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Chapter 11

Methodological needs and perspectives for monitoring ambient air pollution and regional haze: Tools for understanding forest responses

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Abstract

Methodologies for monitoring air pollutants in remote mountain forest locations are discussed, and needs for further development and refinement of such technologies are described. Even the most reliable passive samplers for ozone (O_3) need improvements that would help to account for the effects of wind, temperature, and relative humidity. Passive samplers for monitoring nitrogenous (N) air pollutants have not been widely used, and many new methods are still being developed. These new samplers need to be tested and calibrated against active air pollution monitoring systems before implemented on a larger scale. Portable, real-time air pollution monitors for O_3 have become available and are important for better understanding of the phytotoxic effects of pollutants. Reliable monitoring of particulate matter at the landscape level creates the greatest challenge, and special attention should be given to this issue. Although various optical methodologies are available for monitoring impairment of visibility (i.e., regional haze), methods that would allow for landscape-level evaluation of the chemical composition of particulate matter are lacking. This information is needed for estimates of fluxes of pollutants, especially N species, to forests. The existing and newly developed methodologies make it possible to monitor air pollutants across forest landscapes and develop pollution distribution models. These models and additional biological data will enable the development of biological response models, such as landscape level evaluation of foliar injury, O_3 uptake, or growth changes in pines and changes in other sensitive species. An ultimate goal for the Sierra Nevada is to develop risk assessment models that describe the sensitivity of forests to O_3 and other stressors and the risks associated with air pollution to inhabitants and visitors to the Sierra Nevada. These models are needed for well-informed decision-making regarding management and development needs in the Sierra Nevada.

1. Introduction

Industry, transportation, agricultural activities, as well as natural and prescribed fires are major sources of air pollution in the United States and elsewhere (Wellburn, 1988; Seinfeld and Pandis, 1998; Yokelson et al., 1999). In California, urban pollution from Los Angeles, the San Francisco Bay Area, Sacramento, Fresno, and Bakersfield and emissions from agricultural operations in the Central Valley affect the health of millions of Californians and sustainability and biodiversity of forests and other ecosystems in the Sierra Nevada. Ozone (O_3), a secondary pollutant resulting from atmospheric photochemical reactions, affects the health of humans and sensitive plants (Krupa and Manning, 1988; Krupa, 1997). Nitrogenous (N) pollutants, represented mainly by nitric oxide (NO), nitrogen dioxide (NO_2), ammonia (NH_3), nitric acid vapor (HNO_3), peroxyacetyl nitrate (PAN), peroxypropionyl nitrate (PPN) as well as particulate nitrate (NO_3^-) and ammonium (NH_4^+) are of great importance because of their potential impacts on natural ecosystems. Some N pollutants such as HNO_3, PAN, or PPN have a high phytotoxic potential, and others may alter nutrient cycling processes in ecosystems. Nutrient N is added to plants and ecosystems by rain, fog, cloud, and snow as NO_3^- and NH_4^+ ions, by dry surface deposition of HNO_3, NH_3 and particulate NO_3^- and NH_4^+, and by stomatal uptake of NO, NO_2, NH_3, HNO_3, PAN, and PPN (Hanson and Lindberg, 1991; Bytnerowicz et al., 1999a). Particulate pollutants, both inorganic and organic, especially those with < 10 µm and < 2.5 µm diameters (commonly named $PM_{2.5}$ and PM_{10}) as well as other types of aerosols may also impair visibility and affect human health (Finlayson-Pitts and Pitts, 2000). Particulate matter originating from smoke, dust and made by chemical reactions of gaseous pollutants, as well as moisture and vapor suspended in the air, are responsible for impaired visibility or haze. Haze that impairs visibility in all directions over a large area is called “regional haze” (http://www.epa.gov/oar/oaqps/regusmog/infhaze/html).

Evaluation of landscape level distribution of air pollutant concentrations and deposition to forests, other natural ecosystems, and agricultural systems is important for risk evaluation and proper planning of management practices. In California, O_3 is the main phytotoxic air pollutant at ambient levels. Classic examples of phytotoxic O_3 effects on forests dominated by ponderosa and Jeffrey pines (*Pinus ponderosa* and *P. jeffreyi*) have occurred for more than forty years in the San Bernardino Mountains (Miller et al., 1963, 1969). For the last thirty years such effects have also been seen on pines on the western slopes of the Sierra Nevada (Miller and Millecan, 1971; Duriscoe and Stolte, 1989). Nitrogenous air pollutants may also have significant long-term effects on Sierra Nevada ecosystems. Nitrogenous dry and wet deposition may lead to excess of available N in forest stands, and this in turn may impact forest sustainability and biodiversity, alter species composition, and lead to contamination of ground water and surface waters with excess NO_3^- (Fenn et al., Chapter 5, this volume).

The Sierra Nevada Framework Environmental Impact Statement formulated questions that are important for understanding air pollution issues for the Sierra Nevada (Procter et al., Chapter 15, this volume):

- What are the mass transport patterns, spatial and temporal distributions, and deposition rates of ecologically significant pollutants to the Sierra Nevada?
- What are the effects of O_3, long-term deposition, and the interactions among N and sulfur (S) compounds, O_3, drought, and pests on the composition, structure, and function of Sierra Nevada ecosystems?
- Are models used to examine emissions production and transport adequately representing conditions in the Sierra?
- What are the transport processes that control ambient air pollutant concentrations and delivery in the Sierra Nevada?
- How can we better model/understand future patterns of air pollution from downwind sources?
- What is the natural background of O_3 in the Sierra Nevada?

