Measurements of Gaseous NH_3 and Particulate NH_4^+ in the Atmosphere by Fluorescent Detection after Continuous Air–water Droplet Sampling

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ABSTRACT

Phase partitioning of NH_x (gaseous NH_3 and particulate NH_4^+) in the atmosphere is crucial for the lifetime of NH_x during atmospheric transport. Reliable data for gaseous NH_3 and NH_4^+ in aerosols are necessary to understand phase-partitioning and atmospheric cycles of NH_x. A semi-continuous microflow analytical system (MF system) was developed for measuring gaseous NH_3 and particulate NH_4^+ in the atmosphere. Two inlet lines were used to differentiate total amounts of NH_x and particulate NH_4^+ after gaseous NH_3 were removed by phosphoric acid coated denuder from the sample air stream. Small water droplets were mixed with sample air and separated for liquid phase analysis in the MF system. The NH_4^+ concentration in the liquid was measured using sensitive fluorescence detection after reaction with *o*-phthalaldehyde and sulfite. Based on air sampling at a flow rate of 1 L/min with stripping water at a flow rate of 100 μL/min, the MF system can analyze down to 3 nmol/m^3 of atmospheric NH_3 concentration at 15 min intervals. Comparison with data based on the annular denuder method for gaseous NH_3 and particulate NH_4^+ concentrations indicated reasonable agreement with the MF system. Field tests of the MF system for one month showed good agreement with NH_4^+ concentrations of fine particles collected daily on PTFE filters at the site. The MF system can monitor gaseous NH_3 and particulate NH_4^+ concentrations at 30 min intervals, thereby providing short-term phase partitioning data of NH_x.

Keywords: Ammonia; Gas-particle partitioning; Microflow analysis; Short-term variation.

INTRODUCTION

Ammonia (NH_3), the dominant volatile base in the atmosphere, plays an important role in atmospheric chemistry: it neutralizes precipitation, cloud water, and acidic atmospheric aerosol particles such as sulfate, nitrate, and organic acids. Modification of the aerosol chemical composition by NH_3 neutralization engenders alteration of hygroscopicity and optical properties of aerosols (Seinfeld and Pandis, 2006). Furthermore, NH_3 can enhance new particle formation on a regional scale (Weber *et al.*, 1998; McMurry *et al.*, 2005) and on a laboratory scale (Ball *et al.*, 1999), although NH_3 enhancement of ternary nucleation processes (H_2SO_4–H_2O–NH_3) is controversial (Riipinen *et al.*, 2007; Yu and Turco, 2008).

Atmospheric NH_3 is emitted primarily from livestock waste, volatilization from NH_4^+ containing fertilizer, and other natural (birds, animals, ocean, etc.) and anthropogenic (fuel consumption, biomass burning, etc.) sources, all at the earth's surface (Bouwman *et al.*, 1997; Galloway *et al.*, 2004; Sutton *et al.*, 2008). The NH_3 concentrations in the atmosphere near the ground range from < 0.01 μmol/m^3 in remote regions (Ayers and Gras, 1980; Quinn *et al.*, 1988; Norman and Leck, 2005; Johnson *et al.*, 2008) to approximately 4 μmol/m^3 or more (Theobald *et al.*, 2006; Blackall *et al.*, 2007; Cao *et al.*, 2009; Hsieh and Chen, 2010), largely depending on the proximity to emission sources and deposition processes. However, typical concentrations of sub-micrometer particulate NH_4^+ in the ambient air are < 0.01 μmol/m^3 and approximately 0.3 μmol/m^3 or more (Warneck, 1999; Sutton *et al.*, 2008). Phase partitioning that occurs between gaseous NH_3 and particulate NH_4^+ varies with environmental conditions (temperature and humidity) and acidity of the counteracting aerosols (Stelson *et al.*, 1979; Allen *et al.*, 1989; Mozurkewich, 1993). The complex behavior of gaseous NH_3 and particulate NH_4^+ (hereinafter, NH_x denotes the total amount of gaseous NH_3 and particulate NH_4^+) hampers precise simulation of their temporal and spatial distributions in chemical transport models.

