Abstracts

“Passive Sampling of Gaseous Air Pollutants in Ecological Effects Research”

International Symposium

Mission Inn, Riverside, California

April 9, 2001

USDA Forest Service
Pacific Southwest Research Station
Atmospheric Deposition on Western Forests

Agenda

8:30 – 8:35. Sagar Krupa and Andrzej Bytnerowicz – Organizational remarks

8:35 - 8:40. Mark Poth – Opening of the Symposium

Session I – Development of passive samplers (John Skelly, Chair)

8:40 – 9:10. Sagar Krupa – *Theory and principles of passive sampling of gaseous air pollutants*

9:10 – 9:30. Alan Davison –*Development and types of passive samplers for monitoring* SO_2 *and fluoride concentrations*

9:30 – 9:50. Y.S. Tang, Neil Cape and M. A. Sutton –*Development and types of passive samplers for monitoring* NO_x *and* NH_3 *concentrations*

9:50 – 10:10. Andrzej Bytnerowicz - *Development and types of passive samplers for monitoring* O_3 *concentrations*

10:10 – 10:30 Coffee Break

Session II – Considerations for using passive samplers in field research (Allan Legge, Chair)

10:30 – 10:50. Hongmao Tang – *Principles of proper use of passive samplers in the field research*

10:50 – 11:10. Sagar Krupa and Miloslav Nosal – *Relationship between passive sampler and continuous measurement data in ecological effects research*

11:10 – 11:30. Antonio Ballarin-Denti – *Techniques of ozone monitoring in a mountain forest area: passive vs. continuous sampling, vertical and under crown profiles.*

11:30 – 11:50. J. Mulik and J. Varns – *Factors and costs for daily regional ozone sampling by a publically-operated passive network*

11:50 – 12:00 – Discussion

12:00 – 1:30 Lunch Break

Session III – Case studies, Antonio Ballarin-Denti, Chair

1:30 – 1:45. John Ray – *The National Park Service experience in passive ozone monitoring in California*

1:45 – 2:00. Roger Cox – *Monitoring of ozone concentrations in Canadian forests*

2:00 – 2:15. D.E. Yuska, J.M. Skelly, J.A. Ferdinand, J.E. Savage, J. Mulik and A. Hines - *Detection of tropospheric ozone in north-central Pennsylvania utilizing passive samplers and bioindicator plants*

2:15 – 2:30. Mark Sather – *Regional contributions of a publically-operated Passive Ozone Network in the Dallas/Fort Worth Area, 1998-1999*

2:30 – 2:45. Maria Jose Sanz *et al. – Measurements of ozone in several regions of Spain*

2:45 – 3:00. Rocio Alonso, Andrzej Bytnerowicz and Michael Arbaugh – *Vertical distribution of ozone and N pollutants in the San Bernardino Mountains, southern California*

3:00 – 3:30 Discussion

3:30 – 3:50 Coffee Break

Session IV – Towards development of risk assessment models based on landscape level pollution monitoring, Alan Davison, Chair

3:50 – 4:10. Haiganoush Preisler, Michael Arbaugh, Andrzej Bytnerowicz, Jenny Rechel and Susan Schilling - *Development of models of spatial and temporal distribution of ozone in the Sierra Nevada, California*

4:10 – 4:30. Witold Fraczek, Andrzej Bytnerowicz and Michael Arbaugh – *Application of the ESRI Geostatistical Analyst for development of ozone distribution models in the Carpathian and Sierra Nevada Mountains*

4:30 – 4:50. Antonio Ballarin-Denti –*Ozone risk assessment mapping in European Alps using integrated data from passive samplers and automatic analyzers*

4:50 – 5:00 Discussion

5:00 – 6:00 Session V - Poster viewing, wine and cheese provided (Rocio Alonso, Chair)