To address these questions, a well-designed, long-term air pollution monitoring program must be implemented. These monitoring efforts must be based on reliable, practical, and cost effective techniques that can be implemented at the scale of the entire Sierra Nevada bioregion. Currently used techniques, the latest developments in air pollution monitoring techniques with an emphasis on those easily used in remote locations, and other methodological needs are discussed in this chapter. These needs are discussed based on the data to be obtained for the development of pollution distribution, biological response, and risk assessment models for the Sierra Nevada (Fig. 1).

2. Current monitoring techniques

2.1. Gaseous pollutants

At present, monitoring of O_3, nitrogen oxides (NO_x), or sulfur dioxide (SO_2) has become relatively routine where electric power and adequate funding are available. Availability of reliable electronic analyzers, data loggers, computers, appropriate software for data acquisition and statistical evaluation, as well as new telephone communication capabilities allow for relatively trouble-free monitoring of these pollutants. However, in the mountains and other remote locations, especially in the high elevation subalpine and alpine zones, the availability of electric power is the main limiting factor in deciding what monitoring techniques can be used. Other factors, such as difficulty in moving

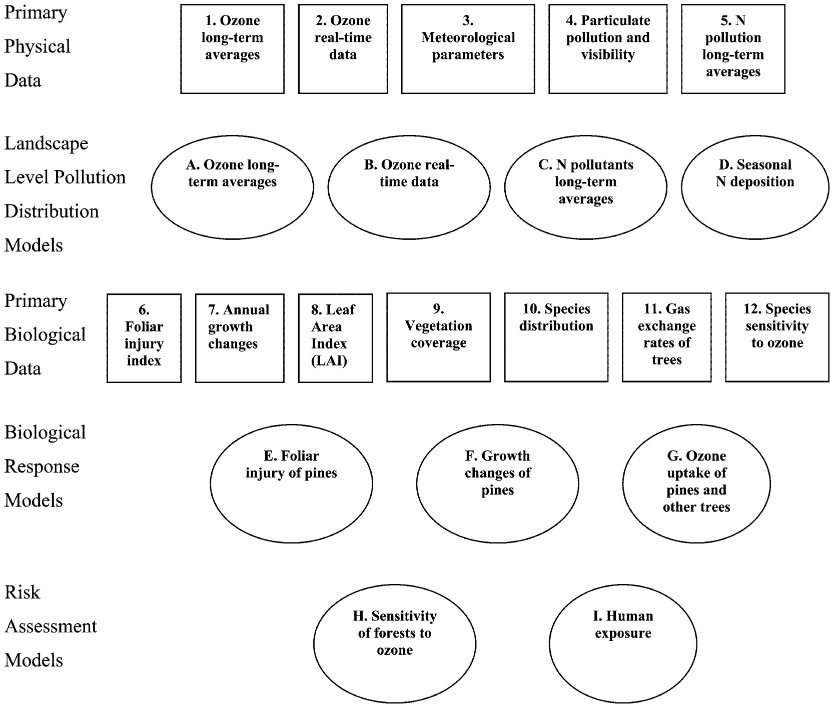

Figure 1. Methodological needs discussed in this chapter required for development of air pollution distribution, biological response and risk assessment models in the Sierra Nevada Mountains (adapted from Bytnerowicz and Arbaugh, 2002). Boxes with numbers contain types of monitoring data; circles with letters contain possible models.

heavy equipment to remote sites, damage during extreme weather conditions, the possibility of vandalism or damage by wildlife, problems with calibration, or funding also limit choices about appropriate monitoring techniques. Instruments that can be powered by solar panels and 12 V DC batteries (e.g., portable electronic analyzers for gaseous pollutants and denuder systems) or techniques not requiring any electric power (e.g., passive samplers) may be an attractive monitoring alternative in such conditions.

2.1.1. *Continuous electronic monitors*

Finlayson-Pitts and Pitts (2000) provide a comprehensive review of the available analytical methods used for measuring concentrations of the major atmospheric contaminants. For instance, for monitoring ambient levels of O_3, the US Environmental Protection Agency (EPA) designated the ultraviolet (UV) absorption, chemiluminescence, or differential optical absorption spectrometry as reference or equivalent methods. Many types of commercially available instruments can be used for air quality monitoring in national and regional networks. Portable instruments not requiring AC power and constant temperature are less expensive than traditional stationary instrumentation and can facilitate monitoring efforts in remote locations. An example of such an instrument for measuring ambient O_3 concentrations is the 2B Technologies UV absorption instrument developed by Bognar and Birks (1996). This instrument is light and compact, easily transported in a backpack, and capable of running on AC power or 12 V DC batteries. When connected to a solar panel, the instrument may operate for many months without recalibration or data downloading. At the moment, similar portable electronic devices are not available for NO or NO_2. The available instruments for NO and NO_2, such as Monitor Labs or Thermo Environmental, require air-conditioned shelters; therefore, monitoring of those pollutants is performed only in limited number of remote field locations. Currently, reliable electronic instruments for NH_3 are not available.

