

Passive Sampler for Measurements of Atmospheric Nitric Acid Vapor (HNO_3) Concentrations

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Nitric acid (HNO_3) vapor is an important nitrogenous air pollutant responsible for increasing saturation of forests with nitrogen and direct injury to plants. The USDA Forest Service and University of California researchers have developed a simple and inexpensive passive sampler for monitoring air concentrations of HNO_3 . Nitric acid is selectively absorbed on 47-mm Nylasorb nylon filters with no interference from particulate NO_3^- . Concentrations determined with the passive samplers closely corresponded with those measured with the co-located honeycomb annular denuder systems. The PVC protective caps of standardized dimensions protect nylon filters from rain and wind and allow for reliable measurements of ambient HNO_3 concentrations. The described samplers have been successfully used in Sequoia National Park, the San Bernardino Mountains, and on Mammoth Mountain in California.

KEY WORDS: air pollution, nitric acid vapor, passive sampler, monitoring, remote sites

DOMAINS: plant sciences, atmospheric systems, ecosystem and communities, environmental management, ecosystems management, analytical chemistry, chemical composition

INTRODUCTION

Nitric acid (HNO_3) vapor, an air pollutant found in photochemical smog, affects the health of people and vegetation. Because of its very high reactivity and deposition velocity[1], HNO_3 provides large amounts of nitrogen (N) to forests and other ecosystems[2]. For example, in forests of the Los Angeles Basin mountain ranges, HNO_3 provides more than 60% of the dry-deposited N to mixed conifer forests[3]. Increased deposition of HNO_3 may lead to eutrophication of sensitive ecosystems and contamination of surface water with nitrate (NO_3^-), especially in locations close to photochemical smog source areas such as mountain ranges in southern California close to Los Angeles[4]. While ambient concentrations of HNO_3 expressed as 24-h averages did not exceed $2.1 \mu\text{g}/\text{m}^3$ in a rural European location[5] and $4.8 \mu\text{g}/\text{m}^3$ as a 12-h daytime average in the Sierra

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Nevada mountains in California[6], in the San Gabriel Mountains of southern California the 12-h daytime concentrations reached $28 \mu\text{g}/\text{m}^3$ [7]. Information on HNO_3 spatial and temporal distribution in forest ecosystems of the western U.S. is essential for a better understanding of its phytotoxic potential and development of N deposition models at a landscape level.

Measurements of HNO_3 concentrations using active sampling, such as annular denuder systems[8] or honeycomb denuder systems[9], although precise, are expensive and labor intensive. Use of these systems on a larger scale (landscape) is very difficult even if battery-operated systems are utilized. Similarly to other pollutants, such as ozone, there is a clear need for simple and inexpensive device which would allow for landscape-level monitoring of the pollutant, including remote locations.

Although HNO_3 may be toxic to plants at elevated concentrations[10], its role as a source of N in different ecosystems is of primary importance. While for evaluation of toxic effects, peak concentration values of pollutants have to be known, for estimates of deposition, information on average concentrations of HNO_3 and its deposition velocity may be sufficient. Results from passive samplers, which integrate concentrations over a collection period, provide such information. Passive samplers, devices that are relatively inexpensive, low-maintenance, and do not require electric power, can be easily used for large-scale monitoring networks providing valuable information for the development of landscape-level pollutant distribution models.

EXPERIMENTAL METHODS

Nylon filters of 47 mm diameter (Nylasorb, Pall Corporation) have been used as a collection medium for HNO_3 . Such filters have been routinely used in annular denuder systems and filter packs for collection of this pollutant[11]. The filters were mounted in PVC double rings of 39 mm inner diameter (total surface of the exposed portion of a filter on both sides = 0.002389 m^2). Evaluation of filter responses to changing levels of HNO_3 , absorption capacity of filters, and performance of various protective caps was done in the continuously stirred tank reactors (CSTR) with controlled concentrations of the pollutant[12]. For testing the absorbing capacity of nylon filters, 30 of those mounted in the PVC rings were exposed to controlled high concentrations of HNO_3 in the CSTR chamber. Every 24 h, three replicate filters were removed from the chamber during 240 h of exposures. For calibration, additional exposures of nylon filters (PVC double rings without caps) were performed at low doses of the pollutant. Calibration curve was developed based on the combined CSTR results below the filter saturation point. Concentrations of HNO_3 and particulate NO_3 in CSTR chambers were monitored with honeycomb denuder/filter pack systems operating at 10 L/min flow rate, which provided $2.2 \mu\text{m}$ cutoff point for particulate matter[9]. Honeycomb denuder/filter pack systems were changed at the same time as passive samplers.