Oral Presentations

Theory and Principles of Passive Sampling of Gaseous Air Pollutants

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There is a rapidly growing interest in passive sampling systems for quantifying ambient concentrations of gaseous air pollutants. Excluding the laboratory analysis costs, passive samplers are inexpensive, easy to use and do not require electricity to operate. Therefore, they are very attractive for use in remote and wilderness areas and in regional scale air quality assessments. Passive samplers allow the quantification of cumulative air pollutant exposures, as total or average pollutant concentrations over a sampling duration (few hours, days and weeks). Such systems function either by chemical absorption or by physical adsorption of the gaseous pollutant of interest onto the sampling medium. While absorption results in an irreversible chemical reaction (resulting in a reaction product that is quantified and inferred linearly to the concentration of the initial pollutant of interest), physical adsorption is reversible leading to the collection and subsequent measurement of the adsorbed species itself. There are five general types of passive samplers: badge, absorption candle, diffusion tube-absorbent surface, packed diffusion tube and cartridge. Selection of a passive sampler must be based on its known or tested characteristics of specificity, linearity and range of response to the chemical constituent being collected. Preparation of the sampling medium must be done with care and laboratory analysis of the adsorbed pollutant or its reaction product with an absorbent must include reliable methods that can yield accurate and reproducible results. In addition, under field conditions, the effects of wind velocity (turbulence), radiation, temperature and relative humidity must be addressed in the context of absorbent - adsorbent performance and sampling rate. Because of all these considerations, passive samplers may provide under- or over estimations of the cumulative exposures, compared to the corresponding data from co-located continuous monitors or active samplers, although such statistical variance can be minimized by taking needed precautions *a priori*.

Development and Types of Passive Samplers for Monitoring NO_X and NH_3 Concentrations

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Passive samplers were originally developed for monitoring personal exposure in the work place. Numerous samplers based on the 'Palmes-tube' have been developed for ambient air monitoring. In each case, the diffusion path length and/or cross-sectional area are modified to achieve the desired sampling rate. The 'tube-type' samplers are low sensitivity samplers suitable for long-term monitoring, whereas the 'badge-type' samplers have faster sampling rates and are suited to short-term monitoring.

In the UK, diffusion tubes are widely used for monitoring NO_2 and NH_3. The open-type tube is prone to positive bias caused by incursion of wind eddies, leading to a shortening of the diffusion path. By using membrane samplers, wind incursions are prevented, but an additional diffusion resistance is imposed and it is necessary to calibrate the tubes against a reference method to obtain an effective sampling rate.

For NO_2 sampling, positive bias also arises from the reaction of NO with O_3 during diffusion within the sampler. The interference from chemical reaction is severe close to NO sources, with errors up to 30% for kerbside locations. In rural areas, where NO concentrations are small relative to NO_2, these errors are small. There may also be negative bias over long sampling periods caused by the degradation of trapped NO_2. Typical detection limits are around 1 ppb over 1 week.

The low sampling rate of diffusion tubes make them too uncertain for use at background concentrations where they significantly overestimate NH_3 concentrations. They are also reported to underestimate NH_3 concentrations at high concentrations and have in the past been subject to a highly uncertain correction factor of 0.42. Badge-type samplers such as the 'Willems badge' samplers permit accurate sampling at low ambient NH_3 concentrations, but suffer from saturation at high concentrations. A passive sampler optimised for monthly measurements of NH_3 is reported here, together with its application in the UK National NH_3 Monitoring Network.

Development and Types of Passive Samplers for Monitoring O_3 Concentrations

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Elevated concentrations of tropospheric ozone damage vegetation and cause serious economic and ecological losses in agriculture, forestry and natural ecosystems. Sufficient information regarding spatial and temporal distribution of O_3 concentrations in forests and other remote locations for evaluation of risks from this pollutant is still missing. Financial and practical constrains seriously limit development of monitoring networks that utilize continuous monitors and active samplers. Passive samplers, the relative simple an inexpensive devices that do not require electric power and continuous maintenance, offer a possibility for landscape-level evaluation of O_3 concentrations. In recent years various types of passives samplers have been developed and used in field conditions in Europe and North America. Various badge, diffusion tube-absorbent surfaces and diffusion tubes providing steady flow of air into the absorption media (DPE, indigo carmine, sodium nitrite, and others) have been developed and used in various field experiments. These developments will be described. A special emphasis will be given to the Ogawa passive samplers widely used in forestry research in the United States and Europe. In these samplers, O_3 reacts with sodium nitrite producing nitrate on a glass/cellulose filter placed within a diffusion badge. Nitrate is H_20-extracted and analyzed with ion chromatography. Ozone concentrations are calculated either by using a formula provided by a developer or by calibration of samplers against collocated continuous active monitors.