2.1.2. Denuder systems

Gaseous HNO_3, nitrous acid (HNO_2), SO_2 and NH_3, as well as ion concentrations in particulate matter can be collected on annular denuder samplers/filter pack systems (Possanzini et al., 1983). Pumps operating on 12 V DC batteries allow for operating of the samplers in locations lacking electric power. Nitric acid deposited on annular denuder tubes is analyzed as NO_3^- ion, HNO_2 as nitrite (NO_2^-), SO_2 as SO_4^{2-}, and NH_3 as NH_4^+. These systems determine average concentrations of the pollutants of interests for periods as short as 4 to 6 hours. Concentrations of NO_3^-, NO_2^-, and SO_4^{2-} are determined with ion chromatography, and concentrations of NH_4^+ are determined colorimetrically. These systems have been used in forest locations in Alberta, Canada (Legge and Krupa, 1989), and California (Bytnerowicz and Riechers, 1995; Bytnerowicz and Fenn, 1996).

Although the annular denuder samplers have been extremely useful, they are rather expensive and difficult to use in field conditions. As an alternative, a glass honeycomb denuder/filter pack system has been developed for collecting HNO_3, HNO_2, SO_2, NH_3, and ions in particulate matter (Koutrakis et al., 1993a). These systems are easier to use in large-scale field monitoring and provide results that are comparable to the classic annular denuder samplers (Possanzini et al., 1983). Similar to the annular denuder systems, HNO_3 deposited on honeycomb denuders is analyzed as NO_3^- ion, HNO_2 as NO_2^-, SO_2 as SO_4^{2-}, and NH_3 as NH_4^+. These systems also allow for determining average concentrations of pollutants for 4 to 6 hours. Concentrations of NO_3^-,

NO_2^-, and SO_4^{2-} are determined with ion chromatography, and concentrations of NH_4^+ are determined colorimetrically. The honeycomb denuder/filter pack systems have been successfully used in California and Central European mountain locations (Bytnerowicz et al., 1999a, 1999b, 2002b).

2.1.3. Passive samplers

Passive samplers allow measuring concentrations of gaseous air pollutants over a relatively long (days and weeks) averaging time. The operative principle is based on the controlled diffusion of air through a diffusion tube, filter, or another type of a screen and contact with a collecting medium (absorbents or colorants), which are specific for individual pollutants. The volume of air reaching the collecting medium is calculated according to Fick's law (Kirchner et al., 1999). The advantages of passive samplers include simplicity of use, small size, low maintenance needs, low costs, possibility for dense deployment, no need for electric power, and integration of long-term exposure regimes. The disadvantages include relatively low sensitivity that does not allow for determining short-term (minutes and hours) concentrations, gradual loss of effectiveness during use or storage, and possible interference from other atmospheric constituents. In recent years various types of passives samplers for O_3 and other pollutants have been developed and used in field conditions in Europe and North America (Krupa and Legge, 2000). Passive samplers for O_3 and N compounds are very important for monitoring air quality in Sierra Nevada ecosystems. Sulfur dioxide, an air pollutant of high phytotoxic potential in Europe and parts of the eastern United States, is present only at background concentrations in the Sierra Nevada (Bytnerowicz and Riechers, 1995; Bytnerowicz et al., 2002b) and therefore is not of concern.

Passive O_3 samplers work on principles of oxidative reactions of O_3 with various chemicals on a collecting medium such as sodium nitrite or dipyridylethlylene (DPE), and various dyes such as indigo or indigo carmine. Examples of O_3 passive samplers include Ogawa samplers (Koutrakis et al., 1993b), CanOxy Plates (Cox and Malcolm, 1999), Maxxam samplers (Tang, 2001), Radiello sampler (Radiello, 2002), the IVL Swedish Environmental Research Institute sampler (Karin Sjoberg, http://www.ivl.se) or the Commonwealth Scientific and Industrial Research Organization (CSIRO) passive gas sampler (http://www.dar.csiro.au/publications/samplers.htm). Analysis of passive sampler extracts is performed with ion chromatography, colorimetry, reflectance spectroscopy, spectrophotometry, fluorometry, or coulometry. The Ogawa sampler (Koutrakis et al., 1993b) has been used in Washington state (Brace and Peterson, 1998; Cooper and Peterson, 2000), California national parks (Ray, 2001), central Europe (Blum et al., 1997; Godzik, 1997; Bytnerowicz et al., 2002a), and in a recent study by Arbaugh et al. (this volume).

