
Appendix B

New passive sampler for monitoring ambient nitric acid (HNO₃) vapor

Andrzej Bytnerowicz¹, Maria Jose Sanz², Michael J. Arbaugh¹, Pamela E. Padgett¹,
David P. Jones¹ and Antonio Davila¹

¹USDA Forest Service, Pacific Southwest Research Station, 4955 Canyon Crest Drive,
Riverside, California 92507, USA

²CEAM, Fundacion Centro de Estudios Ambientales del Mediterraneo, c/Charles R.
Darwin, 14, 469980 Paterna (Valencia), Spain

Fast Track Paper to be submitted to Atmospheric Environment

Abstract

A reliable passive sampler for nitric acid (HNO₃) vapor based on a diffusion of ambient air through Teflon membrane and absorption of the pollutant on Nylasorb nylon filter is described. The sampler is simple in design, easy to make, inexpensive and robust to weather conditions. The sampler is appropriate for use in remote locations for regional-scale monitoring of the pollutant. The sampler has been calibrated against honeycomb denuder systems and tested along air pollution gradients in the California mountains.

Keywords and phrases: air pollution, nitric acid vapor, passive sampler, monitoring, remote sites.

Introduction

Nitric acid (HNO₃) vapor is a principal component of photochemical smog. Because of its high reactivity and deposition velocity (Hanson and Lindberg, 1991), HNO₃ provides large amounts of nitrogen (N) to forests and other ecosystems (Fenn and Bytnerowicz, 1996). For example, in mixed conifer forests of the Los Angeles Basin mountain ranges, HNO₃ typically provides more than 60% of all dry-deposited N (Bytnerowicz et al., 1999). Deposition of HNO₃ may lead to eutrophication of sensitive ecosystems and contamination of surface water with nitrate (NO₃⁻) especially in locations close to photochemical smog sources such as mountains ranges in southern California (Fenn et al., 1998). At high ambient concentrations HNO₃ can cause vegetation damage (Bytnerowicz et al., 2000). At very high concentrations HNO₃ fumes are highly toxic to humans (MSDS, 1998). Although the short-term exposures to HNO₃ concentrations above the highest recorded ambient levels did not cause detrimental lung function effects, the long-term, chronic effects on lung function cannot be excluded (Aris et al., 1996). While ambient concentrations of HNO₃ expressed as 12-hr daytime averages do not exceed 4.8 µg/m³ in Sierra Nevada in California (Fenn et al., 2003), in the mountains surrounding the Los Angeles Basin such averages may be as high as 28 µg/m³ (Grosjean and Bytnerowicz, 1993). Information on HNO₃ spatial and temporal distribution is critical for development of N deposition maps at the landscape and regional levels, which

is important for understanding potential risks associated with the pollutant in forests and other ecosystems.

Measurements of ambient HNO_3 concentrations using active sampling, such as annular denuder systems (Possanzini et al., 1983) or honeycomb denuder systems (Koutrakis et al., 1993), although precise, are expensive and labor-intensive. Therefore there is a need for a simple and inexpensive device, which would allow for a large-scale-level monitoring of the pollutant, particularly in remote areas. Passive samplers measure average concentrations of gaseous pollutants for time periods between a few hours to several weeks (Krupa and Legge, 2000). An existing simple passive sampler for HNO_3 consists of two or three nylon filters protected by a plastic cap from rain and wind (Bytnerowicz et al., 2001). That prototype sampler was used in several monitoring campaigns in California mountains and produced valuable information on ambient HNO_3 concentrations. However, at high wind speeds typical for high elevation mountains, the laminar airflow controlling the HNO_3 deposition to the sampler nylon filters could be impacted by uncontrolled turbulent flow. In such conditions a consistent quantitative measurement of the pollutant was not possible. Therefore, a new sampler that would assure quantitative and reliable measurements of HNO_3 vapor under even harshest environmental conditions, including strong winds, has become evident.

Methodology

Passive sampler. Nylon filters of 47 mm diameter (Nylasorb, Pall Corporation) were used as a collection medium for HNO_3 . Such filters are routinely used in annular denuder systems and filter packs for collection of HNO_3 (Allegrini et al., 1987). Ambient air passes to the nylon filter through a Zefluor Teflon 47 mm diameter filter of 1 μm pore size (Pall Corporation). The filters were housed in a 50 mm commercially available polycarbonate Petri dish and were kept in place by two Teflon rings and one PVC ring. Sampler were protected from wind and rain by a polycarbonate cap (Figure 1).