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To understand the lifetime and behavior of NH_x in the atmosphere, reliable measurements of gaseous NH_3 and particulate NH_4^+ are needed without modification of their phase partitioning in the atmosphere. However, such measurements, especially those for low NH_3 concentration, are difficult because of (1) emissions from measuring personnel, (2) adhesive characteristics of NH_3 molecules, and (3) volatilization from labile particulate NH_4^+ (existing as NH_4NO_3, NH_4Cl, etc.) at the inlet and gas–particle separation parts. Contamination, including that by human emissions, of the measurement system from the surrounding atmosphere can be minimized to automate sample handling and analysis. Stickiness of NH_3 molecules to the wall engenders "inlet problems" such as slower response time and higher detection limits (Yokelson *et al.*, 2003), and "calibration problems" of producing a gaseous standard at sub-ppbv concentration levels. Sampling artifacts from non-ideal separation between gaseous NH_3 and particulate NH_4^+ present another "inlet problem".

Several reports of comparisons for measuring atmospheric NH3 have been published (e.g., Wiebe *et al.*, 1990; Williams *et al.*, 1992; Mennen *et al.*, 1996; Fehsenfeld *et al.*, 2002; Schwab *et al.*, 2007; Norman *et al.*, 2009; von Bobrutzki *et al.*, 2010). Among these measurements, diffusion denuder techniques (Ferm, 1979) have been widely used for sampling and stripping the gas phase NH_3 from the air stream. Most simple diffusion denuders consist of a glass tube coated inside with acidic reagents such as phosphoric and oxalic acids. As a sampling method, the diffusion denuder method presents advantages: it is a simple and low-cost method used for collecting atmospheric NH_3. However, this sampling method has disadvantages: (1) it is time consuming; (2) it has low temporal resolution because of necessary handling and accumulation of sufficient amounts of NH_3 to analyze; and (3) it is labor intensive when high-frequency (e.g. hourly) measurements are needed. Moreover, manual handling, including sample preparation, wet-chemical analysis, and sample storage increase the likelihood of sample contamination. Nevertheless, diffusion denuder techniques have been used to remove the gas phase NH_3 from the air stream, leaving particulate NH_4^+ to be analyzed (Bae *et al.*, 2007; Huang *et al.*, 2009; Thomas *et al.*, 2009).

It is widely recognized that ammonium (NH_4^+) is a major component of sub-micrometer particulates in terms of mass. Usually, collection of aerosol particles onto filters or impactor substrates has been conducted for off-line NH_4^+ analyses. However, sampling artifacts of NH_4^+ resulting from the adsorption and absorption of NH_3 onto deposited particles might occur on filter-based samples (Stelson *et al.*, 1979; Harrison and Kitto, 1990; Kitto and Colbeck, 1999). Recently, several techniques have been developed for real time analysis of sub-micrometer aerosol particles. For instance, Bae *et al.* (2007) compared three semi-continuous NH_4^+ measurement methods. In their analyses, agreement among the three techniques was almost satisfactory, but several issues, especially separation of gas and particles, have been pointed out related as possibly causing discrepancies.

Reliable data for gaseous NH_3 and NH_4^+ in aerosols are necessary to elucidate atmospheric cycles of NH_x. To obtain such data, gaseous NH_3 and particulate NH_4^+ should be measured using the same standard materials and calibrations for both species without modifying their phase-partitioning in the atmosphere. As described herein, we propose a semi-continuous monitoring technique of gaseous NH_3 and particulate NH_4^+ by switching analytical lines for NH_x and particulate NH_4^+ concentrations after removal of NH_3 using a simple diffusion denuder.

METHODS

To accomplish sensitive NH_x analysis, we employed fluorescent detection of the *o*-phtalaldehyde (OPA)–sulfite–NH_3 reaction product (Genfa and Dasgupta, 1989; Genfa *et al.*, 1989) with a microflow (MF) system (Maruo *et al.*, 2001; Kimoto *et al.*, 2003a). As described in this paper, the NH_3 concentration is calculated as the difference between total (NH_x: gaseous NH_3 plus particulate NH_4^+) and NH_4^+ concentrations in liquid samples by application with or without a phosphoric acid denuder at the inlet. Atmospheric NH_x was dissolved in ultrapure water using a continuous air–water droplet sampler (Kimoto *et al.*, 2003b). Herein, we describe the system improvements and performance checks used for measuring NH_3 and NH_4^+ in the atmosphere.

