

Passive permeation sampling of atmospheric HNO₃

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Abstract

Passive samplers based on molecular diffusion are used to measure many organic and inorganic gaseous species in the atmosphere. In this study, the permeation resistance of two types of polytetrafluoroethylene membrane filters (TA300 and PF100, the same manufacturer but different membrane thicknesses) was evaluated and 0.2% NaCl-impregnated and polyamide filters (Nylasorb and Magna, different manufacturers) were compared as adsorbents for nitric acid (HNO₃). As a reference, an annular denuder coated with NaCl was used for measuring HNO₃ concentration. Based on the observed data and effective sampling area of the passive sampler, the sampling velocity (SV) was estimated and compared with reported values from other studies. The NaCl-impregnated filter had a slightly higher SV than the nylon (polyamide) filters. The SV for the thinner permeation filter, with a larger porosity (TA300) was much higher than the less porous filter (PF100). According to these results, the SV for a HNO₃ passive sampler can be adjusted by selecting appropriate permeation filters according to the potential concentration at the sampling site and the maintenance schedule of the sampler.

Key words: Passive sampler, Nitric acid, Permeation membrane

* Elements of HNO₃ passive samplers were examined by comparison with denuder data

* Selection of the permeation filter can be used to control sampling velocity

1. Introduction

Nitrogen oxides in the atmosphere are major air pollutants and influence the reactive nitrogen load at the earth's surface. They are ultimately oxidized to nitrate (NO_3^-) or nitric acid (HNO_3) (Seinfeld and Pandis, 2016). In addition to wet deposition during precipitation, gaseous HNO_3 and aerosol particles containing NO_3^- are removed by dry deposition from the atmosphere. Furthermore, HNO_3 reacts with ammonia (NH_3) in the atmosphere to produce fine particles of ammonium nitrate (NH_4NO_3), and also reacts with alkaline coarse particles, such as sea salts and desert dust, transforming their main components into sodium nitrate (NaNO_3) and calcium nitrate ($\text{Ca}(\text{NO}_3)_2$), respectively. Therefore, understanding the temporal and spatial variation of the atmospheric HNO_3 concentration is important for evaluating air pollution and for estimating the reactive nitrogen load in the atmosphere.

Annular denuders or multi-stage chemical adsorbing filters have been used for measuring the atmospheric HNO_3 concentration (Appel, 1993). These observation methods require electricity to aspirate the sampled air and require a lot of sampler maintenance. Furthermore, spatial observations using many active samplers are difficult to achieve in terms of the labor and maintenance costs. Alternatively the use of passive samplers is a valuable and effective option for long-term and spatially extensive observations because they do not require electricity, and are relatively inexpensive and easy to handle, although the observation data are averaged over relatively long periods, i.e., weekly or longer.

Passive samplers based on molecular diffusion have been developed for many inorganic and organic species (Namieśnik et al., 1984; Górecki and Namieśnik, 2002). There are widely used and commercially available passive samplers for nitrogen dioxide (NO_2) and NH_3 ; therefore, many observations have been reported (Krupa and Legge, 2000; Tang et al., 2001). However, no passive sampler for HNO_3 is commercially available and few observations have therefore been reported (Nishikawa, 2004; Bytnerowicz et al., 2005; Zbieranowski and Aherne, 2012). Passive samplers consist of a collector that adsorbs volatile chemicals and a resistor that relates the adsorbent to the outside air (Namieśnik et al., 1984). In the case of HNO_3 , Nishikawa (2004) and Bytnerowicz et al. (2005) reported passive samplers consisting of polytetrafluoroethylene (PTFE) filters as a permeation membrane and polyamide (nylon) filters as the adsorbent. Nylon filters are commercially available from several manufactures, making them highly convenient for undertaking observations of the atmosphere. Although Perrino et al. (1988) reported sampling

artefacts on nylon filters due to the adsorption of NO₂ and nitrous acid (HONO) in the air and their oxidation into NO₃⁻, Dasch et al. (1989) and Place et al. (2018) indicated that collection of HONO by a nylon filter was not significant. In a comparative study of reagent coatings for an annular denuder sampler (Perrino et al., 1990), sodium chloride (NaCl) was found to be suitable for HNO₃ sampling because it produced few NO₂ sampling artefacts. Further, the NO₂ concentration in the urban atmosphere has been significantly reduced by various emission regulations in recent decades; therefore, NO₂ interference on HNO₃ measurements has also decreased in recent years. Simultaneous measurements using nylon and NaCl impregnated filters would allow us to examine their equivalence as adsorbents in the urban atmospheric environment under reduced NO₂ concentrations. In this study, we conducted a long-term comparison of an NaCl-impregnated filter and commercially available nylon filters obtained from two manufacturers.