Principles of Proper Use of Passive samplers in the Field Research

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Scientific and social interest in monitoring air pollutants indoors and outdoors is manifest in the world. Several sampling methods for monitoring air pollutants in the ambient air and indoor air have been developed and subsequently improved over the past few decades. These methods can generally be classified as active and passive methods. Active samplers such as continuous air pollutant analyzers, filter-packs, high volume samplers etc. need pumps to draw air through collection media. Therefore, electricity cannot be avoided in the active samplers, and the on going operation cost is relative high. A passive sampler is a device, which is capable of taking samples of gas or vapor pollutants from the atmosphere at a rate controlled by a physical process such as diffusion through a static air layer or permeation through a membrane, but which does not involve the active movement of the air through the samplers. Thus, passive samplers, on the other hand, are cost effective and convenient to use. These factors have created a growing demand for passive samplers in the world.

The key factor for using passive samplers is how to determine their sampling rates. The passive sampling rates are affected by many factors, such as temperature, relative humidity, wind speed, wind direction, collection medium, sampler's design etc.

The principles of passive samplers' applications mainly include four parts:

- Program design and passive samplers' installation.
- Determination of passive air sampling rates.
- Air pollution concentrations and air quality.
- Relationship between air pollution concentrations obtained by passive samplers and government standards.

This paper will use Maxxam All-season Passive Sampling System (MAPSS) as an example to discuss how to correctly install passive samplers indoors, personal use, and outdoors, how to use meteorological parameters in different seasons and locations to obtain relatively accurate sampling rates, how to obtain the meteorological information, and how to assess the air quality based on the air pollution concentrations obtained by the MAPSS and the local government standards.

Relationships Between Passive Sampler and Continuous Ozone (O_3) Measurement Data in Ecological Effects Research

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Passive sampling systems yield cumulative exposures of a receptor to gaseous air pollutants, as their total or average concentrations over the sampling period. Frequently such expressions of pollutant dose can not account for the dynamics of pollutant occurrence, its flux and the corresponding plant response that is governed by the physiological characteristics of the plant receptor. These overall processes and relationships are fundamentally stochastic by their nature. Therefore, we developed and verified a stochastic, Weibull probability model to simulate the underlying frequency distributions of hourly ozone (O_3) concentrations (exposure dynamics) using the single, weekly mean values obtained from a passive (sodium nitrite absorbent) sampler. The simulation was based on the data derived from a co-located continuous monitor. Although at the moment the model output may be considered as being specific to the elevation and location of the study site, the results were extremely good. This effort for the approximation of the O_3 exposure dynamics can be extended to other sites with similar data sets and in developing a generalized understanding of the stochastic O_3 exposure-plant response relationships, conferring measurable benefits to the future use of passive O_3 samplers, in the absence of continuous monitoring. Clearly in this context, the dynamics of plant biology must also be understood. Furthermore, the quality of the model results was dependent upon the closeness of the relationship between the passive sampler and the corresponding co-located continuous monitoring data. We provide comparisons of the model output for a site with good relationship between the two measurement techniques and a site with relatively poor correlation. The results show that passive samplers should be deployed with great care, particularly in complex terrains, considering the characteristics of the local topography and the meteorological conditions.

Techniques of Ozone Monitoring in a Mountain Forest Region: Passive vs Continuous Sampling, Vertical and Under-Crown Profiles

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Ozone is the most dangerous air pollutant for plant ecosystems in the Mediterranean and Alpine area due to its heavy effects on both physiological and agronomical parameters of crops and forests. In order to evaluate the relation between ozone exposure and vegetation damage under on-field conditions, suitable ozone monitoring techniques have been investigated. In the framework of a 5-year research project aimed at the ozone risk assessment on forests both continuous analyzers and passive samplers have been employed during the summer season (1994-1998) in different sites of a wide alpine valley in Italy.

Continuous analyzers allowed to record ozone hourly concentration means necessary both to calculate exposure indices such as AOT, SUM, W126 and to record daily time-courses, but their use was limited by power supply, logistic, layout, maintenance and calibration inconveniences. Passive samplers gave only weekly mean concentration values but proved to be much less demanding, cheaper, able to cover much more monitoring sites making also possible the estimate of the altitude concentration gradient. Under-crown ozone profiles were also determined by placing passive sampler at different heights inside the forest canopy.

An inter-comparison between passive (PASSAM, CH) and continuous measurements highlighted the necessity to accurately standardize all the exposure operations, particularly the pre and post exposure conservation at cold temperature to avoid dye (DPE) activity.