For NO_2 passive samplers, triethanolamine (TEA) typically is used as the collection medium (Palmes et al., 1976, 1977; Atkins et al., 1986). A passive sampler for simultaneous determinations of NO_2 and SO_2 with TEA as a collecting medium was developed by Krochmal and Kalina (1997a, 1997b). The Ogawa NO_2/NO_x samplers are of the same physical design as the O_3 passive samplers. The NO_2 sampler uses TEA as the collecting medium, while the NO_x ($NO + NO_2$) sampler uses a mixture of sulfanilamide and N-(1-naphtyl)-ethylenediamine dihydrochloride solution and TEA (Ogawa & Company, 1994). Other absorbents are also used for passive sampling of NO_2 in other types of passive samplers, such as a mixture of sodium iodide and sodium arsenite (Ferm and Svandberg, 1998) or sodium carbonate (De Santis et al., 2001). The diffusion tube samplers for NO_2 have been widely used in the United Kingdom (Colls, 1986; Campbell, 1988; Ashenden and Bell, 1989), the samplers developed by Krochmal and Kalina (1997a, 1997b) in the Carpathian Mountains in Central Europe (Bytnerowicz et al., 2002a), and the Ogawa NO_2/NO_x samplers in the California mountains (Alonso et al., 2002; Bytnerowicz et al., 2002b). Various types of passive samplers for NH_3 measurements have been used in Europe, and they have been described and compared in a field study in an alpine rural environment (Kirchner et al., 1999). That study showed that most of the tested passive samplers could be recommended for ambient measurements. The Gradko diffusion tube samplers for NO, NO_2, and NH_3 (Hargreaves and Atkins, 1987) have been widely used by the authors in Central European and California mountain sites (Alonso et al., 2002; Bytnerowicz, unpublished). More information on NO_2 and NH_3 samplers can be found in a comprehensive review by Tang et al. (2001). A passive sampler for monitoring ambient concentrations of HNO_3, a very important pollutant in the vicinity of photochemical smog source areas, has been recently developed. The sampler uses nylon filters as a selective collection medium for HNO_3 and allows for collection of the pollutant for up to several weeks in highly polluted environments (Bytnerowicz et al., 2001). These samplers have been successfully used in the California mountains (Alonso et al., 2002; Bytnerowicz et al., 2002b).

2.2. Particulate pollution and visibility

Airborne particulates, especially those < 2.5 µm in diameter ($PM_{2.5}$), pose potential health, visibility, safety, and nuisance problems at elevated concentrations. Airborne particulate matter consists of smoke particles resulting from prescribed burning or natural fires, soil dust particles, and particles made by chemical reactions of gaseous air pollutants (Finlayson-Pitts and Pitts, 2000). Particulate matter, moisture, and vapors suspended in air (aerosols) are responsible for deterioration of visibility (Malm, 1999). Visibility impaired at the landscape level, or “regional haze,” has been of great concern for state and federal regulatory agencies as well as for land managers.

In the Sierra Nevada, monitoring of aerosols has been performed as a cooperative effort between the EPA, federal land management agencies, and state air agencies in the Interagency Monitoring of Protected Visual Environments (IMPROVE) measurement program (IMPROVE, 2000). The IMPROVE program monitors current visibility and aerosol conditions in Class I wilderness areas and identifies chemical species and emission sources responsible for existing man-made visibility impairment. The IMPROVE samplers collect one PM_{10} sample on a teflon filter for gravimetric determination of PM_{10} mass concentration, and three $PM_{2.5}$ samples on teflon, nylon, and quartz filters for gravimetric determination of $PM_{2.5}$ mass and for concentrations of selected elements using particle-induced X-ray emission (PIXE), X-ray fluorescence (XRF), and Proton Elastic Scattering Analysis (PESA). The nylon filter is analyzed to determine NO_3^- and SO_4^{2-} aerosol concentrations using ion chromatography. The quartz filters are analyzed for organic and elemental carbon using the Thermal Optical Reference (TOR) method. In addition, transmissometers are used for measuring the light-extinction coefficient and integrating nephelometers for measuring the scattering coefficient. Transmissometers measure the light transmitted through the atmosphere over a distance of 1 to 15 km. Integrating nephelometers measure the scattering of light from a small volume of air (point measurement). Relative humidity of the air is measured continuously at the transmissometers and nephelometers sites. There are three IMPROVE sites in the Sierra Nevada, located in Lassen Volcanic, Yosemite, and Sequoia National Parks (IMPROVE, 2000), with more sites to be installed soon.

The USDA Forest Service’s Missoula Technology and Development Center evaluated real-time particulate monitoring instruments to measure smoke particulate concentrations during the August 2000 wildfires in Montana. Seven nephelometers and two aethalometers (measuring light absorbing aerosols) were tested against the EPA federal reference method (gravimetric sampler) and the EPA equivalent PM_{10} instrument. All the tested instruments provided reliable results; however, the authors recommended that they be corrected for various types of field conditions based on results from the co-located reference methods (Trent et al., 2001).

Annular denuder/filter pack systems (see above) are also used for measurements of NO_3^-, NH_4^+ and SO_4^{2-} concentrations in fine (< 2.5 µm diameter) and coarse (> 2.5 µm diameter) particles in addition to determinations of gaseous pollutants (Possanzini et al., 1983). These systems have been used for determinations of particulates in forest locations in Alberta, Canada (Legge and Krupa, 1989), and California (Bytnerowicz and Riechers, 1995; Bytnerowicz and Fenn, 1996).