Preliminary tests indicated that, due to high reactivity of HNO_3 with surfaces, no pre-screens or diffusion tubes for controlling rate of air moving to sampling media could be used (no detectable amounts of the pollutant reached the nylon filters). Instead, HNO_3 was collected on filters well protected from rain and wind by PVC caps, and calibrated against the co-located honeycomb denuder systems. Tests of several designs of protective caps for nylon filters mounted in the PVC rings were performed in the CSTR chambers.

After exposures, nylon filters were placed in 250 ml Erlenmeyer flasks into which 20 mL of distilled, deionized water was added. The flasks were shaken on a wrist-action shaker for 15 min at middle speed. Amount of absorbed HNO_3 was determined as NO_3^- with ion exchange chromatograph (Dionex Model 4000i). Results of the absorbed NO_3^- were expressed as $\text{mg NO}_3^-/\text{m}^2$ of the total filter surface (two sides). Denuders and filters from honeycomb denuder/filter pack systems were extracted in $0.0024 \text{ M Na}_2\text{CO}_3 + 0.0030 \text{ M NaHCO}_3$ solution. Concentrations of NO_3^- were also determined with ion exchange chromatography (Dionex Model 4000i).

Field tests of samplers were done in Sequoia National Park of the western Sierra Nevada, California. In summer 1999, passive samplers for HNO₃ and honeycomb denuder/filter pack systems were located at five monitoring sites: Ash Mountain, 504 m; Crystal Cave, 1,617 m; Lower Kaweah, 1,905 m; Marble Fork, 2,025 m; and Wolverton, 2,207 m along the Kaweah/Marble Fork drainage in Sequoia National Park. The Kaweah/Marble Fork drainages are directly exposed to airflow from the San Joaquin Valley in California.

Student's *t* test was used for comparison of performance of passive samplers against active monitors/honeycomb denuder systems. Differences are reported as significant at $p < 0.05$ [13].

RESULTS AND DISCUSSION

Deposition of HNO₃ to nylon filters (measured as NO₃⁻) was proportional to the HNO₃ dose in the CSTR exposure chambers up to about 170 mg NO₃⁻/m² (double-sided area of nylon filter). Above that level, nylon filters were not absorbing NO₃⁻ linearly indicating near saturation point with HNO₃ (HNO₃ dose of about 5700 μg/m³ × h). These results indicate that the open-ring filters would saturate after 14 days of exposure to average concentration of HNO₃ of about 17 μg/m³ (6.6 ppb). A strong linear relationship between concentrations of the pollutant and its deposition to nylon filters allowed for precise calibration of passive samplers (Fig. 1). While absorption of NO₃⁻ by nylon filters was closely correlated with HNO₃ ambient concentrations ($R^2 = 0.9954$), no relationship was found with the ambient concentrations of particulate NO₃⁻ (Fig. 2).

The following formulas for calculating HNO₃ concentrations with passive samplers have been developed:

$$\text{NO}_3^- \text{ deposition to nylon filters (mg/m}^2\text{)} = (\text{C}_{\text{NO}_3^-} \text{ of a filter extract} - \text{C}_{\text{NO}_3^-} \text{ of a blank; mg NO}_3^-/\text{L}) \times 0.02 \text{ L}/0.002389 \text{ m}^2 \quad (1)$$

$$\text{HNO}_3 \text{ dose (}\mu\text{g/m}^3 \times \text{h)} = \text{K} \times \text{NO}_3^- \text{ deposition (mg/m}^2\text{)} \quad (2)$$

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

where K values (slope of calibration curves) for various protective caps are listed in Table 1.

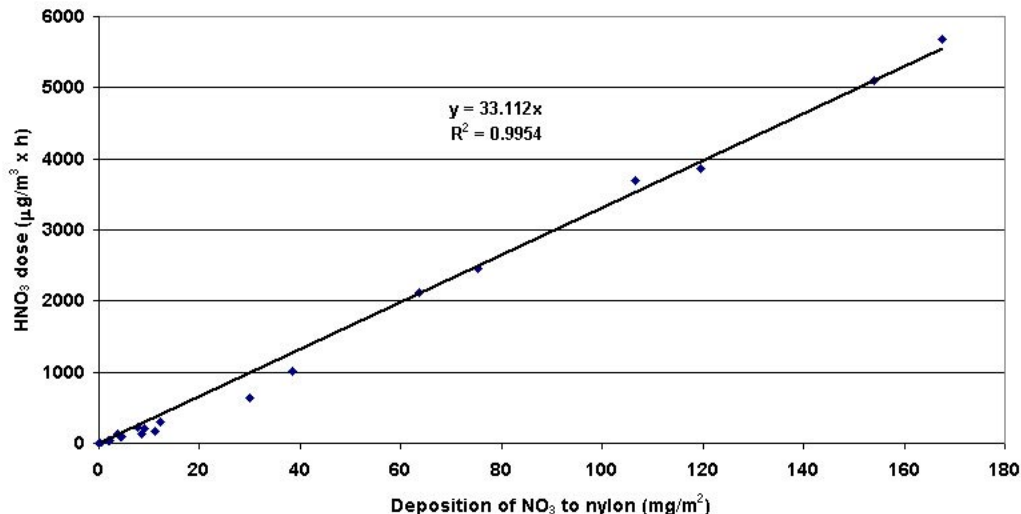


FIGURE 1. Calibration of nylon filters as collecting medium in the HNO₃ passive samplers. Calibration curve was developed in the CSTR chambers with controlled levels of HNO₃.

