

Final Report

Improving Model Estimates of Smoke Contributions to Regional Haze Using Low-cost Sampler Systems

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Abstract

Robust low-cost sampler systems allowing for monitoring of air pollutants important for air quality resulting from forest fires and urban/agricultural activities in remote locations were tested and developed. The main emphasis was placed on passive samplers for ozone and nitrogenous pollutants (nitrogen oxides, ammonia and nitric acid vapor). In addition, a system for evaluation of total inputs of atmospheric nitrogen under vegetation canopies (throughfall collectors) was developed. Passive samplers tested and developed in this study provide information, which is critical for local plume dispersion measures and regional air quality and haze assessments. Passive samplers for ozone, nitric acid and ammonia were used in 2002 summer season in selected areas of the Sierra Nevada (Lake Tahoe Basin, San Joaquin River Drainage, and eastern Sierra Nevada). Effects of local generation of air pollution, long-range transport of pollution plumes, and the McNalley fire (Sierra National Forest, July/August 2002) on distribution of gaseous and particulate air pollutants were evaluated. Geostatistical Analyst software (ESRI) was used for production of maps showing spatial and temporal distribution of measured air pollutants in the studied areas.

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Introduction

The Grand Canyon Visibility Transport Commission (GCVTC) concluded in its analysis that for the Colorado Plateau “emissions from fire, both wildfire and prescribed fire, are likely to have the single greatest impact on visibility at Class I areas through 2040”. Wildland and prescribed fires vary greatly in time and space. Monitoring individual fire emissions, transport and dispersion is difficult and costly, especially for wildland fires. Fire emissions may combine with urban transported pollution to impact regional haze and visibility in Class I areas distant from the fire. Sulfates, nitrates, organics, elemental carbon and soil dust cause most of the visibility deterioration. In addition, nitrogen dioxide is a commonly occurring gaseous pollutant that significantly absorbs light (National Research Council, 1993). Wildfire emissions containing nitrogen oxides and volatile organic compounds (VOCs) also promote the formation of ozone, a criteria pollutant affecting human health and agricultural and natural vegetation (Schultz et al., 1999; Kita et al., 2000). Concentrations of another phytotoxic pollutant, nitric acid vapor, also increase downwind from forest fires (Talbot et al., 1999). Nitric acid vapor is also a very important component of atmospheric dry deposition of nitrogen to forests and other natural ecosystems (Bytnerowicz and Fenn, 1996).

Presently regional haze is measured for Class I areas with the IMPROVE network (IMPROVE, 2000). These monitors are expensive, and require specialized placements that include continuous power sources and air-conditioned shelters. Robust low-cost sampler systems are needed to increase spatial and chemical resolution of this network, especially for Class I areas. As a result there are few monitors placed in Class I areas, and few (6 – 12 per region) established stations over large areas. These stations need to be supplemented with an extensive network of monitors established at more remote locations to quantify the relationship between IMPROVE monitors and air quality conditions in Class I areas.

Recent research indicates that various filter pack, denuder and passive monitoring systems can be used in monitoring of a wide spectrum of air pollutants in remote locations. These pollutants could originate from various sources such as forest fires, and emissions urban, industrial and agricultural activities. Since only Phase I of the original proposal has been funded, serious revision of project objectives and a work plan had to be made. We focused on adaptation of robust low-cost sampler systems to measure gaseous and particulate pollutants significantly contributing to the large-scale air pollution problems, including regional haze. The main emphasis was placed on development of passive samplers for air pollutants and total inputs of atmospheric nitrogenous compounds. Such systems provide information critical for local plume dispersion measures and regional haze assessments. Originally it was intended to use these sampler systems at two key regions in the Western U.S. - the Sierra Nevada in California/Nevada and the Grand Canyon Plateau. However, due to reduced level of funding only the selected areas in the Sierra Nevada areas were monitored. Modeling efforts were limited to the use of Geostatistical Analyst software for evaluation of spatial and temporal distribution of selected air pollutants in the Sierra Nevada Mountains. The results of our research presented in this report reflect those changes.

Project Objectives

Develop and test low-cost self-powered ambient monitoring systems useful for measuring atmospheric components of regional air pollution (haze) caused by emissions from forest fires and other sources.

Develop samplers for atmospheric nitrogen deposition at remote areas.

Assess air pollution status and contribution of forest fires to regional haze in selected Sierra Nevada areas by developing networks of low-cost samplers.

Background

Evaluation of landscape level spatial 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 such as prescribed fires. Visibility is most affected by fine particles in the range of 0.1-1.0 μm diameter, which have the highest light scattering efficiency. Particulate pollutants, both organic and inorganic, also contribute to human health effects and visibility deterioration (National Research Council, 1993). From the point of view of health and phytotoxic effects, ozone (O_3) is the pollutant of primary importance (Krupa and Manning, 1988). From the ecological perspective, deposition of nitrogenous pollutants is important for nutrient cycling in forest and other ecosystems. Ecological and environmental effects related to excess N, include: increased nitrogen nutrient status of normally N-limited plants, alternation of plant physiological processes, degraded water quality, increased emissions of a number of important greenhouse gases, and effects on carbon sequestration (Fenn et al. 1998). Biologically important nitrogenous pollutants that increase N availability to plants are ammonia (NH_3), nitric acid vapor (HNO_3), nitric oxide (NO), nitrogen dioxide (NO_2), particulate ammonium (NH_4^+) and nitrate (NO_3^-) (Bytnerowicz et al., 1998; Bytnerowicz et al., 1999).

Financial and practical constraints seriously limit development of monitoring networks that utilize real-time active monitors for determinations of concentrations of the above listed pollutants. Therefore there is a rapidly growing interest in passive sampling systems for quantifying ambient concentrations of gaseous air pollutants. Excluding laboratory analysis costs, passive samplers are inexpensive, easy to use and do not require electricity to operate. 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 (Krupa and Legge, 2000).

Passive samplers allow for a landscape-level evaluation of air pollution concentrations and deposition. 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. In the reported study, the state-of-the-science active and passive systems of the gaseous pollutants of interest were evaluated. Based on that we recommend a complete system of passive samplers for monitoring ambient concentrations of ozone and key nitrogenous pollutants. We also tested possibility of

using passive sampling for particulate matter determinations. Since diffusion cannot be used for qualitative collection of particulate matter, open-face systems were tried. Our tests showed that qualitative collection of particulate matter that would allow for distinguishing particle size and separation of gaseous and particulate components of an airborne ion of interest (such as NO_3^- or NH_4^+) is impractical. Therefore we believe that portable, battery-operated particulate (PM 2.5 and PM 10) samplers offer the best opportunity for ambient monitoring. As an example of this approach we present in this report maps of particulate matter distribution near the McNalley fire based on data obtained with such samplers. In addition, low-cost battery operated annular denuder/filter pack air pollution sampling systems developed in Great Britain offer new opportunities for landscape level monitoring of a wide spectrum of gaseous and particulate pollutants (Sutton et al. 2001).