Honeycomb denuder/filter pack air pollution sampling systems have also been used for determinations of concentrations of fine particulate NO_3^-, SO_4^{2-} and NH_4^+, in addition to the gaseous pollutants (Koutrakis et al., 1993a). However, a limitation of the honeycomb denuder/filter pack system is that particles > 2.2 µm are not collected, since a critical orifice instead of a cyclone separates coarse particles from the sampled air. The honeycomb denuder/filter pack systems have been extensively used in California and Central European mountain locations (Bytnerowicz et al., 1999a, 1999b, 2002b). Other methods, such as filter packs or tungstic acid denuder systems can also be used for determinations of particulate NO_3^- and NH_4^+ (Anlauf et al., 1985). Modified filter packs have been used for determinations of NO_3^-, SO_4^{2-}, and NH_4^+ in the mountain ranges of Bulgaria and the Czech Republic (Zeller et al., 1997a, 1997b). However, filter packs have been criticized as not accurate for distinguishing between gaseous and particulate N pollutants. The main reason for this is that particulate NH_4NO_3 collected on the Teflon pre-filter volatilizes with HNO_3 vapor and NH_3 as end products. There is also the possibility of chemical reactions between the already collected particulate matter and the gaseous pollutants passing through the filter. Filter packs can, however, be used for measurements of total (gaseous and particulate) NO_3^- and NH_4^+ (Allegrini and De Santis, 1989).

3. Improvements and new approaches to monitoring in remote locations

Although many methodologies are currently used for monitoring air pollutants in remote mountain forest locations, further refinement of the existing techniques and development of new approaches should be considered for a better understanding of responses of mountain forests to air pollution.

3.1. Ground measurements of gaseous pollutants

A good understanding of the operating principles of passive samplers is required for proper monitoring of ambient air pollutants. Protection from abrupt changes in wind velocity at the samplers' inlet is essential for assuring constant diffusion rates of pollutants towards the collecting media, and consequently, reliable performance of the samplers. In this regard, most of the newly developed samplers, such as Maxxam (Tang, 2001) or CanOxy plates (Cox and Malcolm, 1999), provide adequate protection against wind and rain and assure stable diffusion rates. Because diffusion rates change with temperature or relative humidity (RH), additional information on these parameters allows for more precise calculations of pollutant concentrations (Tang, 2001). Therefore, we suggest that, whenever possible, additional meteorological data should be collected and utilized. With some new technological developments, such as miniaturized temperature or RH sensors, measurements of these parameters have become feasible, allowing for improved precision of passive sampler measurements. We recommend calibration of passive samplers against active monitors, and use of experimentally developed equations for calculation of pollutant concentrations. Obviously only reliably calibrated active monitors that are maintained according to generally approved quality assurance protocols should be used.

Although passive samplers for O_3 have been used on a large scale for some years, passive sampling techniques for N pollutants have been used only recently in the United States. Several passive samplers for monitoring of N air pollutants suitable for remote locations have been recently developed (Krupa and Legge, 2000; Tang et al., 2001). Development of new passive samplers that are not affected by changes in environmental conditions and interferences from other pollutants offer new possibilities for reliable sampling of N air pollutants. There is a clear need for laboratory and field studies that would determine the most reliable, sensitive, and accurate systems for monitoring at the large landscape scales. These tests need to be performed under varying environmental conditions (including extreme) and calibrated against active air pollution monitoring systems. Promising new achievements are the NH_3 Alpha samplers developed at the Center for Ecology and Hydrology in Edinburgh, Scotland (Tang et al., 2001), the NH_3 Ogawa samplers (Don Schaeffer, personal commun.), Maxxam samplers for NO_2 (Tang, 2001), or the Radiello samplers for NH_3 and NO_2 (http://pc4.fsm.it:81/padova/radiello.html). In areas where photochemical smog may be a problem, reliable measurements of HNO_3 concentrations are also needed. In this regard, the USDA Forest Service HNO_3 samplers proved to be useful (Bytnerowicz et al., 2001). An improved new sampler in which the collecting medium (nylon filter) is placed behind a diffusion membrane (Teflon pre-filter) controlling air flow is currently being tested in our laboratory (Bytnerowicz, unpublished).

Portable, real-time air pollution monitors are needed, especially for O_3, in order to understand the phytotoxic potential of air pollutants. The 2B Technologies portable O_3 monitors (Bognar and Birks, 1996) offer such possibilities, although some technical problems were found during first years of their use. These instruments are continuously being modified and improved. The Atmospheric Deposition Research Work Unit of the Pacific Southwest Research Station, USDA Forest Service, has performed field trials in which the 2B Technologies O_3 instruments were linked to Campbell weather stations monitoring ambient temperature, RH, radiation, wind speed, and wind direction. These O_3/meteorological monitoring systems powered by 12 V DC batteries coupled with solar panels allow for long-term (2 to 3 months) operation (Rocío Alonso, personal commun.). Information on key meteorological parameters is important for better understanding of O_3 distribution and development of dispersion models (Arbaugh and Bytnerowicz, Chapter 10; Lee, Chapter 7; Preisler and Schilling, Chapter 8; and Frączek et al., Chapter 9, this volume). Judging from the current state of science and new methodological developments, it seems that the problem of adequate monitoring of O_3 in remote locations will be resolved soon using a combination of passive samplers and portable active monitors. Some caution should be maintained, however, since some researchers claim that in extreme environmental conditions, such as highly polluted urban plumes or smoke, performance of the UV absorption O_3 monitors, such as the 2B Technologies monitor, could be affected by the presence of particulate matter and volatile organic compounds (VOCs), especially the aromatic compounds (Robert Yokelson and Ron Sussot, personal commun.). If this is true, in some conditions, instruments operating on principles other than UV-absorption should be considered for use.