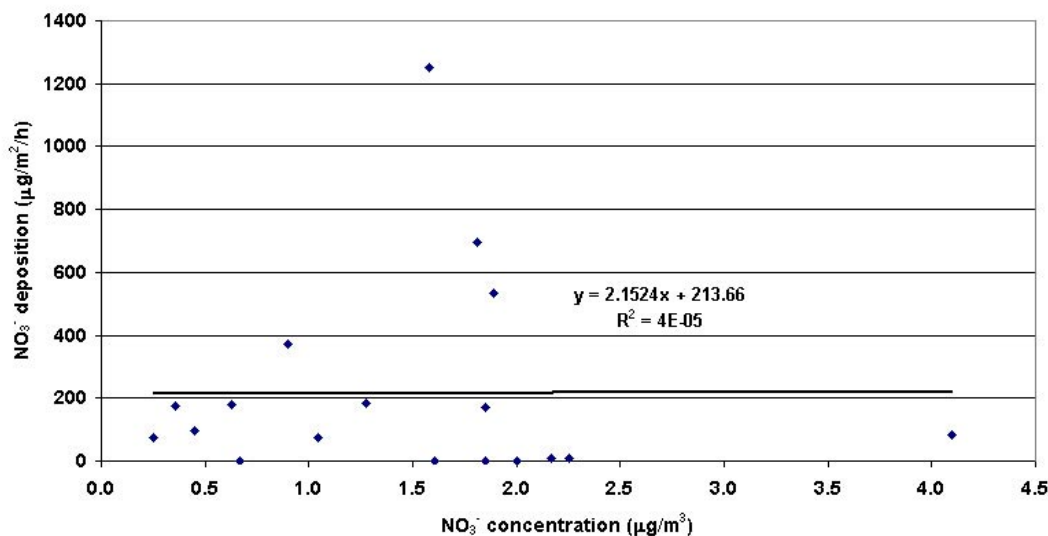


FIGURE 2. Ambient concentrations of particulate NO₃⁻ and rates of NO₃⁻ deposition to nylon filters were not correlated.

TABLE 1
Characteristics of Tested Protective Caps and K Values (Slope of Calibration Curves) for HNO₃ Concentration Calculations

Protective Cap Type	Inner Diameter of a Cap (mm)	Distance between Center of Filter and Bottom Rim of Cap (mm)	Number of Filters in Cap	K Value
Open ring without a cap				33.11
Forest Service cap	90	42	1	49.94
UC Riverside short cap	107	37	2	62.47
UC Riverside long cap	101	247	2	315.33

Protective caps reduced the rate of HNO₃ uptake by nylon filters and increased the K values (Table 1). These tests indicated that enclosure of filters in caps of various designs allows for HNO₃ collection at higher concentrations or longer collection periods.

Field tests in Sequoia National Park indicated that the highest HNO₃ concentrations determined both with passive samplers and honeycomb denuders were recorded at 504 m altitude at Ash Mountain, and the lowest concentrations were at 2,207 m altitude at Wolverton. Ranges of HNO₃ concentrations determined with honeycomb denuder systems and passive samplers were similar (0.6 – 2.1 and 0.4 – 2.9 µg/m³, respectively) (Fig. 3). Statistical evaluation of the HNO₃ data indicated that in four out of five sites where both honeycomb denuder systems and passive samplers were used, concentrations did not significantly differ. This suggests that these HNO₃ passive samplers could be used for estimates of ambient levels of the pollutant in remote mountain locations. However, due to different collection regimes (2-week-long integrated values for passive samplers versus two 24-h measurements per month during the growing season with honeycomb denuder systems), such a comparison has to be viewed with caution. These results also indicate that two different sampling regimes and monitoring methods provided very similar estimates of HNO₃ contamination in the study area. Precision of measurements with the HNO₃