Two types of diffusion resistors between the outside air and the adsorbent have been established, either diffusion in the air to the adsorbent or permeation through a porous inert membrane. For diffusion in the air, factors such as wind speed and temperature greatly affect the sampling rate (Namieśnik et al., 1984; Tang et al., 2001; Górecki and Namieśnik, 2002; Bytnerowicz et al., 2005). Permeation diffusion through chemically inert membrane filters has the advantages of being stable, less sensitive to wind speed, and with negligible particle impaction and deposition on the adsorbent, although the conversion coefficient (sampling rate) must be determined experimentally. Place et al. (2018) discussed various errors in HNO₃ determination using a permeation passive sampler, including negative and positive biases of aerosol particles captured on the permeation filter at the front of the adsorbent filter. In this study, we used a permeation type passive sampler with PTFE membrane filters. Although PTFE membrane filters have been used as a permeation membrane (Nishikawa, 2004; Bytnerowicz et al., 2005; Zbieranowski and Aherne, 2012), no comprehensive and systematic studies of the relationships between different types of permeation filters and adsorbents on the sampling velocity (SV) for HNO₃ have been reported. Therefore, we examined these factors based on simultaneous observations over many years.

2. Experiments

2.1 Observation site

Nagoya is the fourth largest metropolitan urban area in Japan. Although the population of Nagoya City is ca. 2.3 million, the air pollution levels in Nagoya are relatively low. For example, the annual mean PM_{2.5} and NO₂ concentrations in recent years are about 12 µg m⁻³ and 15 ppb, respectively (Nagoya City, 2020). Atmospheric observations were conducted on the roof of the seven-story Environmental Studies Hall (51 m above sea level; 35.16°N, 136.97°E) of Nagoya University from October 2016 to February 2020.

2.2 Passive permeation sampler

A commercial available polystyrene filter holder (micro-slide holder, ADVANTECH) was used as the sampler, with a modification enabling the addition of a deflection protector at the center (Fig. 1). The inner diameter of open surface was 41 mm. All filters used in this study were 47 mm in diameter. A cellulose filter (Toyo filter paper 5A) impregnated with 300 µL of 0.2% NaCl solution [1:9 of H₂O:MeOH by volume; quickly (ca. 3 min) dried in an incubator at 40 °C in the laboratory] per filter, and polyamide filters (Nylasorb, 1.0 µm nominal pore size, Pall Corporation and Magna, 5.0 µm nominal pore size, GVS Filter Technology) were used as adsorbents for HNO₃. Nylasorb filters are not currently available, so comparisons with other filters are valuable and unique. The HNO₃ in ambient air permeated through the PTFE filters (TA300, 3.0 µm nominal pore size, and PF100, 10.0 µm nominal pore size, both manufactured by ADVANTECH). The PTFE and adsorbent filters were housed in the micro-slide holder with no spacing between the PTFE and the adsorbent filters. The holder was attached to a steel frame material on the roof with magnetic clips. The holder was placed in a well-ventilated area, without direct solar radiation and rain (Supplemental Fig. 1). After collecting the samples, the adsorbent filter of the passive sampler was placed in an airtight 15-mL polypropylene centrifuge tube (IWAKI) and kept frozen prior to chemical analysis. For the chemical analysis, 13 mL of pure water was added to the tube to extract NO₃⁻.

2.3 Annular denuder sampler

An annular denuder system (ADS) was used for collecting HNO₃ (Song and Osada, 2020). The temporal resolution of the ADS sampler was typically 2–3 days, and occasionally shorter intervals (8 to 24 h). The ADS data were collected until the end of February, 2019. After removing coarse particles, HNO₃ was collected using an annular denuder (2000–30x242–3CSS; URG Corp.)

coated on the inside with NaCl (Perrino et al., 1990). Ambient air was drawn into the ADS at a flow rate of 16.7 L min^{-1} (25°C , 1 atm). To extract NO_3^- , 10 mL of pure water was added to the denuder samples, and the solutions were stored in airtight polypropylene tubes in a refrigerator prior to chemical analysis.