For the nitrogenous pollutants, in addition to passive samplers, mini-denuder systems provide another possibility for active monitoring of some important N pollutants (NH_3, HNO_3) in remote locations. The new miniaturized DELTA systems for long-term (up to a month) monitoring of NH_3 and NH_4^+ with battery-powered air pumps have been recently implemented in 50 locations in the United Kingdom as a part of a new national monitoring network (Sutton et al., 2001). The detection limit of this method is < 0.01 µg/m^3, and the sampling is accurate and inexpensive. Other gaseous pollutants such as HNO_3 and SO_2 can also be monitored with such systems. By adding a critical orifice and a filter pack, a collection of fine particulate matter is also possible (Sim Tang, personal commun.).

3.2. Ground measurements of particulate pollutants

Reliable monitoring of particulate matter at the landscape scale is a challenge to scientists, and land managers and special attention should be given to this issue. Although various optical methodologies are available for evaluation of visibility impairment (regional haze issues), methods that would allow for landscape-level evaluation of chemical composition of particulate matter are still lacking. This information is required for estimates of fluxes of pollutants, especially N species, to forests. There is a great need for real-time fast response instruments to measure particulate pollutants.

Several types of commercially available optical instruments tested after the Montana forest fires in summer 2000 (later called “Fire Storm 2000”) allow for reliable determinations of $PM_{2.5}$, PM_{10}, and total particle mass (Trent et al., 2001). However, information on chemical composition of the collected particulate matter is also very important from the point of view of nutrient deposition to forests and other ecosystems and effects on biogeochemical cycling. In that regard some newly developed instruments offer a possibility for collection of total, PM_{10} or $PM_{2.5}$ particulate matter for chemical analysis. An example of such instruments is DataRAM 4 produced by the MIE (Monitoring Instruments for the Environment, 2000). There is a major knowledge gap regarding long-term temporal and spatial patterns of particulate pollutant concentrations at the scale of the entire mountain range. Weekly average concentrations of SO_4^{2-}, NO_3^-, and NH_4^+ from the Clean Air Status and Trends Network (CASTNET) databases are available only for three Sierra Nevada national parks. Because this network uses a filter pack techniques for collection of particulate matter and HNO_3, distinguishing between gaseous and particulate fractions of NO_3^- and NH_4^+ is not possible (Allegrini and De Santis, 1989). Some new advances in development of passive technologies have been reported (Brown et al., 1998) and provide hope that wide-scale monitoring efforts will be feasible in the future. Development of new technologies for monitoring particulate matter in remote locations should be encouraged.

3.3. *Remote sensing of pollutant concentrations and deposition*

Remote sensing techniques and satellite and aircraft imagery offer some new opportunities for evaluation of air pollution distribution and its effects on global, regional, landscape, or ecosystem scales as a support (and means to extrapolate) to the ground-based data. Aircraft-carried lidar instrumentation has been used for measuring O_3 and aerosol concentrations over the Pacific Ocean during the 1996 fire season (Fenn et al., 1999). A considerable number of satellite-based remote-sensing systems have been used for determining the column-integrated concentration or the vertical profile of the constituents in the stratosphere and upper troposphere. However, to date none of these systems has been able to detect O_3, NO_2, CO, or SO_2 with success. In the case of satellite imagery for O_3, the problem is trying to detect relatively small concentrations of O_3 in the lower troposphere through the stratosphere where the O_3 signal is extremely large. For NO_2, CO, and SO_2, the tropospheric concentrations are close to or at the detection limits with the presently used space-borne instruments. There is, however, considerable research underway on the potential to determine O_3 in the troposphere with remote sensing systems. It is expected that in the future, remote sensing systems that are being developed using newer technologies, such as the Tropospheric Emission Spectrometer (TES), or Ozone Monitoring Instrument (OMI), offer the potential of measuring O_3, NO_x, and SO_2 in the lower troposphere directly and can be used to detect their transport and emissions. A system that may greatly help in understanding the transport of gaseous pollutants in the lower troposphere of the United States is GEO-TRAPSAT, a geostationary orbiting satellite that will measure a variety of trace gases (EPA, 2002). Therefore, it is expected that in the near future the results of remotely-sensed air quality measurements will allow for a better understanding of regional and landscape level distribution of key air pollutants. However, for development of such methodologies and eventual applications, calibration against well-established ground-based measurements of pollutants will be essential.

Remote sensing should also help in evaluation of air pollution deposition to vegetation at the landscape, ecosystem, and forest stand levels. For this task, information on real- time concentrations of air pollutants, vegetation coverage, as well as distribution, gas exchange dynamics and leaf area indices (LAI) of key forest species, are needed. Land-use maps showing distribution of basic forest types and other landscape categories based on the Corine satellite imagery have been developed for the entire Carpathian Mountains of Central Europe (Frączek et al., 2001). Nikolov et al. (1995) has used satellite images for estimates of LAI for the western United States, including the entire Sierra Nevada range. It is only a matter of time until more advanced remote sensing techniques will allow for more precise evaluation of vegetation at the forest stand to landscape levels. This information, verified by field observations, will facilitate evaluation of deposition of O_3 and N pollutants to forest canopies at various spatial scales.