The throughfall method has been extensively used for estimating atmospheric deposition to forests and other ecosystems (Thimonier, 1998). Deposition of N in throughfall is the hydrologic flux of N from the canopy to the forest floor. Throughfall measurements of N deposition generally underestimate total N deposition to the forest because of canopy retention of a portion of the N intercepted by the canopy, and because deposition to understory vegetation and direct deposition to the ground surface are usually not measured. Nonetheless, throughfall collection and analysis seems to have greater potential than other methods for widespread monitoring of atmospheric deposition to forests and other ecosystems. Throughfall is often the method of choice because of the impracticality of other methods of monitoring dry deposition at the scale needed for characterizing atmospheric deposition over large forested landscapes. However, traditional throughfall methods are labor intensive and analytically expensive to implement at broad scales----because of the need to frequently collect and analyze a large number of replicate samples (generally on a precipitation-event basis). Therefore we modified throughfall collection technique by using ion exchange resin (IER) columns. IER, usually deployed in resin bags, have often been used for nutrient cycling studies (Binkley and Hart, 1989; Susfalk and Johnson, 2002), although less frequently for atmospheric deposition measurements (Köchy and Wilson, 2001; Kjønnaas, 1999a; Simkin et al., 2004). We chose the resin column design with the expectation that this would be a highly efficient technique for ion capture from throughfall or precipitation samples as the flow is directed through the IER column, enhancing contact of the solutions with the resin. Other advantages of the IER column design used in this study are that the resins are not in contact with the soil or forest floor and that the resins can be easily extracted in the laboratory from the same columns used during the field exposure.

An alternative approach to emission models originally planned for the study is to use Geographic Information System (GIS). The GIS software and methodologies offer solutions to many specialists including foresters, natural resource managers, and air pollution professionals. Using powerful tools for better analysis and decision making, GIS is able to provide the "big picture" about the considered resources and lets to perform various complex tasks. The objective of this application of GIS methods was to produce mapped distributions of ambient O_3 in selected areas of the Sierra Nevada Mountains in summer season of 2002, using a combination of passive O_3 samplers and active O_3 monitoring station data.

Materials and Methods

Air pollution monitoring systems

Passive samplers

In the Ogawa passive badge type, O₃ sampler (Ogawa & Co. USA, Inc. Pompano Beach, FL) a filter coated with sodium nitrite, which gives a measure of O₃ through the oxidation of nitrite (NO₂⁻) to nitrate (NO₃⁻) is used. The badge is double-ended, requiring two absorption filters (one at each end). The sampler is protected from rain and sunlight with the use of a PVC shelter (Koutrakis *et al.*, 1993b). The rate of NO₃⁻ formation (amount of NO₃⁻ formed on a filter over time of exposure) serves as a measure of O₃ concentration. The H₂O extracted nitrate is determined with ion chromatography (Dionex Ion Chromatograph Model 4000i). In comparison, the CanOxy PlateTM (Canadian Forest Service, Fredericton, NB) consists of a small plastic dish, supporting a paper impregnated with Indigo dye, which reacts with ozone to produce a yellow compound (isatin). A white Teflon diffusion membrane covers the paper to reduce turbulent diffusion related variability in the sampling rate. Each “sampler” consists of two CanOxy Plates suspended in a PVC shelter, which protects the plates from precipitation and direct sunlight. Ozone exposure is determined by eluting the reaction product (isatin) from the paper and measuring the optical density using a spectrophotometer (Cox and Malcolm, 1988). Normally, both types of O₃ passive samplers are placed in the field for 1 to 4 weeks; however, the exposure time should be planned based on the local characteristics to provide the desired resolution of O₃ data. Concentrations of O₃ measured with passive samplers were compared with real-time O₃ measurements with the UV absorption Thermo Environmental Model 49. The empirically derived coefficients were used for calculating O₃ concentrations from all the passive sampler sites.

Nitric oxide (NO) and nitrogen dioxide (NO₂) were monitored with the Ogawa (Pompano Beach, FL) passive samplers of the same design as the O₃ samplers. These two gases are absorbed on cellulose filters coated with triethalonamine (TEA). After water extraction concentrations of NO₃⁻ and NO₂⁻ resulting from NO and NO₂ absorption are analyzed with ion chromatography (Dionex Ion Chromatograph Model 4000i) (Mulik *et al.*, 1989; Ogawa Company, 1997). In addition, Gradko (Gradko Laboratories, UK) samplers of the diffusion tube type (Hargreaves and Atkins, 1987) were also used in this study. Diffusion tubes of standardized dimensions provide a steady flow of air to the absorbing medium so concentrations of the pollutant can be calculated by an equation provided by the manufacturer. Samplers consist of a diffusion tube with a diffusion membrane and stainless steel grids coated with triethanolamine (TEA) as a collection medium (Palmes *et al.*, 1976, 1977). The original colorimetric method for determining the absorbed NO₂ was replaced by more precise ion chromatography (Gair *et al.*, 1991). The diffusion tube NO₂ samplers have been used in several studies, e.g., in the United Kingdom (Ashenden and Bell, 1989; Campbell, 1988; Colls, 1986) and in Lithuania (Perskauskas and Mikelinskiene, 1998), although they were found to overestimate NO₂ concentrations by about 24-27% in weeklong exposures. Oxidation of NO by O₃ inside the diffusion tube is believed to be a possible cause of this problem. However, with longer collection periods losses of the collected NO₂ due to photolysis may offset the over estimation by the samplers (Heal *et al.*,

1999). Most recently Tang et al. (2001) have shown that under certain conditions and with prolonged sampling periods, the instability of TEA is a problem.

Ammonia (NH_3) concentrations were determined with the Gradko diffusion tubes (Hargreaves and Atkins, 1987). In samplers of a similar design to the NO/NO_2 samplers, NH_3 reacts with H_2SO_4 coating on stainless steel mesh enclosed in diffusion tubes. Ammonium sulfate produced was extracted on the ultrasonic bath. The extract was analyzed for ammonium (NH_4^+) colorimetrically (Technicon Autoanalyzer). Ammonia concentrations were also monitored with Ogawa samplers of the same design as used for O_3 , NO , and NO_2 . Ammonia is absorbed on cellulose pads coated with citric acid forming ammonium citrate. Ammonium is extracted with water and analyzed colorimetrically (Technicon Autoanalyzer). Concentrations of NH_3 from passive samplers were calculated based on a comparison with co-located annular denuder systems (Koutrakis et al., 1993a).