Vertical ozone soundings by mean of tethered balloons (kytoons) revealed ozone reservoirs aloft and were useful to explain the ozone advection dynamic in mountain slopes where ground measurement proved not to be adequate. More sophisticated 3-D space-temporal ozone distribution detection was obtained by a LIDAR system in a pilot study. Advantages and disadvantages from each mentioned technique are discussed.

__Factors and Costs for Daily Regional Ozone Sampling by a Publically-operated Passive Network__

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An extensive passive sampling network (Passive Ozone Network *of* Dallas; POND) was operated by the public to provide daily tropospheric ozone measurements in a 25,000 km^2 region of northern Texas for 14 weeks during the 1998 and 1999 summer ozone seasons. The resulting product is a quality-based database (> 4000 Ogawa sampler deployments) that is being actively applied in formulating the ozone management strategies for this and surrounding regions. It is suggested that similarly sized networks, sampling for ozone and additional key pollutant species, could be deployed nationally to accelerate and/or supplement the siting changes needed in current US air monitoring networks to address the new 8 hr NAAQS guidelines for ozone. The factors considered in the quality assurance program for POND, as they would apply in the planning of a similar network, i.e., selection, training and motivation of the public, logistics of mailing and analysis, geographics and siting, system design and durability of materials, ample sensitivity for daily sampling, etc., will be discussed.

Experience dictates a direct cost analysis for any proposed field operation must be provided before any serious consideration of implementation. We present procedures for estimating the costs to install regional passive networks and obtaining the air quality database desired. Secondly, we provide comparative costs between establishing 30 site (i) instrumented versus (ii) passive monitoring systems in one US region and then moving and reestablishing the respective networks elsewhere.

The National Park Service Experience in Passive Ozone Monitoring in California

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The National Park Service has tested and used passive ozone samplers for several years to get baseline values for parks and to determine the spatial variability within parks. Experience has shown that the Ogawa passive samplers can provide ± 15% accuracy when used with a quality assurance program consisting of blanks, duplicates, collocated instrumentation, and a standard operating procedure that carefully guides site operators. Although the passive device does not meet EPA criteria as a certified method (mainly, that hourly values be measured), it does provide seasonal summed values of ozone. The seasonal ozone concentrations from the passive devices can be compared to other monitoring to determine baseline values, trends, and spatial variations. This point will be illustrated with some Kriged interpolation maps of ozone statistics.

A refinement is to use the passive samples to get elevation gradients and spatial distributions of ozone within a park. This has been done in varying degrees at Mt. Rainier, Olympic, Sequoia-Kings Canyon, Yosemite, Joshua Tree, Rocky Mountain, and Great Smoky Mountains National Parks. The ozone has been found to vary by factors of 2 and 3 within a park when average ozone is compared between locations. Specific examples of the spatial distributions of ozone in 3 California will be given using interpolation maps. Positive aspects and limitations of the passive sampling approach will be presented.

Monitoring Ozone Exposure of Canadian Forests

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Air quality objectives, established for the protection of crops and other plants, are now being exceeded over large forested areas of Canada, giving rise to the need for both extensive and intensive monitoring programs to determine long-term critical exposure values for forest damage. Ozone may also predispose plants to other injuries caused by thaw-frost cycles or drought, and may exacerbate nutrient deficiency by reducing carbon allocation to roots. Currently, air quality monitoring is being carried out at "continuous" monitoring stations, however, these are limited to a few urban sites and fewer rural sites. The requirement for an inexpensive monitor for atmospheric oxidants (specifically ozone) that can be use in remote locations prompted the development of CanOxy Plate™ passive ozone monitor by the air pollution research group. The monitors underwent operational trials during 1997-2000. These trials involved the exposure of the monitor in the upper canopy, and at an adjacent forest opening at selected ARNEWS sites across the country. The operational trial was for 4 exposure periods of 2 to 3 weeks. The CanOxy Plate monitors were co-located nearest continuous ozone air quality monitor. This allowed for the production of a field calibration for quality assurance assessment. Results from 1996 indicate significant correlations with accumulated ambient ozone concentrations (r=0.93) suggesting a high degree of quality assurance under field conditions. Analysis of CanOxy Plates exposed at plots in forest openings indicated no relationship with the amounts of ozone (ppmh) monitored with the nearest continuous air quality monitor, often hundreds of kilometres away. Spatial differences in ozone exposure between the continuous air quality monitors and the forest plots together with our knowledge that strong gradients of ozone exposure found within the canopy, underlines the importance of *in situ* monitoring of ozone exposure of Forest Health plots in areas of elevated ground level ozone. Development of a passive ozone monitoring protocol and analysis techniques will be shown for forest exposure on different scales.