3.4. Using air pollution data to better understand forest responses

Recent developments of passive sampler technologies allow for a dense deployment of monitoring sites and better understanding of landscape-level distribution of O_3. However, passive samplers can only provide information on average concentrations of the pollutant during relatively long exposures (typically 1 to 2 weeks). Although this approach helps to understand trends of dispersion of the polluted air masses, it does not provide information on acute exposures potentially phytotoxic to O_3 sensitive plants or humans. There are some interesting developments in the area of using long-term average O_3 data for estimates of short-term O_3 concentrations. Krupa et al. (2001) has proposed that a Weibull probability model could simulate frequency distribution of hourly O_3 concentrations based on the single, weekly mean values obtained from passive samplers. The simulation was based on data derived from co-located continuous monitors and passive samplers. Tuovinen (2002) suggested that in most cases changes in O_3 concentrations follow the Gaussian distribution and that 14-day average values from passive samplers can be used for reestablishing diurnal curves of the pollutant. Data from eight different forest locations in Europe were used for calibration and testing of the proposed model. Despite simplifying assumptions on typicality of O_3 distribution in various mountain conditions, the model performed reasonably well for the accumulated exposures in most of the tested locations. Based on those data, a statistical model for estimating AOT40 values (an index that describes O_3 exposure and potential phytotoxic effects in terms of hourly accumulated exposure over a threshold of 40 ppb during daylight hours for vegetation season) has been offered.

Models that would describe biological responses of forests to air pollution (landscape level evaluation of foliar injury, growth changes, or alteration of gas exchange of pines and other sensitive species) are needed. These models would be based on the pollution distribution models and additional biological data. An ultimate goal for the Sierra Nevada is to develop risk assessment models that would describe sensitivity of forests to O_3 and other stressors and that would also describe risks associated with air pollution to inhabitants and visitors to the Sierra Nevada. These models are needed for well-informed decision-making by managers and in considering development needs for the Sierra Nevada. Because it is now generally accepted that O_3 exposure indices based on ambient concentrations do not adequately explain phytotoxic effects of O_3, development of new approaches is rapidly advancing (Emberson et al., 2000; Grünhage et al., 2001). Within the European International Cooperative Program (ICP) Vegetation, flux oriented indices are being developed (ENEPE ICP, 2000/2001). In mountain forests of California, the SUM0 O_3 exposure index poorly correlates with the observed foliar injury of ponderosa and Jeffrey pines evaluated according to the ozone injury index (OII) and Forest Pest Management (FPM) systems (Arbaugh et al., this volume). It seems that the responses of conifers to O_3 exposure as measured with these indices are very difficult, or maybe impossible, to explain by using ambient O_3 exposure indices for a single growing season (as typically collected in remote locations). This difficulty is mainly because both the OII and FPM scores are based on cumulative responses of foliage to the pollutant over several years (Grulke, Chapter 3, this volume). Goldstein et al. (Chapter 4, this volume) also point out that a large portion of the O_3 uptake by pines occurs outside of the summer season for which O_3 exposure indices are calculated. In addition, because of the poorly understood responses of trees to long-term exposures to O_3 and other environmental stressors, effects of changing levels of available N, increasing CO_2 concentrations, complex biochemical defensive systems, and compensatory mechanisms of trees, it is extremely difficult to understand and predict growth responses of trees.

Based on this evidence, it seems that the next logical step towards a better understanding of O_3 injury in California forests would be to try to correlate O_3 uptake by pines with their injury indices (Panek et al., Chapter 14, this volume). As these authors suggest, one of the urgent future needs for the Sierra Nevada forests would be to characterize spatial patterns of O_3 at the regional scale. An opportunity for landscape level assessments would be a linkage between spatially explicit, modeled O_3 uptake with remotely-sensed spectral reflectance data showing chlorotic mottle or biochemical signatures related to O_3 damage (Panek et al., Chapter 14, this volume).