2.4 PTFE and adsorbent filter combinations

Various combinations of the PTFE (TA300 and PF100) and adsorbent (NaCl, Nylasorb, and Magna) filters were tested in this study. From 2016 to 2017, simultaneous measurements were made using the ADS and two passive samplers (NaCl and Nylasorb both with TA300). In 2018, the type of nylon filter was changed from Nylasorb to Magna because Nylasorb was no longer available in Japan. A thicker permeation filter (PF100) was also added for testing. Although parallel measurements using the ADS ended in February 2019, a comparison of the three passive samplers (Magna with TA300 and PF100, NaCl with TA300) was conducted for the later part of the observation.

2.5 Chemical analysis and operational blanks

Filter water extracts were filtered using a membrane filter ($0.45 \mu\text{m}$ pore size, 13AI; GL Science Inc.) prior to an ionic analysis using ion chromatography (LC-10A series, Shimadzu Corp., Japan, with modification). The instrument was equipped with a separation column for anions (AS-12A, Dionex, USA) and a suppressor (AERS-500, Dionex) with a flow rate of 1.3 mL min^{-1} . The injection volume was $500 \mu\text{L}$. Major anions were eluted isocratically using $2.7 \text{ mM Na}_2\text{CO}_3$ and 0.3 mM NaHCO_3 . A daily calibration was performed using four mixed standard solutions at the beginning of the analysis and a check was performed using mid-level standard solutions at the end of the measurement series. All standard solutions were diluted from 1000 ppm certified ionic standard solutions (Japan Calibration Service System) supplied by FUJIFILM Wako Pure Chemical Corp. (Japan). The relative standard deviation of repeated measurements for the mid-level standard solution was better than 10%. The operational blank values of the adsorbent filters were also measured approximately every 2–3 months, and the blank values ($0.47 \pm 0.08 \mu\text{g}$ per 0.2% NaCl impregnated filter, $n = 11$; $0.35 \pm 0.14 \mu\text{g}$ per Nylasorb filter, $n = 10$; $1.55 \pm 0.30 \mu\text{g}$ per Magna filter, $n = 33$; $0.92 \pm 0.62 \mu\text{g}$ per annular denuder, $n = 23$) were subtracted from the

value of the actual sample. In this study, blank values with the error for the entire study period were used to calculate the atmospheric concentration from the actual sample.

3. Results and Discussion

3.1 Long-term comparison of the permeation passive sampler and ADS

The HNO_3 concentrations (ppbv, left axis) based on the ADS data from October 2016 to February 2020 were high in summer and low in winter (Fig. 2). The daily accumulated NO_3^- (nmol day^{-1}) collected by the combinations of the PTFE (TA300 and PF100) and adsorbent (NaCl, Nylasorb, and Magna) filters are also superimposed on Fig. 2. The range of HNO_3 concentrations based on the ADS was larger than the variation of the accumulated amounts of the passive samplers. The duration of the ADS sampling (< 3 days) was shorter than the sampling intervals for the passive samplers (1 week). The longer sampling interval for the passive samplers had an averaging effect on the temporal variation in the atmosphere. The trends of the temporal variations in HNO_3 concentrations and daily amounts were very similar, such as the declines in 2017 observed in early June and early August and the peaks in mid-May, late June, and late July to early August.

The HNO_3 dose estimated as the product of the volume-weighted mean concentration (nmol m^{-3}) measured by the ADS with the sampling duration correlated well with the accumulated NO_3^- amount (nmol) per adsorbent filter (Fig. 3). The volume-weighted mean concentration of HNO_3 was calculated by taking the sample volume of the ADS into account to align the sampling interval of the passive sampler. The results of the weighted least-square regression analysis (r^2 , fitting equation with uncertainty for the slope and intercept, and the number of data points) are also indicated in Fig. 3. As speculated from the similarity of temporal variations in Fig. 2, the results of all combinations showed high r^2 values (> 0.94) for the relationship between permeation membranes (TA300 for Figs. 3a and b, PF100 for 3c) and adsorbents (NaCl for 3a, two nylon filters for 3b and 3c). Comparisons of two nylon filters (Magna and Nylasorb) in Fig. 3b are shown separately in Supplemental Fig. 2. The slopes (0.91 and 0.77) in Figs. 3a and 3b, respectively, indicate the difference in efficiency of the adsorbents, showing that the NaCl impregnated filter had a higher (ca. 15%) adsorption efficiency than the nylon filters with the same permeation membrane (TA300). The slopes in the figures of Magna and Nylasorb versus the HNO_3 dose were nearly the same (Supplemental Fig. 2). The difference in the slopes was not significant at the $P =$