Detection of Tropospheric Ozone in North-Central Pennsylvania Utilizing Passive Samplers and Bioindicator Plants

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Field research was performed to measure ambient concentrations of tropospheric ozone and to determine foliar injury to black cherry (*Prunus serotina*) and common milkweed (*Asclepias syriaca*) in North Central Pennsylvania from May 29 to September 5, 2000. Ogawa passive ozone samplers were used at 15 rural, open-area sites, of which, 6 sites had co-located TECO continuous ozone monitors. Results of this first year of a planned two-year investigation indicated a high correlation between the Ogawa passive samplers and the continuous ozone monitors with an r-value of 0.9441 ($p<0.0001$). There was also a high correlation between ozone concentration and elevation ($r = 0.86126$, $p <0.0001$) showing that higher elevations received greater ozone concentrations. Highest seasonal ozone concentrations among all sites were recorded at Skyline Mountain (580 m,msl). Lowest concentrations were recorded less than 3 miles away in the city of Williamsport (202 m,msl). Black cherry and common milkweed were observed for foliar injury at each of the sites using a modified Horsfall-Barratt rating system. Average injury to both black cherry and common milkweed was analyzed by recording the sum of the leaves injured per plant with the sum of the area per leaf injured out of the total number of injured plants. The highest combined plant injury occurred at the Moshannon State Forest site while lowest injury occurred at the State College site. There were no significant relationships noted between sites and foliar injury on the two ozone-sensitive bioindicator species due to the very low ozone presence during the latter part of the 2000 growing season; this result is consistent with our expectations of a cool and rainy late summer and early fall season. In contrast, significant relationships between ozone exposures and symptom expressions had been reported for the 1999 growing season when ozone was much higher and weather conditions favored late-season uptake of ozone by black cherry and milkweed.

Regional Contributions of a Publically-operated Passive Ozone Network in the Dallas/Fort Worth Area, 1998-1999

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This presentation will summarize key results from a two year intensive passive/continuous ozone study in an approximate 25,000 km^2 area around Dallas-Fort Worth, Texas. Specifically, this presentation will discuss the value of the two year Passive Ozone Network of Dallas (POND) database to scientists and modelers working on ozone pollution research, and describe in detail ozone concentration results from a series of 11 contiguous passive/continuous monitored days in not only the Dallas-Fort Worth area, but also including rural continuous sites in neighboring Oklahoma and Arkansas. With 30 passive ozone sites in 1998, and 10 passive ozone sites in 1999, the POND studies added valuable additional 24-hour ozone data for scientists and modelers to use in future photochemical grid model exercises. Further, the 1999 POND passive samplers also recorded 12-hour day and night ozone samples for diurnal analysis. Both urban and rural sites were represented in the POND studies, providing important ambient ozone concentration data for both public health and ecological effects (e.g. crop effects) research.

Measurements of ozone in several regions of Spain

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Ambient concentration of tropospheric ozone are measured in two different networks, twelve Intensive Monitoring Plots (IMP) of the Pan-European International Cooperation Program for Forest (UN/EC) and a local network of eleven sites around Madrid City (DGCN). Since all plots were in remote sites without power and the number was relatively high, passive samplers (Ogawa & Co. USA) were use instead of continuos monitors. The measurements started in April 2000 and will continue several years. Samplers ere located next to two continuous monitoring stations from Valencia Air Quality Network for calibration purposes. Here the data from 2000 are presented for both networks, the results show that the IMP plots experience lower levels of ozone in general respect to the Madrid Network ones. The highest daily averaged values (70 ppb) for the biweekly sampling periods were found during 2000 in the South facing slopes of the mountains located Northwest of Madrid in the City network during summer (August). In the IMP network the highest values were reordered in Alicante were values for August reached 64 ppb as a daily average of the first two weeks. For all sampling stations both networks a yearly common behaviour was observed, with one maximum in late Spring (beginning of June) followed by a decrease and a new broad maximum in mid Summer (beginning of August) that slowly decreased during September.