In addition to a need for better understanding of O_3 deposition to forest canopies at a landscape scale (Panek et al., Chapter 14, this volume), similar understanding of deposition of N pollutants is also needed. Although wet-deposited N is easy to measure or model, easy methodologies for measuring dry deposited atmospheric N to trees and other landscape features are not presently available. Because knowledge on deposition of fine particles tends to be empirical or based on theories untested in natural outdoor settings, a comprehensive understanding of particle deposition has not been achieved. Direct measurements of fluxes are required for improved model parameterization for the deposition of gases and particles (Wesely and Hicks, 2000). As a result, reliable models describing dry deposition of air pollutants to complex mountain terrains do not exist. However, new attempts to develop such models are encouraging (Peter Finkelstein, personal commun.). Despite these difficulties we suggest that even with the currently available technologies, reasonable estimates of N dry deposition to some forest stands in complex mountainous terrains can be made. Information on long-term (1 to 2 weeks) average concentrations of major gaseous N pollutants such as NO, NO_2, NH_3 and HNO_3 vapor can be obtained with passive samplers, while the shorter-term (4 to 24 hours) average concentrations of NH_3, HNO_3, and fine particulate NH_4^+ and NO_3^- can be obtained with annular denuder systems. Internal uptake of NO, NO_2, NH_3, and HNO_3 to plants can be calculated based on information on ambient concentrations of the measured gases, information on stomatal conductance to H_2O vapor of major plant species, and correction of stomatal transport of the gases of interest (Bytnerowicz and Riechers, 1995). The branch rinsing technique (Lovett and Lindberg, 1984) can be applied for determinations of surface deposition of NH_4^+ and NO_3^- particulate matter for selected plant species (those with a relatively impermeable cuticular layer). With the assumption that foliar surface-NH_4^+ comes mostly from particulate deposition since NH_3 is almost entirely taken up by stomata (Van Hove et al., 1989), deposition velocities of particulate NH_4^+ to foliar surfaces could be calculated. The NO_3^- deposited to foliar surfaces is a combination of HNO_3 vapor and NO_3^- particulate deposition. The portion of deposition from HNO_3 vapor can be calculated by multiplying deposition velocity values for that gas (v_{HNO_3}), obtained from chamber experiments and literature, by its ambient concentrations. By subtraction, the portion of NO_3^- surface flux originating from NO_3^- particulates can be calculated. Dividing this by ambient levels of particulate NO_3^- will allow for estimates of particulate NO_3^- deposition velocities to various plant surfaces. Subsequently, the calculated deposition velocities for key plant species in a given stand or ecosystem as well as ambient levels of NO_3^- can be used for calculations of landscape level fluxes of that pollutant (Bytnerowicz and Riechers, 1995; Bytnerowicz et al., 1999a). It should be remembered, however, that for various reasons (leaching of NO_3^- and NH_4^+ from the leaf interior, absorption of deposited ions by plant surfaces, particulate matter resuspension or volatilization, etc.), the precision of such estimates might be questionable or impossible to determine for some plant species.

In addition to estimates of N deposition to vegetation, determinations of N deposition to soils are also needed. These are especially important for ecosystems with low LAI values, such as subalpine, alpine, or desert ecosystems. Total deposition (fluxes) of NO_3^- and NH_4^+ to soil surfaces can be measured by direct measurements to soil samples exposed in Petri dishes in ambient air (covered vs. open plates) (Padgett et al., unpublished). In addition, calculations of HNO_3 vapor deposition to different types of soils can be done based on deposition velocities calculated from experimental exposures to known concentrations of the pollutant (Padgett and Bytnerowicz, 2001).Throughfall techniques have been used for evaluation of integrated (wet and dry) flux of nutrients to the forest floor (Schaefer and Reiners, 1990). The typical throughfall approach is difficult to use at a landscape scale, since a large number of replicate collectors is needed and samples have to be collected immediately after each rain event (Thimonier, 1998). However, by using mixed bed ion exchange resin columns, collection of throughfall samples can be done much less frequently, typically one to three times per year (Kjønaas, 1999).This allows for relatively easy and inexpensive evaluation of integrated deposition of N species (NO_3^- and NH_4^+) over a long period (months, seasons, years) at a scale from forest floors and stands to landscapes (Fenn et al., 2002).

Fig. 1 summarizes the methodological needs required for the development of air pollution distribution, biological response, and risk assessment models in the Sierra Nevada. The monitoring methodologies assist in gathering data on ambient concentrations of the air pollutants important for forest health, human health, and visibility (boxes 1, 2, 4, and 5). Information on meteorological parameters (box 3) is needed as auxiliary data for development of pollution distribution models (models A, B, C and D). The three models described in this book (Lee, Chapter 7; Preisler and Schilling, Chapter 8; and Frączek et al., Chapter 9, this volume) testify that reliable models of air pollution distribution in complex mountain terrain can be developed (model A). Similarly, data on N pollutant can also be used for development of models of distribution of N pollutants concentrations (model C). Statistical models translating long-term average O_3 concentrations into real-time O_3 concentrations (model B) can also be developed based on comparison of the collocated passive and active O_3 monitors and historical information on real-time concentration trends. Reliable models of seasonal distribution of N deposition (model D) that would take into account all forms of N deposition to various landscape components in all seasons still need to be developed. This is not an easy task, especially for complex mountain terrain.

Models describing biological responses of forests to air pollution (landscape level evaluation of foliar injury, growth changes, or O_3 uptake of pines and other sensitive species—models E, F, and G) would be based on the pollution distribution models and additional biological data such as foliar injury index (box 6), annual growth changes (box 7), leaf area index (box 8), vegetation coverage (box 9), species distribution (box 10), gas exchange rates of trees (box 11), or information on species sensitivity to O_3 (box 12). An ultimate goal for the Sierra Nevada is to develop risk assessment models that would describe sensitivity of forests to O_3 and other stressors (model H) and would also describe risks associated with air pollution to inhabitants and visitors to the Sierra Nevada (model I). These models are needed for well-informed decision-making by land managers and in evaluating development needs in the Sierra Nevada.

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