A simple and inexpensive passive sampler for nitric acid vapor (HNO_3) was 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 co-located honeycomb annular denuder systems. 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 (Bytnerowicz, 2001 a). A new, improved sampler in which quantitative flow of contaminated air to Nylon filter is controlled by a diffusion membrane (Teflon filter) was recently developed and is described in this report.

Active air pollution monitors

Ozone was monitored with a Thermo Environmental Model 49 UV absorption instrument widely used for ambient air pollution monitoring (Cambridge, MA). In addition, a miniaturized single-beam UV absorption instrument (2B Technologies) with a novel airflow system and advanced electronics and computing systems was used in selected locations. The design of this instrument allows for a smaller size, lower power requirements and insensitivity to temperature and atmospheric pressure changes. The instrument may also be operated by the 12 V battery or solar panels (Bognar and Birks, 1996) and may be linked to battery/solar panel charged Campbell meteorological stations.

A fully instrumented mobile active monitoring system was developed for deployment at sites downwind of active fires. Instruments using EPA equivalency method for continuous analysis of NO_x , CO_2 , and O_3 will be utilized. In addition, gaseous and particulate N compounds can be monitored in this portable system with honeycomb denuder filter packs. The instruments, calibration equipment, and data logger are housed in a mobile trailer for rapid deployment as needed. The trailer is located at a site with AC line power, but can become operable for full analysis within a short time of arrival at the monitoring site. The data obtained with this system will be used as an EPA equivalency database for comparison with to field data from the passive and portable active network set up in the area. The trailer is presently housed at the USDA FS Rocky Mountain Research Station (contact person – Dr. Robert Musselman).

Annular denuder systems

Originally we planned to use two types of denuder systems: glass honeycomb denuder/filter pack systems suitable for short-term very precise determinations (Koutrakis et al., 1993a) and miniaturized denuders allowing for long-term and landscape-level monitoring (Sutton et al., 2001). However, due to technical difficulties that we experienced with the second system (mainly caused by high temperatures and high solar radiation in the Riverside location), we were not able to use them as planned. Therefore all calibrations of passive samplers for HNO_3 and NH_3 were based on the honeycomb denuder data.

In the honeycomb denuder systems, acidic gaseous pollutants (HNO_3 and SO_2) are collected on a honeycomb denuder coated with the sodium carbonate and ammonia on another honeycomb denuder coated with citric acid. A filter pack consisting of Teflon, nylon and citric acid-coated glass filters is used for collecting fine particulate ($<2.5 \mu\text{m}$) nitrate, ammonium and sulfate (Koutrakis et al., 1993a). Pollutants collected on honeycombs and filters are extracted in H_2O or weak carbonate solutions and analyzed with ion chromatography (Dionex 4000i) or colorimetrically (TRAACS autoanalyzer).

Throughfall Collectors for Atmospheric Deposition

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. This method will typically require only 1-3 samplings per year. Precipitation is collected by a rain collector or snow tube and ions are retained by the ion exchange resin as the solution moves through the column. Ions retained by the resin are then extracted in the same column with 2N KCl and analyzed for nitrate and ammonium. A previous study in Sweden suggested that ion exchange methods for estimating throughfall inputs hold promise (Kjønaas, 1999).

The resin used for the passive collectors is a mixed bed anion and cation exchange resin (Amberlite™ MB150). Thirty five grams of the resin is added to each column (0.5 inch PVC tubing). Polyester floss is inserted at the bottom and top of the resin and the bottom is closed with a slit cap to allow the throughfall solution to percolate through the column. Liquid throughfall or rainfall samples are collected in containers in the usual manner except that the liquid is allowed to drain through a resin column where the ions are adsorbed by the ion exchange resin.

In many studies ion exchange resins are placed in nylon mesh bags during exposure to soil or atmospheric deposition (Kjønaas, 1999; Skogley and Dobermann, 1996). An advantage of the ion resin column design used in this study is that the resins can be easily extracted from the same columns used during the field exposure by percolating KCl solution through the column. At the end of the exposure period, nitrate and ammonium adsorbed onto the resin are extracted from the columns by adding 200 ml of 2N KCl. The KCl extracts are then analyzed for nitrate and ammonium on a TRAACS Autoanalyzer.

Preliminary results suggest that the passive ion exchange throughfall collectors provide very good results and hold promise as an inexpensive throughfall monitoring technique that can be applied on a larger scale than otherwise possible with traditional throughfall methods.

Field Tests of Air Pollution Monitoring Systems

Concentrations of major N air pollutants and O₃ were monitored with passive samplers and annular denuder systems during a field study performed in summer 2002 at the USDA Forest Service Fire Laboratory in Riverside, CA. Annular denuder systems provided information on short-time (typically 6 to 24 hours) concentrations of HNO₃, HNO₂, NH₃ and fine (<2.5 μm diameter) particulate NO₃⁻, NH₄⁺ and SO₄²⁻. Passive samplers provide (typically 1 to 4 weeks) average concentrations of ozone and nitrogenous gaseous pollutants (NO, NO₂, NH₃ and HNO₃ vapor).

Large-scale Air Pollution Monitoring Campaign

The Sierra Nevada Mountains contain national parks and wilderness areas that provide a unique panoramic visual experience. People from around the world travel to Yosemite, Sequoia-Kings, or Lassen Volcanic National Parks and other national parks and wilderness areas in the region. The quality of their experience depends on maintaining high air quality, which is threatened by haze and toxic pollutants resulting from projected population growth over the next fifty years. Congress has set a national goal of remedying existing human-caused visibility impairment, and preventing future impairment, at these national parks and wilderness areas. Fire plays a significant role in visibility in these areas. Aggressive prescribed fire programs aimed at reducing the buildup of biomass have the potential to conflict with regional haze programs and goals initiated by States and Tribes. This could lead to a cycle of reduced prescribed fire activity, and increased wildland fire occurrence and severity. These regions are priority areas in the Western U.S. for implementing monitoring and modeling systems to support prescribed fire programs.