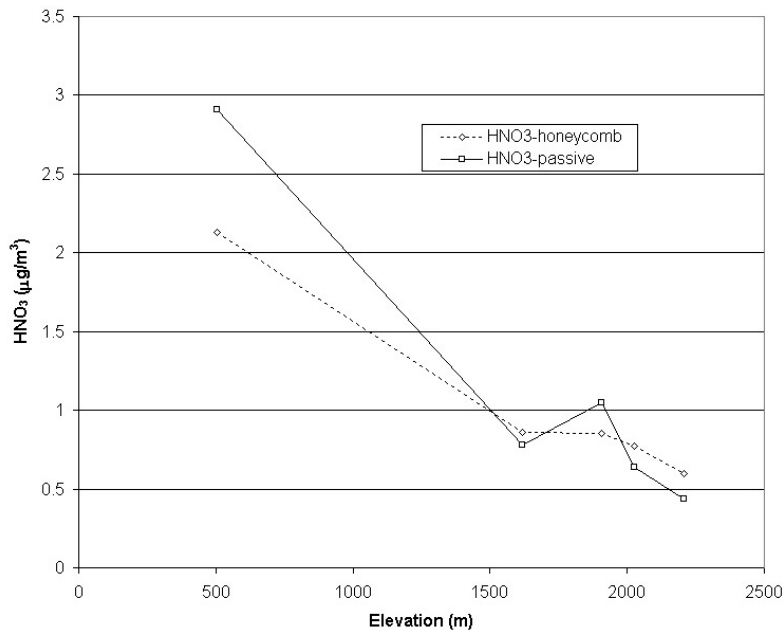


FIGURE 3. Changes of seasonal average HNO₃ concentrations measured with honeycomb denuder/filter pack systems and passive samplers along the Kaweah/Marble Fork drainage in Sequoia National Park in summer 1999.

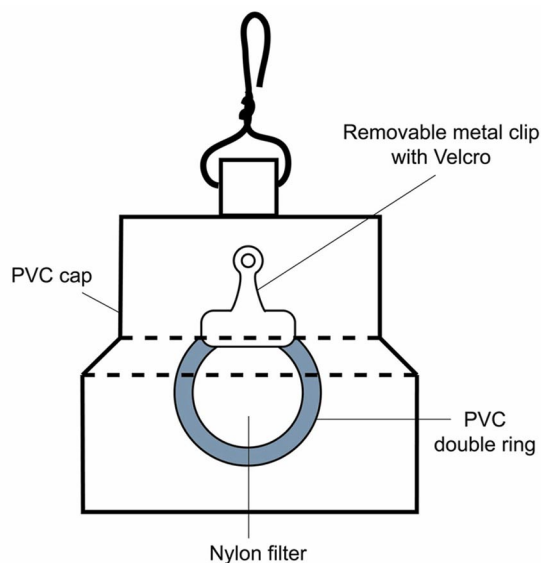


FIGURE 4. Schematic of HNO₃ protective cap designed at the University of California, Riverside. Two nylon filters enclosed in PVC double rings were inserted in metal clips that were attached to the cap's inner wall with Velcro tape.

passive samplers was good — the coefficient of variation of three replicate measurements stayed between 0.8 and 25.4% (average 9.2%) during the entire monitoring period. Precision of HNO₃ passive samplers could be additionally improved if a diffusion barrier providing uniform flow of air to the collection medium could be used.

A protective cap developed at the Department of Environmental Sciences of the University of California (UC-Riverside short cap) provided good protection of nylon filters against wind and rain (Fig. 4). This type of a protective cap has been successfully used in monitoring studies in

remote mountain ranges of the San Bernardino and Mammoth Mountains. Results of these experiments are presented in other papers published in this volume [14,15].

In summary, it can be said that the developed sampler provides much-needed information regarding ambient levels of HNO₃ vapor on a large scale. However, in order to improve performance and reliability of the sampler, especially in conditions of high winds (a situation quite typical for these mountain environments), additional tests of diffusion barriers controlling flow of air to the collecting medium are needed. The USDA Forest Service scientists will perform such tests during the 2001 summer season.

CONCLUSIONS

1. A strong relationship between ambient concentrations of HNO₃ and nitrate collected to nylon filters was determined in the CSTR chambers. The nylon filters used in this study (effective double-sided area of 0.002389 m²) have a capacity of collecting 5,700 μg HNO₃/m³ × h which allows for long-term (several weeks) monitoring of the pollutant. Protective caps of various designs reduce rate of HNO₃ deposition and amount of nitrate absorbed on the collecting medium and extend potential time of HNO₃ collection.
2. Field tests demonstrated that results obtained with passive samplers were similar to the values recorded with honeycomb annular denuder/filter pack systems. Therefore, we conclude that passive samplers can reliably measure ambient levels of HNO₃.
3. Low price, simple design, and easy operation of the samplers allow for a large (landscape) level monitoring of HNO₃. This offers a possibility for evaluation of risks to ecosystems and humans.
4. Additional tests are needed for improving performance of the samplers. Enclosing nylon filters in collection devices providing steady airflow by diffusion barriers will be tested.

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