Vertical distribution of ozone and nitrogenous pollutants in the San Bernardino Mountains, southern California

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Information about spatial and temporal distribution of air pollutants is essential for a better understanding of environmental stresses affecting forests and the estimation of potential risks associated with air pollutants. Ozone and nitrogenous air pollutants were monitored along an elevation gradient in San Gorgonio Wilderness area (San Bernardino Mountains, California, USA) during the summer of 2000 (mid-June to mid-October). Passive samplers were exposed for two-week periods at six sampling sites located at 300m intervals ranging from 1200 to 2700m elevation. Elevated concentrations of ozone were found in this area with seasonal means ranging from 53 to 59 ppb. The highest ozone concentrations were detected in the period 25 July-8 August, reaching values of 64-72 ppb expressed as two-week mean. Passive-sampler ozone data did not show a clear relationship with elevation although during the periods with higher ozone levels, ozone concentrations were higher at those sites bellow 2000 m than at sites located above that elevation. All nitrogenous pollutants studied showed a consistent decrease of exposure with elevation. Nitrogen dioxide (NO_2) levels were low, decreasing with increasing elevation from 6.4 to 1.5 ppb seasonal means. Nitric oxide (NO) concentrations were around 1-2 ppb, which is within the range of the detection levels of devices used. Nitric acid concentrations were lower at higher elevations (seasonal means 1.9-2.5 : g m^{-3}) than at lower elevations (seasonal means 4.3-5.1 : g m^{-3}). Summer concentrations of ammonia were slightly higher than nitric acid ranging from 6 : g m^{-3} at the lowest site to 2.5 : g m^{-3} registered at the highest elevation. Since complex interactions between ozone and nitrogenous air pollutants have been already described on forests, simultaneous information about the distribution of these pollutants is needed. This is particularly important in mountain terrain where there are not reliable models of air pollutant distribution.

Statistical Approaches for the Analysis of Ambient Ozone Levels from Passive Samplers in the Sierra Nevada, California

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Statistical approaches for modeling spatially and temporally explicit data are discussed for 79 passive and 9 active monitors distributed across the Sierra Nevada, California. A generalized additive regression model was used to estimate spatial patterns and relationships between ozone and explanatory variables as well as to predict ambient ozone exposure levels in non-monitored sites. The fitted model was then used to estimate probability maps for risks of exceeding critical ozone levels in the Sierra Nevada region.

Preliminary results indicate the explanatory variables elevation; maximum daily temperature; precipitation and ozone level at closest active monitor, were significant in the model. There also was a significant (mostly east-west) spatial trend. The between site variability had the same magnitude as the error variability. This seems to indicate that there still exist some important site features not captured by the variables used in the analysis. There also were a few outliers (3% of the data) spread among all the sites. The fitted model using robust techniques (i.e., assigning less weight to outliers) had an overall R^2 value of 0.58. The mean standard deviation for a predicted value was 7 ppb per hour.

Application of the ESRI Geostatistical Aanalysts for development of ozone distribution modesl in the Carpathian and Sierra Nevada Mountains

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The newly developed by ESRI Geostatistical Analyst has been used to determine spatial interpolation parameters of ozone (O_3) concentrations and to generate maps of ozone distribution in two big mountain ranges, the Carpathians in Central Europe and the Sierra Nevada in California. Development of methods used in this study will be explained and examples of the results obtained in the two studies will be presented. A sufficient number of sample points is a key factor determining the accuracy and reliability of the ozone concentration surface resulting from geostatistical analysis. In case of the Carpathian Mountains, a small number of monitoring sites resulted in a generalized surface of ozone distribution, partly due to only a slight correlation of ozone concentration and elevation observed in that study. In the Sierra Nevada Mountains, the ozone monitoring network was much denser and broader collateral geographic and climatologic information could be associated with the ozone data. The final maps of ozone concentrations for Sierra Nevada were derived from cokriging algorithm based on two secondary variables - elevation and maximum temperature as well as the determined geographic trend. Consequently, the resulting maps of ozone concentrations in the Sierra Nevada are more precise and more reliable than those created for the Carpathians. An effort to determine an optimized sampling density will also be explained.