Calibration of passive samplers. Calibration was performed in two continuously stirred tank reactors (CSTR) with controlled low and high concentrations of the pollutant (Padgett et al., 2004). Thirty-six passive samplers (eighteen per chamber) were used for the calibration. All samplers were placed in the chambers in the beginning of the calibration experiment. The first batch of 3 replicate samplers was collected after 3.6 hours of the exposures from the low concentration chamber. The subsequent collections of 3 replicate samplers from each chamber were made every 24 hours until all the samplers were collected. Concentrations of HNO_3 in the CSTR chambers were monitored with honeycomb denuder/filter pack systems operating at 10 L/min flow rate (Koutrakis et al., 1993). Honeycomb denuders were coated with 1% CaCO_3 water/methanol/glycerol solution. Two denuders in line were used in each system to assure that the pollutant was completely captured. Honeycomb denuder systems were changed at the same time as the passive samplers.

Chemical determinations. After the exposures, nylon filters were placed in 250 mL Erlenmeyer flasks into which 0.02 L of distilled/deionized water was added. The flasks

were shaken on a wrist-action shaker for 15 minutes at middle speed. The amount of absorbed HNO₃ as NO₃⁻ was determined using an ion exchange chromatograph (Dionex Model 4000i) and was expressed as μg NO₃⁻/filter according to the following formula:

$$(1) \text{ NO}_3^- \text{ deposition to nylon filters } (\mu\text{g}/\text{filter}) = ([\text{NO}_3^-]_{\text{filter extract (mg/l)}}] - [\text{NO}_3^-]_{\text{blank (mg/L)}}]) \times 0.02 \text{ L} \times 10^3$$

Denuders were extracted in 0.0024 M Na₂CO₃ + 0.0030 M NaHCO₃ solution. Concentrations of NO₃⁻ in denuder extracts were also determined with ion exchange chromatography (Dionex Model 4001i). Calculated concentrations of HNO₃ were expressed as μg/m³.

Results & Discussion

A strong linear relationship between concentrations of HNO₃ vapor measured with honeycomb denuder systems and its deposition to nylon filters of the passive samplers measured as NO₃⁻ ion was found (Figure 2). On the contrary, during field testing no relationship between NO₃⁻ collected on nylon filters and ambient concentrations of fine particulate NO₃⁻ was found (Bytnerowicz et al., 2001).

Based on the relationship shown in Figure 2, the following formulas for calculating ambient HNO₃ concentrations with passive samplers were developed:

$$(2) \text{ HNO}_3 \text{ dose } (\mu\text{g}/\text{m}^3 \times \text{h}) = 69.498 \times \text{NO}_3^- \text{ deposition to nylon filters } (\mu\text{g}/\text{filter})$$

$$(3) \text{ HNO}_3 \text{ concentrations } (\mu\text{g}/\text{m}^3) = \text{HNO}_3 \text{ dose } (\mu\text{g}/\text{m}^3 \times \text{h}) / \text{exposure time (h)}$$

A strong linear relationship between ambient HNO₃ vapor and NO₃⁻ collected on a Nylasorb nylon filter was measured up to 200.68 μg NO₃⁻/filter (Bytnerowicz et al., 2001). Accordingly, the maximum HNO₃ dose measured is 200.68 * 69.498 = 13,947 μg/m³ x h. Consequently, during a period of 2 weeks the sampler has a capacity of measuring at least 41.5 μg m⁻³ (13,947 μg/m³ x h /336 h). Such concentrations are much higher than ambient HNO₃ levels ever determined (Bytnerowicz and Fenn, 1996). Precision of the measurements with the HNO₃ passive samplers was good – relative differences between the 3 replicate measurements stayed between 0.2% and 14.9% (average 5.0%) during 2003 summer monitoring in the San Bernardino Mountains (Andrzej Bytnerowicz, personal communication).

The described passive samplers can reliably measure ambient HNO₃ concentrations at wide environmental ranges for extended periods of time (typically between 1 to 4 weeks). Low price, simple design and easy operation of the sampler allow for a large-scale (landscape, region) monitoring of HNO₃. This offers a possibility for evaluation of HNO₃ vapor risks to ecosystems and humans.

Acknowledgements:

Formatted
Deleted:

The authors thank Diane Alexander and Edgar Romo for help with chemical analyses and Dorota Shortell for technical drawings of the sampler. The Joint Fire Science and National Fire Plan programs supported this study.