Inlet and Air–Water Droplet Sampler

Fig. 1 depicts the continuous air–water droplet sampler connected to the MF analytical part. Two physically identical air–liquid lines were prepared for subtracting total NH_x – particulate NH_4^+ in the atmosphere. At the inlets, coarse particles were removed using Nuclepore filters (pore size: 5 μm, 25 mm diameter) having aerodynamic diameter of ca. 2 μm for 50% cut-off at an air flow rate of 1 L/min (John *et al.*, 1983). Then 50-cm-long 3 mm i.d. glass tubes etched inside were connected after the inlet. One glass tube (Line 1 in Fig. 1) was coated inside with 3% H_3PO_4 and 5% glycerine in 48% methanol and 44% pure water by weight. To develop laminar flow, 5 cm of the uncoated part was left at one end of the tube. The glass tube of the Line 2 was not coated with reagents, but was placed to ensure identical flow conditions. Assuming that the coated wall behaves as a perfect sink of gaseous NH_3, the collection efficiency of this denuder is estimated as > 99% at the air flow rate of 1 L/min according to formulae presented by Dasgupta (1993). However, the actual collection of gaseous NH_3 is expected to be less efficient because of non-ideal conditions in use. That is, the collection efficiency depends on the relative humidity, NH_3 concentration, and other parameters. Because the denuder performance deteriorates after use over a long period, we changed the inlet denuder every week. These coated and uncoated glass tubes were connected by short silicon tubes to PTFE T-shape tubes having different diameters (1/8 and 1/16 inch) at the ends. At a flow rate of 100 μL/min, ultrapure water drops were added at the T-shape tube into the sample air stream, and transferred to a
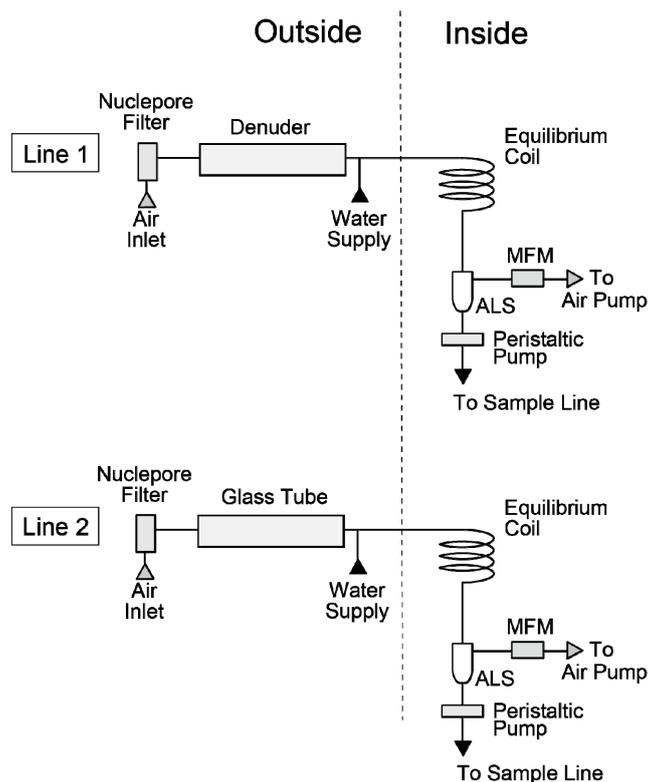
Fig. 1. Schematic diagram of inlet system with acidic denuder (Line 1) and without acid denuder (Line 2). Aside from the coating, the acidic reagent (3% H_3PO_4 and 5% glycerine in 48% methanol and 44% water by weight), lines 1 and 2 are physically identical. Ultra-pure water droplets were supplied using a syringe pump at 100 μL/min. Nuclepore filter, pore size, 5 μm, 25 mm diameter; MFM, mass flow meter; ALS, air–liquid separator made by glass; Sample air flow rate is 1 L/min. The dotted line represents the observation room wall.