In the previous study (Bytnerowicz et al., 2003) ninety-four passive ozone monitors were located at sites in the Sierra Nevada Bioregion between Lassen Volcanic National Park and the Sierra National Forest. At nine of the sites passive monitors were co-located with active ozone monitors. Passive monitors were exchanged every two weeks between May and October 1999. In a similar study, passive ozone, nitrogen dioxide and sulfur dioxide monitors were located at 33 sites in the Carpathian Mountains during 1997-1999 (Bytnerowicz et al, 2001). Preliminary results of the Carpathian study indicated that adequate spatial coverage required roughly one sampler per 1000 km², or samplers located on a 32 x 32 km grid. The results of these studies compare well with the Scottish monitoring grid density for regional evaluation of NH₃ exposure (Drs. Neil Cape and David Fowler, personal communication). Therefore we propose that the 1000 km² spacing be used as the minimum grid size for this study. The actual grid resolution will depend on sampler cost, and frequency of visits (and the associated difficulties of filter changes), which will be determined during the testing period

Technology Transfer

Sampler systems developed as part of this project will be made available to NFS, NPS and other interested agencies for use in routine periodic monitoring of Class I areas, and for monitoring project level smoke emissions from prescribed fire. The relatively low cost and portability of these systems should reduce costs of equipment that management agencies will need for monitoring of prescribed fire treatments, while providing greater spatial monitoring coverage and detailed chemistry than is possible using present PM monitoring systems. Training, instruction manuals and chemistry laboratory support will also be provided to air resource management personnel for the sampler systems developed.

Results and Discussion

Evaluation of air pollution monitoring systems

The following systems were tested during the campaign:

Passive O₃ samplers (Ogawa, CanOxy)

Passive NO₂ and NO_x samplers (Ogawa, Gradko)

Passive NH₃ samplers (Ogawa, Gradko, Alpha)

Passive HNO₃ vapor samplers (USDA FS - two designs)

Data Ram samplers and prototype passive samplers for particulate matter

Delta mini-denuder systems for NH₃

Active O₃ monitors (Thermo Environmental Model 49 UV absorption instrument) were used for evaluation of the O₃ samplers' performance and their calibration. Honeycomb denuder/ filter pack air pollution monitoring systems for gaseous and particulate N pollutants (HNO₃, HNO₂, NH₃, fine particulate NO₃⁻ and NH₄⁺) were used for evaluation and calibration of HNO₃ and NH₃ passive samplers. Concentrations of NO and NO₂ were calculated based on algorithms provided by the manufacturers and by direct comparison with readings from active monitors.

Passive O₃ samplers

Ogawa (Koutrakis et al., 1993) and CanOxy (Cox et al., 2001) O₃ samplers were tested during the summer 2002 study. The samplers were exposed for 1, 2, 3 and 4 weeks and collocated with the active O₃ monitor.



Figure 1. Field tests of air pollution monitoring systems at the USDA Forest Service Riverside Fire Laboratory in summer 2002.



Figure 2. Ogawa passive samplers (left picture) and CanOxy plates (right picture) were tested as the O₃ monitoring devices.

Calibration curve for the Ogawa O₃ sampler shows a very good agreement between the passive samplers and the reference active monitor ($R^2=0.9949$) for a linear relationship (Figure 3). The samplers were also characterized by high precision (relative standard deviation between 1.6 and 6.4% for four replicate measurements). Linear relationship between active monitors and Ogawa samplers was maintained during the entire experiment up to 26,600 ppb x h O₃ dose. Such a dose is equivalent to average concentration of about 40 ppb O₃ during a period of four weeks. For the CanOxy plates and active O₃ monitors a logarithmic relationship was found during four weeks of the exposures (Figure 4). This may be an indication of saturation of the samplers after prolonged periods of the exposure. However, the CanOxy samplers were characterized by precision similar to the Ogawa samplers. Relative standard deviation for these samplers ranged between 0.9 and 6.7%.

Additional tests of the Ogawa O₃ passive samplers were performed in winter 2003 in continuously stirred tank reactor (CSTR) chambers at controlled levels of the pollutant. The main goal of that study was to evaluate a capacity of the samplers for O₃ collection (see Appendix A).

Ogawa O₃ Calibration - Summer 2002

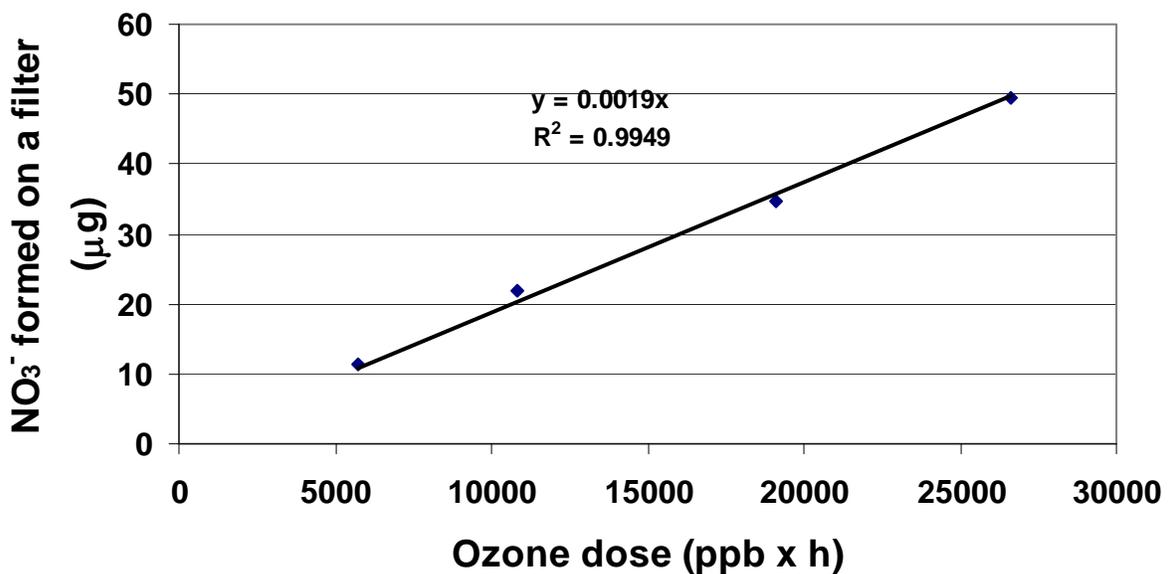


Figure 3. Calibration curve for the Ogawa O₃ passive samplers.