References

- Allegrini, I., DeSantis, F., Di Palo, V., Febo, A., Perrino, C., Possanzini, M. 1987. Annular denuder method for sampling reactive gases and aerosols in the atmosphere. *The Sci. Tot. Environ.*, 67, 1-16.
- Aris, R., Christian, D., Hearne, P. Q., Balmes, J. R. 1996. The Effects of Nitric Acid Vapor Alone and in Combination with Ozone in Exercising, Healthy Subjects as Assessed by Bronchoalveolar and Proximal Lavage, California Environmental Protection Agency, Air Resources Board, Research Notes No. 96-6, October 1996.
- Bytnerowicz, A. Fenn, M. E. 1996. Nitrogen deposition in California forests: a review. *Environ. Pollut.*, 92, 127-146.
- Bytnerowicz, A., Fenn, M., Miller, P., and Arbaugh, M. (1999). Wet and dry pollutant deposition to the mixed conifer forest. In: P. R. Miller and J. McBride (eds) *Oxidant Air Pollution Impacts in the Montane Forests of Southern California: The San Bernardino Mountains Case Study*, Springer, Ecological Series 134, New York, 235-269.
- Bytnerowicz, A., Padgett, P. E., Arbaugh, M. J., Parker, D. R., Jones, D. P. 2001. Passive sampler for measurements of atmospheric nitric acid vapor (HNO₃) concentrations. *The ScientificWorld*, 1, 815-822.
- Bytnerowicz, A., Padgett, P., Percy, K., Krywult, M., Riechers, G., and Hom, J. (1999). Direct effects of nitric acid on forest vegetation. In: P. R. Miller and J. McBride (eds) *Oxidant Air Pollution Impacts in the Montane Forests of Southern California: The San Bernardino Mountains Case Study*. Springer, Ecological Series 134, New York, 270-287.
- Fenn, M. and Bytnerowicz, A. (1996) Summer throughfall and winter deposition in the San Bernardino Mountains of southern California. *Atmos. Environ.*, 31, 673-683.
- Fenn, M. E., Poth, M. A., Bytnerowicz, A., Sickman, J. O., Takemoto, B. K. 2003. Effects of ozone, nitrogen deposition, and other stressors on montane ecosystems in the Sierra Nevada. In: A. Bytnerowicz, M. J. Arbaugh and R. Alonso (eds) *Ozone Air Pollution in the Sierra Nevada: Distribution and Effects on Forests*. *Developments in Environmental Science 2*, Elsevier, Amsterdam, 111-155.
- Fenn, M. E., Poth, M. A., Aber, J. D., Baron, J. S., Bormann, B. T., Johnson, D. W., Lemley, A. D., McNulty, S. G., Ryan, D. F., and Stottlemeyer, R. (1998) Nitrogen excess in North American ecosystems: predisposing factors, ecosystem responses, and management strategies. *Ecol. Appl.*, 8, 706-733.

Grosjean, D., Bytnerowicz, A. (1993) Nitrogenous air pollutants at a southern California mountain forest smog receptor area. *Atmos. Environ.*, 27A, 483-492.

Hanson, P. J. and Lindberg, S. E. (1991) Dry deposition of reactive nitrogen compounds: a review of leaf, canopy and non-foliar measurements. *Atmos. Environ.*, 25A, 1615-1634.

Koutrakis, P., Sioutas, C., Ferguson, S. T., Wolfson, J. M., Mulik, J. D., and Burton, R. M. (1993) Development and evaluation of a glass honeycomb denuder/filter pack system to collect atmospheric gases and particles. *Environ. Sci. & Technol.*, 27, 2497-2501.

Krupa, S. V., Legge, A. H. 2000. Passive sampling of ambient, gaseous air pollutants: an assessment from ecological perspective. *Environ. Pollut.*, 107, 31-45.

MSDS. 1998. Material Safety Data Sheets, J. T. Baker,
<http://www.jtbaker.com/msds/englishhtml/m7718.htm>

Padgett, P. E., Bytnerowicz, A., Dawson, P. J., Riechers, G. H., Fitz, D. R. 2004. Design, evaluation and application of a continuously stirred tank reactor system for use in nitric acid air pollutant studies. *Water, Air and Soil Pollution*, 151, 35-51.

Possanzini, M., Febo, A., Liberti, A. 1983. A new design of a high performance denuder from the sampling of atmospheric pollutants. *Atmos. Environ.*, 17, 2605-2610.