0.01 level, suggesting that both had the same adsorption efficiency even though they were supplied by different manufacturers and had different pore sizes. Although the slope was higher for NaCl, the r^2 value was the same for Figs. 3a and 3b. This suggested that both were equally good for monitoring HNO_3 . However, each needed an additional calibration to provide a more accurate measurement.

Perrino et al. (1988) reported positive sampling artefacts due to the adsorption of NO_2 and HONO when using a nylon filter, especially during the photochemically active period. At the nearest atmospheric pollution monitoring station, which was located about 2 km from Nagoya University, the annual average NO_2 concentration was about 10 ppb during the study period (Aichi Prefecture, 2020). Using monthly averages during the study period, the average NO_2 concentrations in winter (December, January, and February; $n = 12$) and summer (June, July, and August; $n = 9$) were 14.3 ± 0.9 ppb and 6.3 ± 0.9 ppb, respectively. The NO_2 concentration was low and conditions conducive to photochemical smog were very rare at the site. In addition, the NO_2^- peak was absent in the extracts of passive samples in this study. Therefore, any NO_2 artefacts on the nylon filters during NO_3^- accumulation were negligible in this study. Similarly, Dash et al. (1989) and Place et al. (2018) reported that NO_2 and HONO interferences were minimal on nylon filters.

The slope (0.41) of the scatter plot (Fig. 3c) between the permeation membranes (PF100) and the nylon filter (Magna) was 53% of the slope (0.77) between the TA300 and nylon filters (Fig. 3b). This suggested that the diffusion resistance of the PF100 was much larger than that of the TA300.

3.2 Comparison of the sampling rate with previous results

Table 1 summarizes the various parameters of the permeation sampler used in this study, such as pore size, filter thickness, porosity, adsorbent type, and SV; porosity data for some studies were not available. Based on a theoretical consideration of permeation sampling (Namieśnik et al., 1984), the SV (m day^{-1}) was estimated as follows:

$$\text{SV} = M / (A \cdot C \cdot t) \quad (1)$$

where M is the accumulated amount of NO_3^- (nmol) in the adsorbent during a collection time of t (day), A is the area of the permeation sampler ($12.2 \times 10^{-4} \text{ m}^2$ for this study), and C is the HNO_3 concentration during sample collection (nmol m^{-3}). The values of M and C are the results of simultaneous observations using passive and active (ADS) samplers, respectively. The SV for a given gaseous species is related to the efficiency of the adsorbent and the resistance, which depends on the thickness and permeability of the permeation filter. Many passive samplers used previously have a long (lower SV) or short (higher SV) diffusion length between the PTFE and adsorbent filters to control the SV. In addition to the distance between the permeation and adsorbent filters, three other factors contributed to the diffusion resistance: the thickness of the permeation filter, the porosity, and the pore size. In this study, the highest SV was observed for the combination of the TA300 as a permeation filter and a 0.2% NaCl impregnated filter as an adsorbent. For nylon filters, the adsorbing ability was the same for the Nylasorb and Magna filters (Fig. 3b and Supplemental Fig. 2). The SV for the combination of the PF100 as a permeation filter and the Magna filter as an adsorbent was 53% of the SV for the TA300 and Magna filters. The nominal pore size of the TA300 (3 μm) was smaller than that of the PF100 (10 μm), but the TA300 (75 μm) was much thinner than the PF100 (1,000 μm), suggesting more resistance for the thicker PF100 filter. From the comparison, it was apparent that the difference in thickness made the largest contribution.