CanOxy Plates, summer 2002, logarithmic

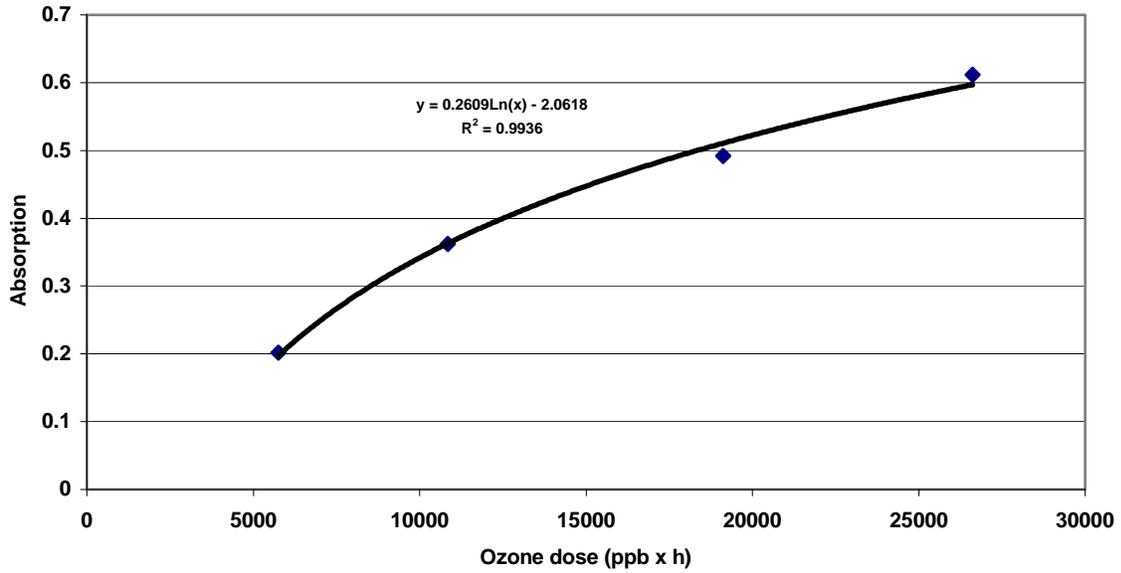


Figure 4. Calibration curve for the CanOxy plates O₃ samplers.

Passive NO₂/NO_x samplers

NO₂ Ogawa sampler, summer 2002

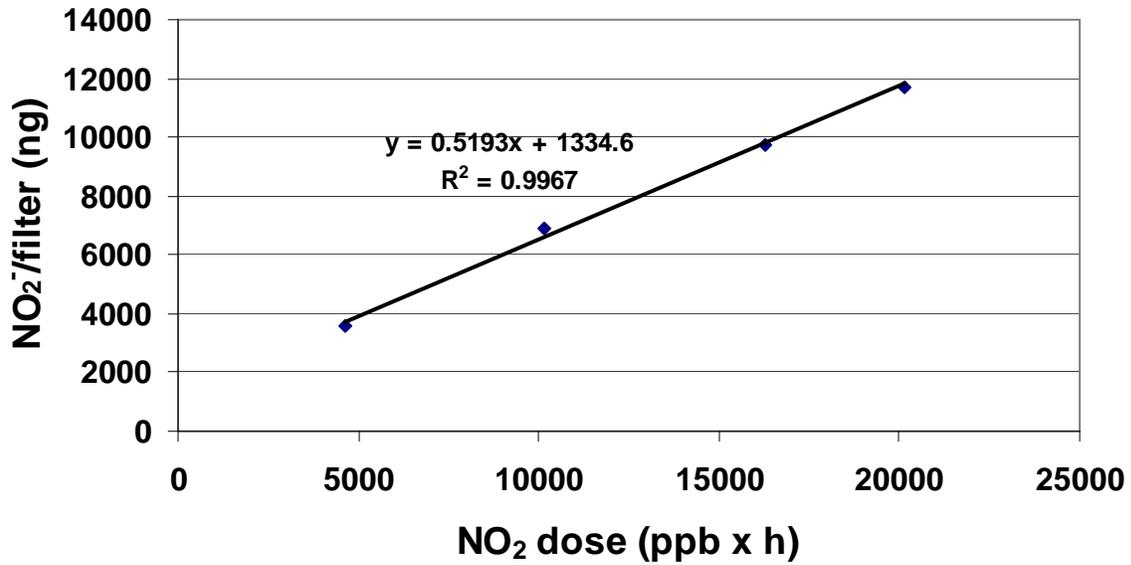


Figure 5. Calibration curve for the Ogawa NO₂ passive sampler.

NO_x Ogawa sampler, summer 2002

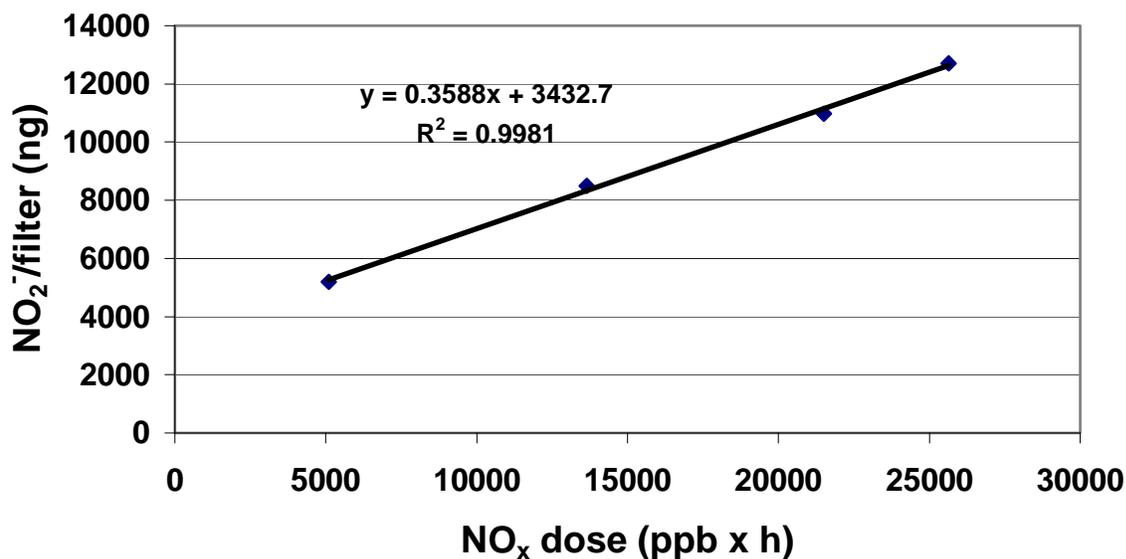


Figure 6. Calibration curve for the Ogawa NO_x sampler.