Ozone risk assessment and mapping in the European Alps using integrated data from passive samplers and automatic analyzers

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As a part of a five years integrated study on the atmospheric pollution in a southern Alps area, an ozone risk assessment has been carried out in 1998 in the Italian Province of Sondrio. The area (90x40 Km^2) is characterized by a long valley and a complex orography, which prevents an accurate definition of spatial patterns and temporal evolution of ozone levels by automatic analyzers or mobile stations.
The ozone risk assessment procedure has been performed by employing passive samplers in 15 sites during the summer season (May 11 to August 17) integrated by a limited number (4) of automatic analyzers (both fixed and placed on mobile labs). Data were collected weekly from sites ranging in altitude from 252 to 1985 m asl.
Spatial patterns of ozone concentrations were estimated using geostatistical techniques. Ordinary kriging was applied to generate weekly maps on a grid base of 2x2 Km^2. Interpolations were corrected with a proper function to account for altitude and related ozone daily courses. This function of time and altitude, carefully fitted to the passive collected ozone weekly means, was essential to obtain modeled estimates of the hourly ozone values necessary to calculate the AOT40 exposure index. On this basis weekly spatial distribution maps of AOT40 were calculated. The results were compared with on-field observations of visible leaf injuries on several forest plant species collected from 81 sites.
For the years 1999 and 2000 the ozone risk assessment was extended to the whole Lombardy Region (240x220 Km^2). Level I exceedances maps were produced for both forests and crops.

Poster Presentations

1. Flaviu Popescu, Vladimi Gancz, Ovidiu Badea, Andrzej Bytnerowicz and Robert Musselman – *Correlation between ozone pollution and meteorological conditions in the Retezat National Park of the Carpathian Mountains, Romania*

2. Andrzej Bytnerowicz – *Passive sampler for nitric acid vapor*

3. Dennis Fitz – *Development of monitoring techniques for measurements of* NH_3 *fluxes*

4. Andrzej Bytnerowicz, David Parker and Pamela Padgett – *Vertical distribution of ozone and* HNO_3 *vapor on Mammoth Mountain, eastern Sierra Nevada, California*

5. Marcus Schaub, Maria Sanz et al. – *Assessment of ozone injury on European vegetation – the ICP–Forests Program*

6. Antonio Ballarin-Denti, Brambilla E., Fumagalli I., Gerosa G., Mazzali C., Mignanego L., and Sormani L. – *Ozone monitoring in the Province of Milan (Italy) by means of passive samplers and plant bioindicators.*

7. Mark Fenn, Mark Poth and Michael Arbaugh - *A passive throughfall collection method for measuring atmospheric deposition of nitrogen*

Passive sampler for nitric acid vapor

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Nitric acid (HNO_3) is one of the most important air pollutants responsible for increasing deposition and saturation of forests with nitrogen. Nitric acid may cause injury of plants and has a potential to modify development of injury caused by ozone. Better understanding of HNO_3 spatial and temporal distribution in forest ecosystems of the western United States is essential for better understanding of its phytotoxic potential, estimates of N deposition and development of N deposition models at a landscape level. A simple and inexpensive passive sampler has been developed in the USDA Forest Service Pacific Southwest Research Station in Riverside, CA. Nitric acid is selectively absorbed on 47 mm nylon filters with no interference from particulate NO_3^-. Concentrations determined with the passive samplers closely corresponded with those calculated with the collocated honeycomb annular denuder systems. Due to a very high deposition velocity of HNO_3, our attempts of placing nylon filters in a diffusion tube or diffusion badge to provide a steady flow of sampled air to the absorption medium failed (no detectable amounts of the pollutant reached the nylon filters). The PVC protective caps of standardized dimensions protected nylon filters from rain and wind and allowed for reliable predictions of ambient HNO_3 concentrations. Our samplers have been successfully used in several studies in California (the Sequoia National Park, the Mammoth Mountain and the San Bernardino Mountains elevational gradient studies).