Nishikawa (2004) reported a slightly lower SV for the combination of the PF100 and Ultipor N66 filters, which is another polyamide (nylon) filter frequently used for air sampling. The other three reports listed in the lower part of Table 1 used combinations of various permeation and Nylasorb filters. The SV values for these combinations were estimated from the sampling rate and area based on sampler descriptions, and their SV values were found to be in a similar range to that reported by Nishikawa (2004) and about one third or less of the results for the combination of the TA300 and Nylasorb or Magna in this study. To mount a passive sampler outside, many other studies have employed weather shields around the filters for protection from wind and rain, which will increase the diffusion resistance toward the passive samplers from the ambient atmosphere. Sampler housing dimensions (diameter to height ratio) will influence the SV (Place et al., 2018). Because our sampler was exposed without a weather shield, the SV was higher in this study than in other studies. In addition, most samplers used in previous studies had a gap (diffusion length) between the permeation and adsorbent filters. As mentioned earlier, a millimeter-scale gap

provides resistance from the outside to the adsorbent filter; therefore, SV becomes dependent on the length. However, it might be difficult to keep the gap constant for the entire area of the permeation filter without deflection, which could be a potential source of error in the SV variation. In addition, the TA300 might be more porous than other filters. Based on these comparisons, the selection of a suitable permeation filter based on its SV depends on the ambient HNO_3 concentration and the sampling schedule applied for HNO_3 accumulation.

4. Summary and Conclusions

Passive permeation samplers for HNO_3 were examined to determine the efficacy of various PTFE permeation membranes (TA300 and PF100) and adsorbents (0.2% NaCl-impregnated filters, Nylasorb and Magna filters). This was based on simultaneous observations with an annular denuder coated with an NaCl sampling system. The SV was estimated for various combinations of permeation and adsorbent filters. The NaCl-impregnated filter had a slightly higher SV than the nylon filters. A comparison of permeation filters with almost the same porosity suggested that the SV for the thinner filter (TA300, 75 μm thickness) was much higher than that for the thicker filter (PF100, 1000 μm thickness). As a permeation filter, the TA300 is therefore suitable for short-term sampling of low HNO_3 concentrations, whereas the PF100 is more appropriate for long-term sampling (e.g., monthly) of high HNO_3 concentrations. In addition to the effective area and diffusion length of a passive sampler, the selection of the permeation filter is an important parameter that can be used to control SV.

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Table 1 List of materials used in passive samplers and their sampling velocity (SV)

	Permeation filter	Pore size (μm)	Thickness (μm)	Porosity (%)	Adsorbent type	Sampling velocity (m/day)
This study (1)	TA300	3.0	75	83	0.2% NaCl 5A impreg.	748
This study (2)	TA300	3.0	75	83	Nylasorb	633
This study (3)	TA300	3.0	75	83	Magna	
This study (4)	PF100	10.0	1,000	77	Magna	279
Nishikawa (2004)	PF100	10.0	1,000	77	Ultipor N ₆₆	185–238
Bytnerowicz et al. (2005)	Zefluor	2.0	152	na	Nylasorb	190
Place et al. (2018)	Zefluor	1.0	165	na	Nylasorb	135
Zbieranowski and Aherne (2012)	TE38*	5.0	265	na	Nylasorb	213

na: not available, TA300 and PF100: manufactured by ADVANTECH, Zefluor, Nylasorb, and Ultipor: manufactured by Pall Corp., TE38: manufactured by Whatman, Magna: manufactured by GVS Filter Technology.

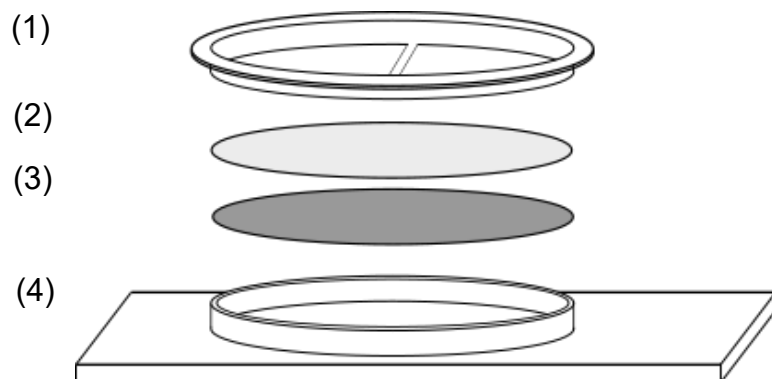


Figure 1 Schematic of the HNO₃ passive sampler. (1): filter cap, (2): permeation PTFE (TA300 and PF100) membrane filter, (3): adsorbent (NaCl impregnated filter and nylon filter), (4): sample holder base. Parts of (1) and (4) are available as a micro-slide made from polystyrene and manufactured by ADVANTECH (P/N: MISL-47). To prevent the deflection of filters, we added a narrow (2.5 mm width) bridge made of polyethylene and attached to the bottom of (1) with plastic glue. The internal diameter of (1) was 41 mm.