Ogawa NO₂ and NO_x (NO₂ + NO) passive samplers are of the same design as the Ogawa O₃ samplers (Figure 2). Highly significant linear relationship was determined between the passive samplers and the real time electronic instrument ($R^2 = 0.9981$ for NO_x and $R^2 = 0.9967$ for NO₂). The samplers were also characterized by high precision – for four replicate measurements the relative standard deviation for the NO₂ samplers ranged between 2.5 and 4.9%, and for the NO_x samplers between 3.1 and 3.5%.

Gradko diffusion tube was another NO₂ sampler tested during the summer 2002 campaign (Figure 7).

There was a strong relationship between the Gradko samplers and the active monitor ($R^2 = 0.9734$), however the precision of the sampler was quite poor (relative standard deviation for 4 replicate measurements ranged between 2.8 and 20.4%). Our study confirms that diffusion tube passive samplers are less precise than other samplers in which diffusion membranes control flow of air to the collecting medium (Heal et al., 1999; Krupa and Legge, 2000).

Gradko NO₂ samplers, summer 2002

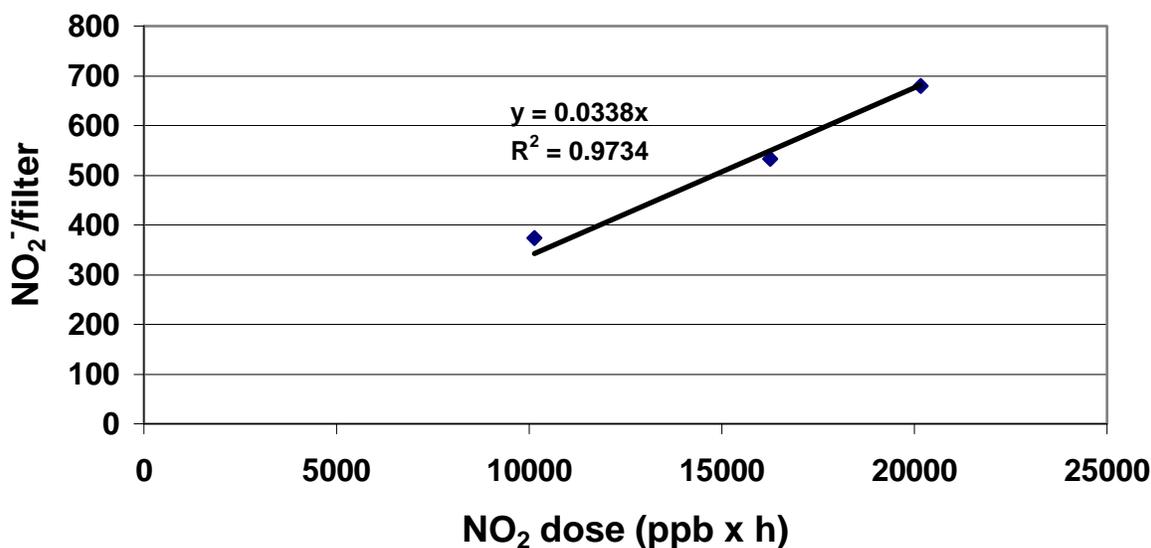


Figure 7. Calibration curve for the Gradko NO₂ sampler.

Passive NH₃ samplers

Three different NH₃ samplers tested during the summer 2002 field tests performed well. All of the samplers showed an excellent correlation with the ambient concentrations measured with the honeycomb denuder systems with the R² values for Gradko sampler 0.9885 (Figure 8), for Alpha sampler 0.9931 (Figure 9), and for the Ogawa sampler 0.9955 (Figure 10). Precision of the Gradko sampler was the worst (relative standard deviation ranging between 2.8 to 20.9% for 4 replicate measurements), and for Ogawa samplers the best (relative S.D. for 4 replicate measurements ranging between 0.8 and 6.4%). Precision of the Alpha samplers measured as relative S.D. for 2 replicate measurements was between 3.9 and 13.5%.

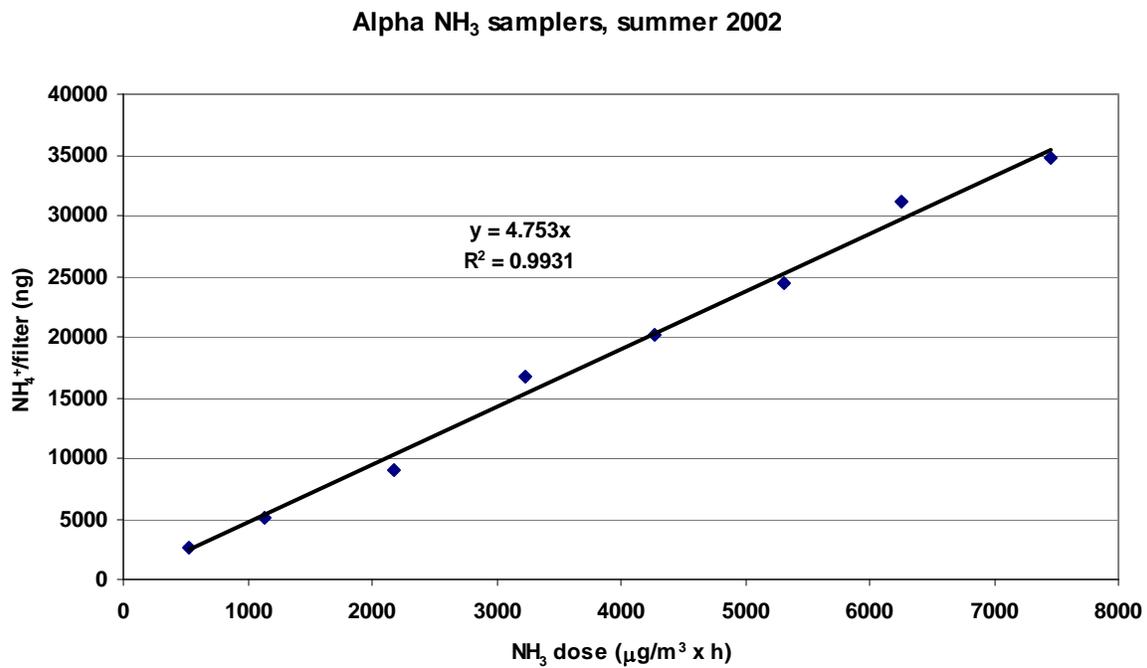


Figure 8. Calibration of the Alpha NH₃ sampler.