PTFE tube coil (1/16 inch i.d., 5 m length). Sample air of 1 L was washed using 100 μL water every minute. Preliminary experiments showed that water is sufficiently effective as an absorber for measuring ambient levels of NH_3 (Genfa *et al.*, 1989; Kimoto *et al.*, 2003b). The length of the washing PTFE coil was necessarily greater than 3 m (Kimoto *et al.*, 2003b). In our study, the air inlets, glass tubes, and the droplet mixers were placed outside within a white-colored weather shield to minimize heating by sunlight. At the ends of the washing PTFE coil, liquid phase droplets were separated by glass air–liquid separators in a temperature-controlled box. Sample air flow rates were controlled and monitored using mass flow meters. Liquid samples were delivered to the porous degassing tubes by a peristaltic pump in the MF system. The sample lines were switched by computer controlled three-way valves. The liquid sample was loaded into a 200 μL sample loop on a six-port valve (Fig. 2) and injected to the MF system.

Microflow Analysis

The basic system of microflow analysis is almost identical to that reported by Maruo *et al.* (2001). Fig. 2 portrays a schematic diagram of the MF system. The R1 solution was composed of 30 mM of *o*-phthalaldehyde (biochemical grade; Wako Pure Chemical Industries Ltd.) in 70% methanol (fluorometric grade, Luminasol; Dojindo Laboratories, Japan). The R2 solution contained 10 mM of
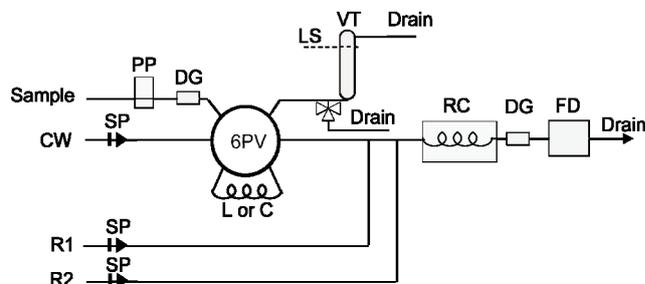

Fig. 2. Schematic diagram of a microflow analytical system with fluorescence detection of NH_4^+ and *o*-phthalaldehyde/sulfite products. Sample: sample solution from the inlet system at about 100 μL/min. CW, carrier water (ultrapure water, 100 μL/min); R1, OPA reagent (10 μL/min); R2, phosphate buffer and sulfite solution (10 μL/min); SP, syringe pump; 6PV, six-port valve with 200 μL sample loop or cation concentrator column; LS, liquid level sensor; VT, volumetric tube; RC, reaction coil heated at 85 ± 1°C; DG, degassing tube (Gore-Tex); FD, fluorescence detector (optimized for excitation, 360 nm; emission, 420 nm); PP, peristaltic pump.

disodium sulfite (analytical grade; Wako Pure Chemical Industries Ltd.) and 50 mM of potassium dihydrogen phosphate (analytical grade, Wako Pure Chemical Industries Ltd.) with 5 mM trisodium citrate (analytical grade, Wako

Pure Chemical Industries Ltd.) at pH 11.0 adjusted by adding 1-M sodium hydroxide. The R1, R2 and ultrapure carrier water were supplied to the reaction coil (RC) by precise syringe pumps at a flow rate of 10 µL/min for the R1 and R2, and 100 µL/min for the carrier water. The reaction coil was curled in a heating block maintained at 85 ± 1°C. A porous degassing tube (Gore-Tex) was connected between the reaction coil and the fluorescence detector that uses excitation at about 360 nm and emission greater than 420 nm. Using a six-port valve with a 200 µL sample loop, a constant volume of the liquid sample was injected to the MF system. The volume of sample loop can be reduced for higher atmospheric concentrations. The time required for one sample analysis was 15 min in this study. Switching analytical lines 1 and 2 at every 15 min, a pair of data for NH_x and particulate NH_4^+ in the atmosphere was obtained for 30 min intervals. Three-port and six-port valves, syringe and peristaltic pumps, and other system components were all controlled using a built-in computer in the MF system which also records data of air flow rates, fluorescent detector voltages, temperatures in the equilibrator box, etc. All digital data can be monitored on a PC screen using a LAN connection with the MF system.