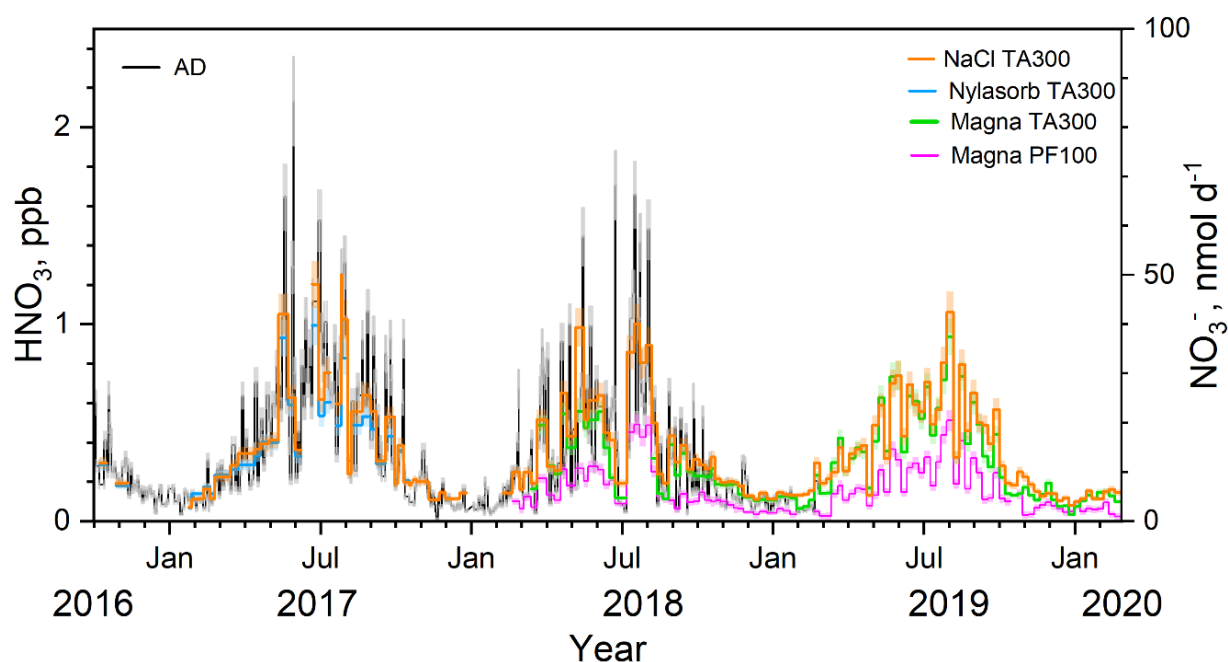


Figure 2 Variations of the HNO₃ concentration (ppb) measured by the annular denuder system (ADS) and the daily accumulated amount of NO₃⁻ collected by passive samplers using NaCl impregnated Nylasorb and Magna filters as adsorbents. Combinations of adsorbents and permeation filters are indicated by the different line colors with reduced intensity for error bars used in the figure.