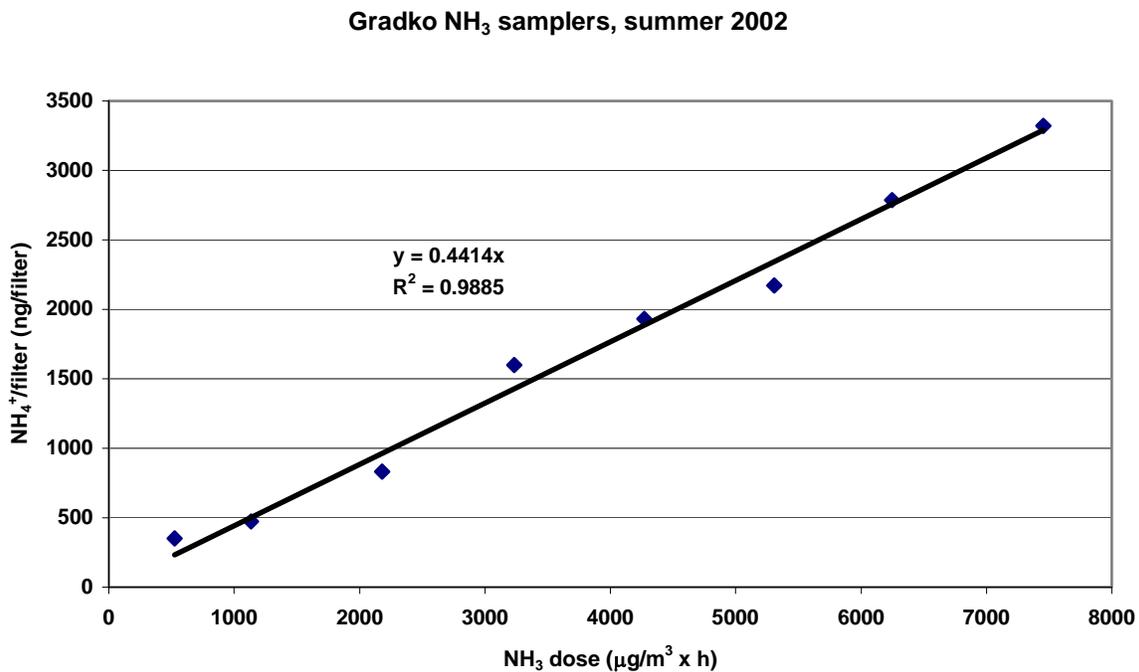


Figure 9. Calibration of the Gradko NH₃ samplers.

Ogawa NH₃ sampler, summer 2002

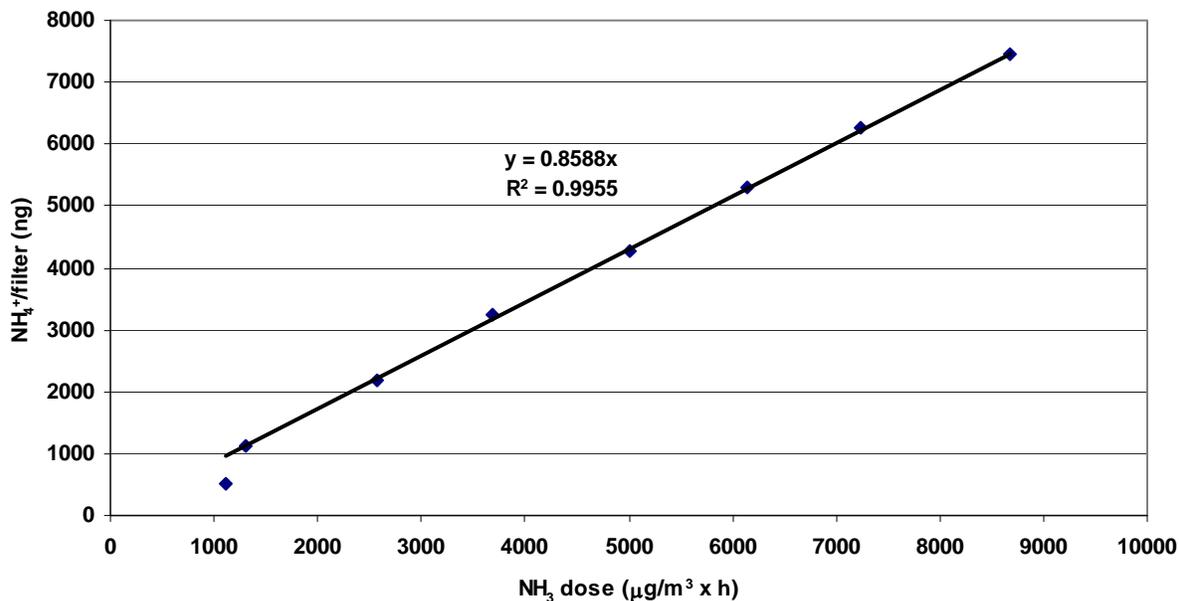


Figure 10. Calibration of the Ogawa NH₃ samplers, summer 2002.

Passive HNO₃ samplers

Old HNO₃ passive samplers (Bytnerowicz et al., 2001) and prototype new samplers with Teflon filter as a diffusion membrane were tested. The old sampler showed a good agreement with HNO₃ concentrations measured with honeycomb denuder systems ($R^2 = 0.9902$), while for the new sampler this relationship was weaker ($R^2 = 0.962$). Both samplers had moderate precision – for the old sampler the relative S.D. ranged between 1 and 25%, while for the new sampler the relative S.D. was in general between 3 and 21%. Our tests indicated that the prototype new sampler performed well. Additional tests and calibration of the new sampler in continuously stirred tank reactor (CSTR) chambers were performed in winter 2003 (results of those tests shown as Appendix B).

