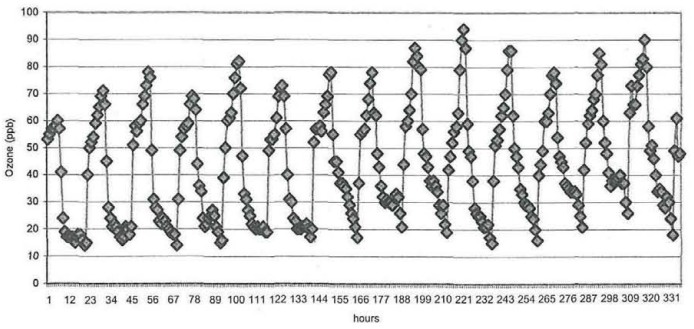
Results and Discussion

Ozone concentrations decreased from SW to NE as the polluted air masses from California Central Valley moved into the Sierra Nevada range with prevailing winds (Fig. 3). Summer-time average concentrations of the pollutant were well above 70 ppb in the SW part of the study area. These spatial trends were also supported by the data from active monitors. At Shaver Lake (Fig. 4a) the maximum concentrations in late afternoon stayed <100 ppb while the minimum values at night often were <20 ppb. At Fence Meadow (Fig. 4b) maximum concentration in the afternoon reached ~115 ppb and the minimum values at night never dropped below 40 ppb. At Wishon Reservoir (Fig. 4c) maximum values in the afternoon on a few occasions exceeded 100 ppb, and during the night concentrations dropped to about 40 ppb. Comparison of the results from these three sites indicates that although all of them were under the influence of the Central Valley photochemical smog, each of them had different characteristics of the temporal O_3 distribution. At the Shaver Lake site, sharp diurnal changes and low night values indicate a strong influence of the Fresno agglomeration (reduction of O_3 concentrations at night hours to very low values caused by reactions with NO emitted from combustion engines). High daytime O_3 values at Fence Meadow indicate a very strong urban effect. However, high nighttime O_3 concentrations suggest that at Fence Meadow a potential for the nighttime titration of O_3 by NO was low. This is somewhat surprising since the Wishon Reservoir site, located farther away from the Valley pollution sources, had lower nighttime O_3 concentrations than the Fence Meadow site. Our results support earlier findings by VAN OOY & CARROLL 1995 that showed high variability of diurnal O_3 concentrations between several western Sierra Nevada sites.

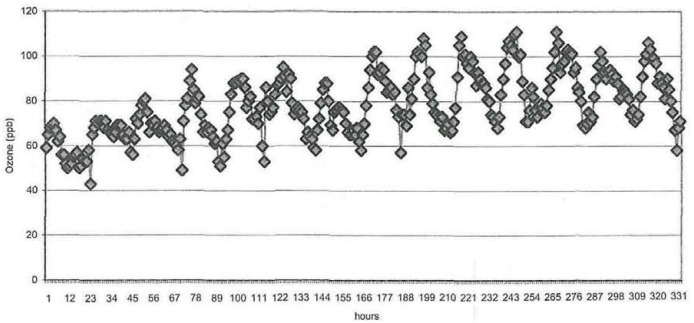
Clearly more information on chemical, topographic and meteorological characteristics of each individual monitoring site is needed for better understanding of O_3 spatial and temporal distribution in complex mountainous terrain. Parameters such as wind speed, wind direction, ambient temperature, elevation, slope, and aspect could explain differences between the individual sites and general patterns of the larger-scale changes. By combining various data sets (average O_3 concentrations from a dense network of passive samplers, real-time O_3 concentrations from a subset of locations, and meteorological and physical characteristics in the area of interest), reliable geostatistical maps can be developed. Such maps could show "hot spots" for O_3 and point to the areas that should be more intensively studied. In such areas denser networks of active monitors could be established for better understanding of the real-time O_3 patterns. Such information is crucial for understanding risks to ecosystems and human health from O_3 exposures.

Two-week long average O_3 concentrations from passive samplers can be reasonably transferred into AOT40 values used in Europe for evaluation of risks to various terrestrial ecosystems (TUOVINEN 2002). More emphasis should also be placed on development and utilization of models that could translate average concentrations of O_3 from passive samplers into real-time values. This could be

a. Shaver Lake, Aug. 6, 12:00 - Aug. 20, 13:30, 2003



b. Fence Meadow, Aug. 5, 14:00 - Aug. 19, 11:30, 2003



c. Wishon Reservoir, Aug. 5, 14:00 - Aug. 20, 9:30, 2003

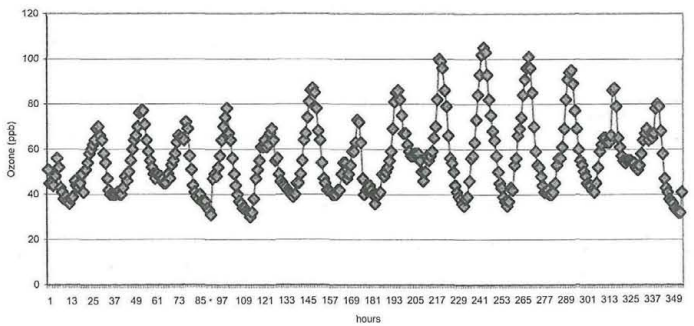


Fig. 4. Diurnal changes in O_3 concentrations in three Kings River Project's locations monitored in August 2003 with 2B Technologies UV absorption monitors.

done based on comparing historical data from collocated passive and active monitors (KRUPA & al. 2001). Such information is needed for development of the secondary, biologically based O_3 standards recommended by the National Research Council 2004. Similar standards based on potential O_3 flux are currently being developed in Europe (ASHMORE & al. 2004).

Distribution of ambient O_3 in complex mountain terrain is difficult to predict just with air pollution dispersion models. The approach of monitoring ambient O_3 with passive samplers, application of geostatistical models that take into account not only multiple O_3 point data but also climatic and topographic information, greatly helps in understanding distribution trends and selection of areas of highest risk from O_3 exposures. This is important since elevated levels of O_3 affect many sensitive plant species. These include key tree species such as ponderosa pine (*Pinus ponderosa*) in mixed conifer forests of California mountains (MILLER & LONGBOTHAM 1983) or Swiss stone pine (*Pinus cembra*) in subalpine forests of the Carpathians (MANNING & GODZIK 2004) and the Alps (DALSTEIN & al. 2002). The USDA Forest Service methodology may also help in ground-level verification of the pollution dispersion models or results of the remote sensing assessments of ground-level O_3 concentrations. Information on distribution of ambient O_3 may also be helpful in predicting wildfire risks since elevated O_3 concentrations predispose forests to drought, bark beetle attacks, premature dieback and dead biomass accumulation.

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