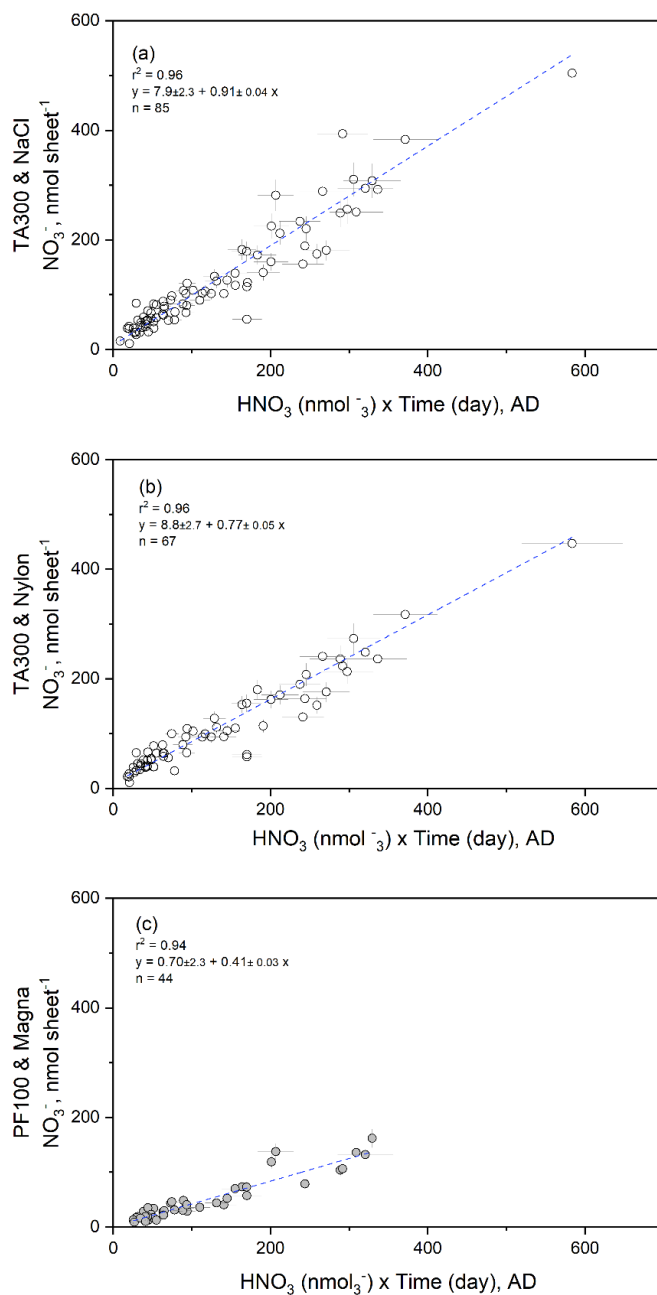
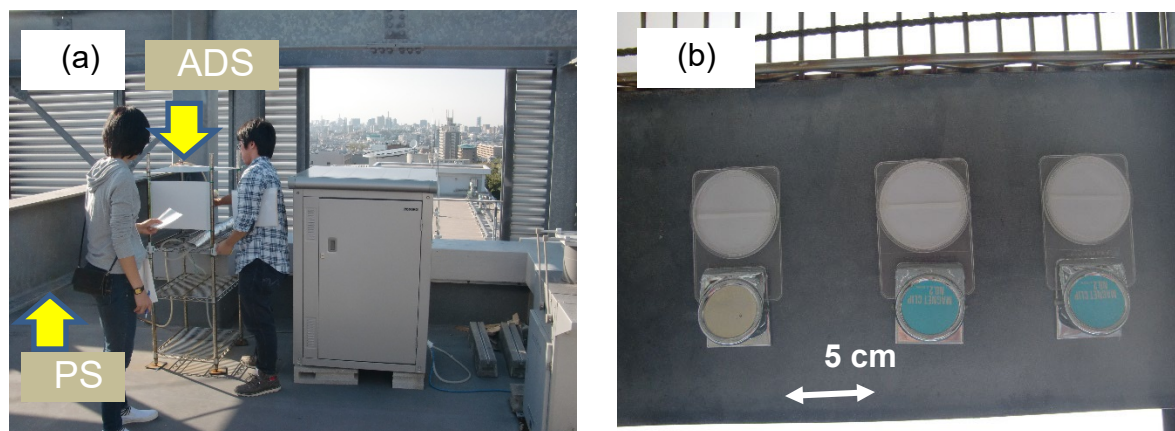


Figure 3 Scatter plots of the accumulated amount of NO_3^- on the adsorbent (y axis) and the products of the HNO_3 concentration determined by the annular denuder and time of sample collection of the permeation sampler (x axis). a): NaCl impregnated filter as the adsorbent and TA300 as the permeation membrane, b): Nylon filters (Nylasorb and Magna) as the adsorbent and TA300 as the permeation membrane, and c): Magna filter as the adsorbent and PF100 as the permeation membrane.

Supplemental Materials



Supplemental Figure 1 Atmospheric sampling on the rooftop. (a) downward arrow: location of the annular denuder system, upward arrow: location of passive samplers, (b) passive samplers mounted at the bottom of the steel frame