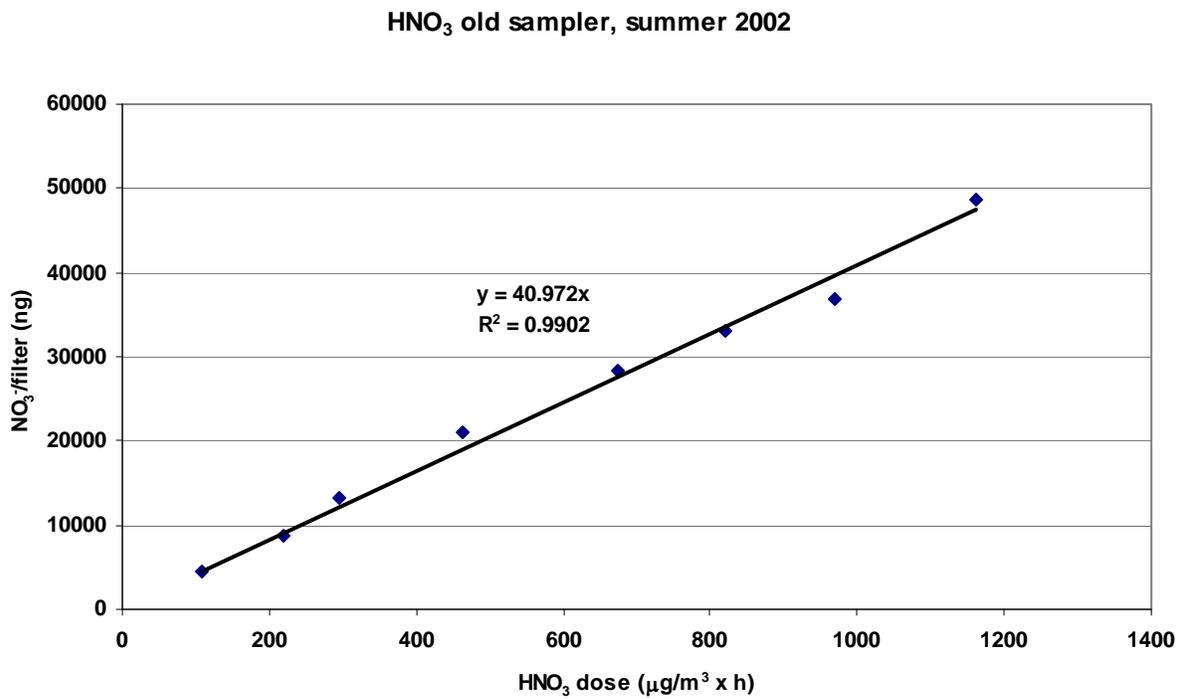


Figure 11. Calibration of old HNO₃ passive samplers.

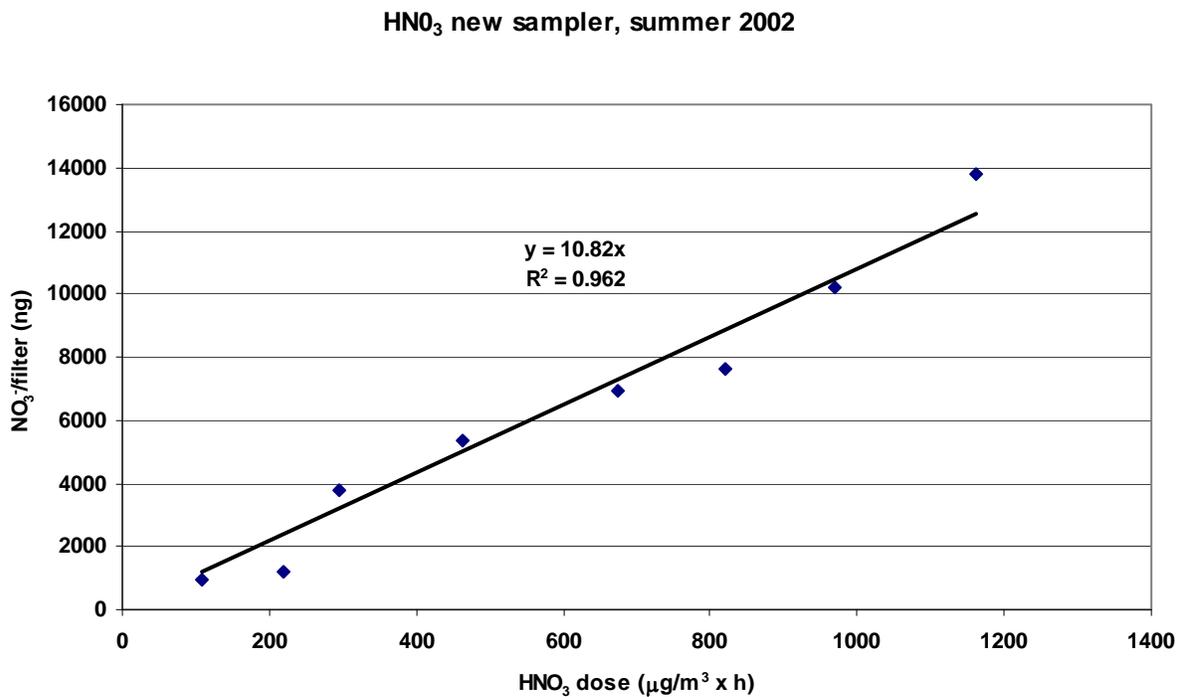


Figure 12. Calibration of new HNO₃ samplers.

Test of Delta NH₃ samplers

Two Delta systems (Tang et al., 2001) were tested in parallel with the honeycomb denuder/filter pack air pollution systems (Figure 13). Unfortunately, due to technical problems (pump of one of the systems was broken), the tests were not completed. More tests of that promising sampling system will be performed in the future.

Development of passive systems for particulate matter

During the summer 2002 and later in the laboratory settings, a feasibility of developing passive samplers for particulate matter was tested. Results of those trials are summarized in Appendix C.

Development of passive samplers for total atmospheric deposition

Passive samplers for collection of throughfall (dry and wet deposition washed from plant canopies) based on ion exchange resins have been developed by Drs. Mark Fenn and Mark Poth of the USDA Forest Service Fire Laboratory in Riverside (see Appendix D).

Field application of passive samplers for O₃, HNO₃ and NH₃

Results from the summer 2002 air pollution monitoring campaign in selected areas of the Sierra Nevada are presented in Appendix E.

Conclusions and Recommendations

1. Various commercially available passive samplers can be successfully used for accurate measurements of gaseous ozone, ammonia and nitrogen oxides. However, since the Ogawa passive samplers can be used for monitoring multiple pollutants, they seem to be most practical for large-scale monitoring in complex mountain areas.
2. Nitric acid vapor samplers developed by the USDA Forest Service Riverside Fire Laboratory provide an inexpensive, simple and reliable method for monitoring ambient concentrations of the pollutant in remote locations.
3. Due to complexity and variability of aerosol formation processes and their presence, development of passive samplers for particulate matter that would allow full separation of gaseous components from particulate matter and separation into various particulate sizes is impractical.
4. Ion exchange resin samplers provide an inexpensive, simple and reliable methodology for monitoring total nitrogen deposition under plant canopies in remote locations.



Figure 13. Delta NH₃ sampling system at the USDA Forest Service Riverside Fire Laboratory.

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