Calibration

For the liquid-phase standard, 1 g/kg NH_4^+ standard solution (ion chromatography grade, Wako Pure Chemical Industries Ltd.) was used as a primary stock solution. Working standard solutions were prepared by diluting the stock solution down to 0.05 µM immediately before measurements. Responses of the fluorescent detector of 0.05–1.09 µM are depicted in Fig. 3(a). Fig. 3(b) portrays a calibration plot of data depicted in Fig. 3(a). Strong linearity was obtained for the plot. The 43 consecutive replicate measurements of 0.05 µM NH_4^+ solution indicated standard deviation (σ) of peak areas as 0.173. Assuming constant σ-independence from concentration levels, the limit of quantification (Miller and Miller, 2010) of the analyte (x_Q) can be estimated as

$$x_Q = 10\sigma/b, \tag{1}$$

where b is the slope of the regression line. In this case, we obtained $x_Q = 0.03$ µM, corresponding to 3 nmol/m³ of atmospheric concentration, assuming perfect collection of gaseous NH_3 into the liquid. Regarding reproducibility associated with the MF system, 10 consecutive replicate measurements of 1.13 µM NH_4^+ solution indicated standard deviation (σ) of concentration as 0.04. In other words, the relative standard deviation was 3.5%.

We also performed comparisons with the gas phase NH_3 standard. The NH_3 standard (48.58 ppmv in N_2; Takachiho Chemical Industrial Co. Ltd.) was diluted using a two-step dilution system: changing mass flow ratio and micro-orifices (Fig. 4). The first dilution was performed using two mass flow controllers (MFC1 and MFC2 in Fig. 4) for dilution from 1/92 to 1/4000 of the original gas concentration. In fact, the NH_3 gas adheres to the wall of the apparatus. For that reason, use of mass flow controller
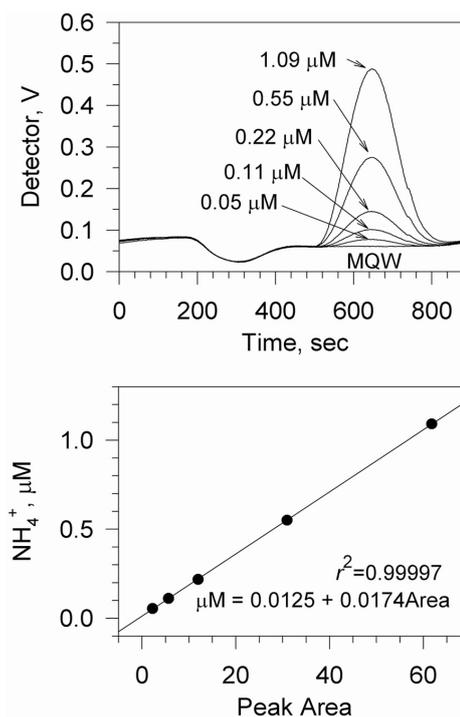

Fig. 3. Detector responses (a) and calibration line (b) of liquid standards.

should be avoided for dilution at sub-ppbv concentration levels. Therefore, micro-orifices were used at the second stage to produce sub-ppbv standards as a fixed 1/200 flow ratio under constant temperature and back-pressure conditions. All parts after the first stage were produced using PTFE.

Fig. 5 portrays the relation between gas standards and the MF response calibrated using the liquid standards, as depicted in Fig. 3(b). The regression line slope was 0.86, which suggests that (1) collection efficiency of NH_3 in this system was 86% on average, (2) part of NH_3 gas was lost in the dilution system, or (3) differences might exist in between primary gas and liquid standards used. According to test results for changing the air flow speed from 0.5 to 1.5 L/min at a constant gas concentration (ca. 30 nmol/m³), the collection efficiency was equal from 0.5 to 1.2 L/min; it decreased slightly at 1.5 L/min (not shown; similar flow dependency was reported in Kimoto *et al.* (2003b)). In contrast, a strong linear relation was obtained for gas standards, which implies that the loss of diluted NH_3 is unlikely to be the cause of the difference. For our study, we primarily used liquid standards for calibration because of traceability. Gaseous NH_3 standard was secondarily used for checking the system performance.