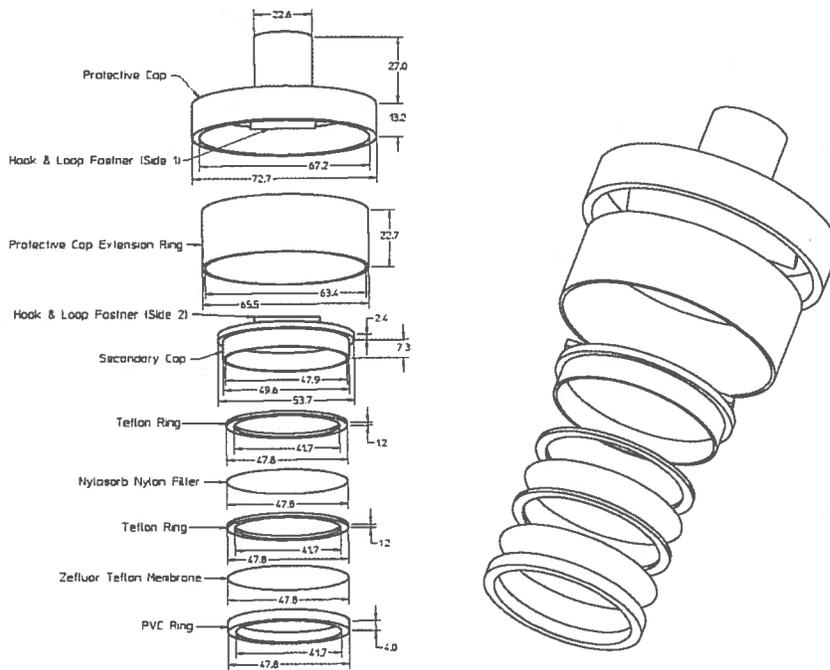


Figure 1. Schematic of the HNO₃ passive sampler designed at the USDA Forest Service, Pacific Southwest Research Station, Riverside, California. A Nylasorb 47 mm diameter nylon filter collecting HNO₃ is sandwiched between two Teflon rings at the base of the Millipore Petri dish of 50 mm diameter. Airflow is controlled by a 47 mm diameter Zeffluor filter of 1 μm pore-size hold in place by the PVC ring. Passive sampler is held with Velcro tape inside of a cap protecting the sampler from wind and rain.

Calibration July 2003 - new FS samplers

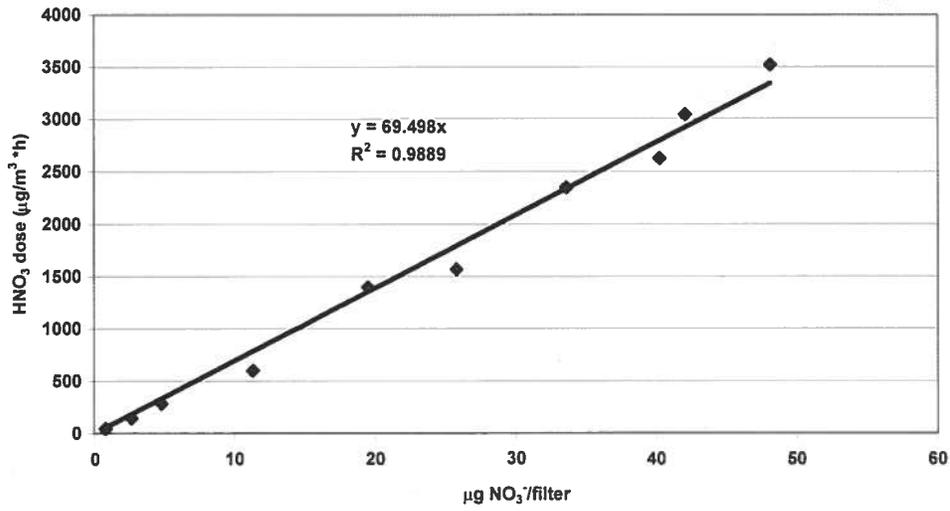


Figure 2. Calibration of HNO_3 passive samplers against honeycomb denuder systems. Calibration curve was developed in the Continuously Stirred Tank Reactor (CSTR) chambers with controlled levels of HNO_3 . Values on the “x” axis represent amount of NO_3^- extracted from the passive sampler nylon filters, while values on the “y” axis represent a dose of HNO_3 determined with collocated honeycomb denuders systems.

Figure Captions

Figure 1. Schematic of the HNO_3 passive sampler designed at the USDA Forest Service, Pacific Southwest Research Station, Riverside, California. A Nylasorb 47 mm diameter nylon filter collecting HNO_3 is sandwiched between two Teflon rings at the base of the Millipore Petri dish of 50 mm diameter. Airflow is controlled by a 47 mm diameter Zefluor filter of 1 μm pore-size held in place by the PVC ring. Passive sampler is held with Velcro tape inside of a cap protecting the sampler from wind and rain.

Figure 2. Calibration of HNO_3 passive samplers with honeycomb denuder systems. Calibration curve was developed in the Continuously Stirred Tank Reactor (CSTR) chambers with controlled levels of HNO_3 . Values on the "x" axis represent amount of NO_3^- extracted from the passive sampler nylon filters, while values on the "y" axis represent a dose of HNO_3 determined with the collocated honeycomb annular denuders.