A Passive Monitoring Technique for Measuring Ammonia Fluxes

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Fabric diffusion denuders have been developed at our laboratory to sample semi-volatile species such as nitric acid and ammonia. Simple cloth fabrics have been found to be as efficient for sampling such species as the more complex honeycomb and annular designs constructed of metal or glass. Cut into 47mm circles, these fabric denuders are simply mounted in an open-face filter holder in place of a filter. We have recently used these denuders to sample ammonia fluxes from fertilized cropland, a dairy operation and a pig farm. The denuders were coated with phosphoric acid and two of them were placed in holders that were open-faced on both sides. Two denuders were used since the collection efficiency at 10 L/min was typically 90-95%. One such holder was placed on each end of 1¼" inch PVC pipes that were six inches long. One pipe was placed horizontally in a north-south orientation, another in an east-west orientation. The amount of ammonia collected depended on the flow rate in the pipe due to the prevailing wind and concentration of ammonia, thus giving a measurement related to the ammonia flux. Samples collected downwind of the three sources always showed most of the ammonia was collected by denuders pointing toward the source. The fluxes measured by this approach were consistent with fluxes calculated from the ammonia measured with actively sampled denuders with similar substrates multiplied by the wind velocity.

Vertical distribution of ozone and HNO_3 vapor on Mammoth Mountain, eastern Sierra Nevada, California

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Mammoth Mountain near Mammoth Lakes in Eastern Sierra Nevada Mountains is a popular recreational location for thousands of Californians, visitors from other states and abroad. Eastern Sierra Nevada Mountains has been considered as an area with very low air pollution. Air pollution monitoring was performed during the summer class "Acquisition and Analysis of Environmental Data" that was organized by the Department of Environmental Sciences of the University of California in Riverside. In August and September 1999 and 2000 concentrations of ozone (O_3) and nitric acid vapor (HNO_3) were monitored on an elevational gradient (2184 – 3325 m) on the Mammoth Mountain with passive samplers. The Ogawa passive samplers were used for O_3 monitoring and the samplers developed by the USDA Forest Service for HNO_3 monitoring. Close agreement between concentrations of two pollutants was determined for two years of the study. No clear effects of elevation on concentrations of the two pollutants detected. In general, concentrations of HNO_3 were low and at the background levels expected for the Eastern Sierra Nevada, however, the measured concentrations of O_3 were elevated. High concentrations of ozone in the area were confirmed with an active O_3 monitor (2B Technologies, Inc.) placed at the Mammoth Mountain Peak. Possible explanation of elevated concentrations of O_3 will be presented.

Ozone Monitoring in the Province of Milan (Italy) by Means of Passive Samplers and Plant Bioindicators

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The Province of Milan (northern Italy) is characterised by high population density and diffuse industrial activities both responsible of high levels of pollutant emission and critical air quality. Among the different air pollutants subjected to control regulations particular attention is being paid to ozone, as its thresholds are often exceeded in the summer.
The network of existing monitoring stations covers much better urban areas than rural sites where however higher is ozone concentration during the summer and its damage on crops. Since the extension of air pollution monitoring based on automatic analysers requires large investments and maintenance costs, efforts are under way to integrate the base network with passive analysers and/or bioindicators. During 1998 and 1999 two campaigns have been carried on to evaluate ozone pollution by means of tobacco plants (*Nicotiana Tabacum*) and passive samplers (PASSAM, CH).
Tobacco plants were periodically exposed to atmospheric ozone (May-August) and an appropriate index of ozone damage evaluated. Weekly values of AOT0 were calculated and relations between AOT0 and Leaf Injury Index investigated. Passive samplers were exposed to ambient ozone and collected every week supplying a dataset of weekly values for several sites. Spatial distribution of weekly ozone concentrations were estimated in an area of 70x60 km^2 on a grid base of 2x2 km^2. Kriging interpolation was performed on the base of an anisotropous variogram.

A Passive Throughfall Collection Method for Measuring Atmospheric Deposition of Nitrogen

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Measurement of nutrient deposition in throughfall is a widely used method for estimating atmospheric deposition inputs to forest ecosystems. Many studies have been published, providing a large database of throughfall deposition inputs to forests. However, throughfall collection and analysis is labor intensive and expensive due to the large number of replicate collectors needed and because sample collection and chemical analyses are required on a repetitive precipitation event-based schedule. Therefore we developed and tested a passive throughfall collector system based on a mixed bed ion exchange resin column. We anticipate that this method will typically require only one or two samplings per year. Precipitation is collected by a rain collector or snow tube and ions are retained as the solution moves through the resin column. Ions retained by the resin are then extracted in the same column with 2*N* KCl and analyzed for nitrate and ammonium. Preliminary results from the first three months of exposure at a high and low deposition site in the San Bernardino Mountains will be compared to results from traditional throughfall collectors co-located with the passive samplers.