PERFORMANCE TESTS

Comparison with Annular Denuder Method at an Urban Site

The MF system developed in this study was compared with the annular denuder method designed for sampling NH_3 and NH_4^+ in the atmosphere, similar to basic
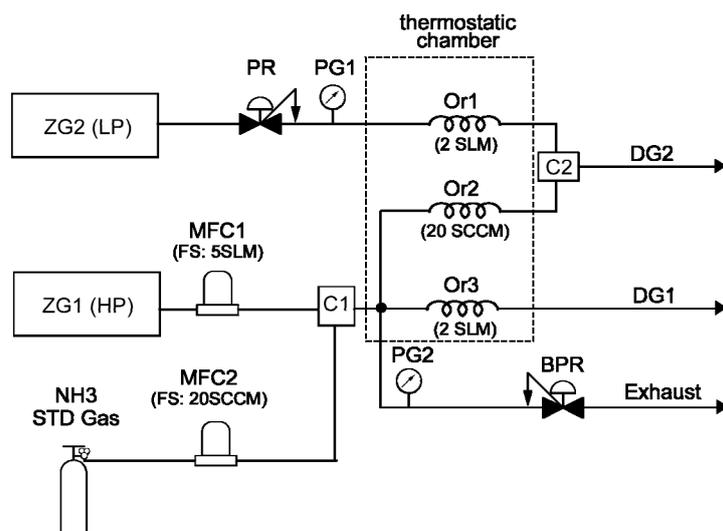
Fig. 4. Dilution system used for preparing low concentration NH₃ gas standards. ZG1 (HP), high-pressure zero-gas supply; ZG2 (LP), low-pressure zero-gas supply; PR, pressure regulator; PG, pressure gage; MFC, mass flow controller; Or, micro orifice; BPR, back-pressure regulator; DG, diluted gas port (DG1 for higher concentrations at several tens of ppbv levels and DG2 for lower concentrations at sub-ppbv levels).
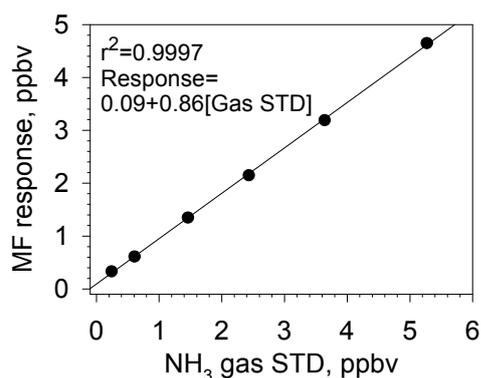

Fig. 5. Relation between gaseous standards and MF system response.

configurations used in Matsumoto and Okita (1998). The annular denuder system consists of a cyclone separator (2000-30EH; URG Corp.) cutting particles larger than 2.5 μm in diameter, an annular denuder (28 mm OD × 242 mm length, -2000-30x242-3CSS; URG Corp.) coated with 2% oxalic acid in methanol and glycerol for collecting NH₃, a PTFE filter (nominal pore size, 1.0 μm; filter size, 47 mm diameter; Advantec Toyo Kaisha Ltd.) for collecting aerosol particles, and a backup oxalic acid impregnated filter (impregnated 300 μL of 0.01M oxalic acid in a 16/84 glycerol/methanol solution by volume, 47 mm diameter) for collecting gaseous NH₃ evaporated from particles on the PTFE filter. We used data from the annular denuder as gaseous NH₃ and the sum of PTFE and the oxalic acid impregnated filter as particulate NH₄⁺. The sample flow rate was 16.7 L/min for the annular denuder system. It was monitored using a mass flow meter (SEF-51; STEC Inc.).

Fig. 6 presents results of atmospheric measurements at Nagoya University on February 29, 2008. Although the comparison data were few, concentrations of gaseous NH₃

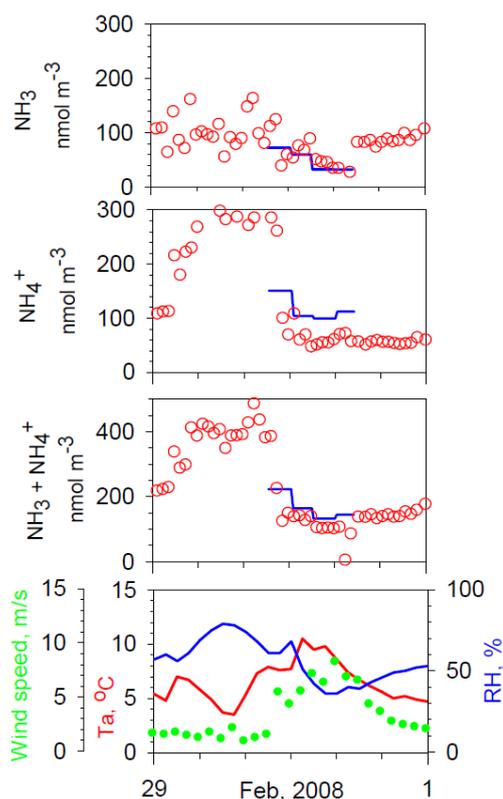

Fig. 6. Comparison with the annular denuder method (stepwise blue lines) and the MF system (open red circles) observed in Nagoya, 29 February 2008. Meteorological data at Nagoya were obtained from the Japan Meteorological Agency.

agreed well. Concentrations of particulate NH₄⁺ and NH$_x$ of the denuder system were slightly higher than that in our MF system. Differences in cut-off diameters between the

cyclone (> 2.5 μm) and the Nuclepore filter (> 2.0 μm) at the inlets might engender the differences observed for the denuder and the MF systems. During the comparison of NH_4^+ in aerosols, difficulty in producing identical inlet conditions was noted also in Bae *et al.* (2009).

Field Testing at a Background Site

The MF system was used for field work conducted from mid-March to mid-April, 2008. During the field campaign, standard solution (approximately 1 μM) was measured automatically every day. Fig. 7 presents response variation of the standard solution from 22 March to 17 April. Response of the standard solution decreased gradually from 1.12 to 0.90 μM during 4 weeks, possibly because of the degradation of reagents stored at room temperature and accumulation of stain within the detector and PTFE tubing in the MF system. Biological activity in the tubing might also have reduced the response of the standard solution, as discussed later in detail. According to various examinations of the MF system after the campaign, degradation of the OPA reagent showed the highest potential for decreasing response during the measurement. Using data presented in Fig. 7, atmospheric NH_3 and NH_4^+ concentrations were corrected for the response variation.

The field campaign was conducted at Cape Hedo Atmosphere and Aerosol Monitoring Station (CHAAMS), Okinawa, Japan (26.87°N, 128.25°E, 60 m a.s.l., Takami *et al.*, 2007; Takami *et al.*, 2010). The station is located at the northern end of Okinawa Island, far away from populated areas of this island. Westerly winds prevail during winter to spring. Therefore, this station has been used to study the outflow of pollution from continental Asia. At this station, because numerous parameters of atmospheric aerosols and gases have been monitored (http://www.nies.go.jp/asia/hedomisaki/outline_e.html), it is suitable to test our system for a longer time period. In addition, stacked filter pack samples were collected daily using an automated sampler (GS-10; Tokyo Dylec Corp.) with a typical air flow rate of 23 L/min. The stacked filter pack consisted of an impactor, a Nuclepore filter (pore size: 8 μm), and a PTFE backup filter for collecting particles

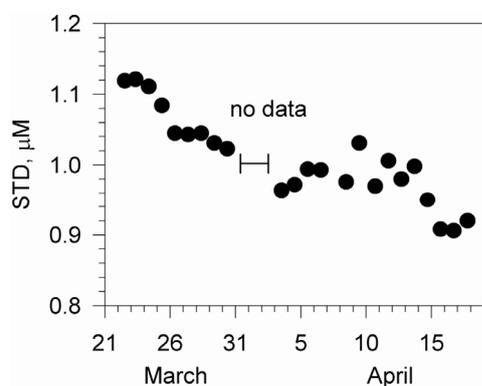**Fig. 7.** Response variation of system check standard (1 μM NH_4^+) during 22 March–17 April, 2008 at Cape Hedo, Okinawa, Japan. No data were obtained during 31 March–2 April because of malfunctions.

having aerodynamic diameters of > 7, > 1.5, and < 1.5 μm, respectively. We compared NH_4^+ concentrations in fine particles of the stacked filter pack samples.

Fig. 8 shows the wind direction (green), wind speed (black), and the results (red lines) of the MF system with the NH_4^+ concentration (blue line) of fine particles obtained from the stacked filter pack. Although large short-term variations were apparent in NH_4^+ concentrations measured using the MF system, the MF data averaged for the duration of the filter pack samples agreed well with filter pack data (Fig. 9). Large variation was also found for NH_3 concentrations, but most large spikes in NH_3 concentrations were out of phase in peaks of NH_4^+ concentrations. Comparison with local meteorological parameters reveals some high NH_3 peaks that occurred during periods of wind from directions from 90 (E) to 240 (SSW), as indicated by arrows at the top of Fig. 8. At these directions from the site, many farms had been cultivating sugar cane. March is the season of harvesting and planting new sugar cane near the site. Natural fertilizers such as poultry manure were used for planting new sugar cane. For that reason, NH_3 and amines might be evaporated from fertilized farmland. However, primary amines were not detected on chromatograms of cation analysis for filter packs during this period. In addition, as Kérousel and Aminot (1997) reported, interference from primary amines was < 0.5% for the reaction of NH_4^+ with OPA and sulfite. Consequently, high NH_3 peaks during wind directions from 90 (E) to 240 (SSW) were attributed to NH_3 emission from fertilized farmland, engendering changes in NH_4^+/NH_x (particle fraction of NH_x), for example, the gradual change of NH_4^+/NH_x from nearly 1 to almost 0 during March 22–23.

In contrast, the drastic change of NH_4^+/NH_x from nearly 0 to almost 1 during March 23–24 might be attributed from rapid and large variation of NH_4^+. Rain (several millimeters per hour at maximum) was observed during 12–19 h on March 23. During 17–19 h, the NH_4^+ concentrations were almost zero, but they increased to 400 nmol/m³ at 4 am on March 24. The minimum concentration of NH_3 was about 10 nmol/m³ at around 16 h for this period. The NH_3 concentrations were almost constant at about 30 nmol/m³ from 19 h on March 23 to 07 h of the next day. Consequently, values of NH_4^+/NH_x increased from nearly zero to > 0.9 during this period concomitantly with increased NH_4^+ concentrations. This example demonstrates one advantage of the MF system. It is unrealistically labor intensive to use the denuder method manually for such a large variation of NH_4^+/NH_x within a short (< 12 h) duration. For that reason, the MF system is more useful to observe short-term variation of NH_4^+/NH_x.

High NH_4^+ concentrations are often found in the air masses transported from China (Takami *et al.*, 2007, 2011). Under conditions of continental outflow with high NH_4^+ concentrations from the Asian continent, NH_3 concentrations were low. Local wind directions during the continental outflow were mostly westward to northward. Therefore, the influence of NH_3 emanating from local farmland was expected to be small.
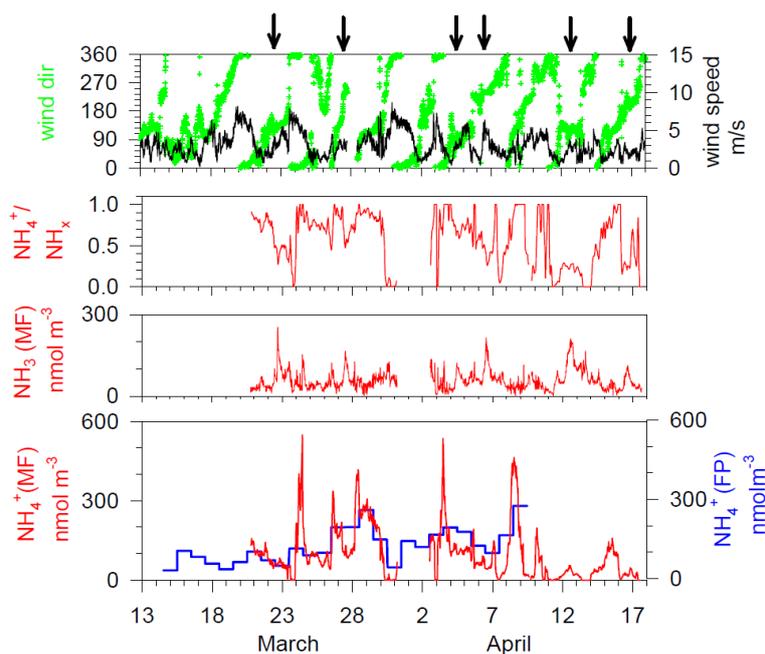
Fig. 8. Results of field measurements at Cape Hedo, Okinawa, Japan obtained during March–April, 2008. Red lines show results for the MF system. No data were obtained during 31 March–2 April because of malfunctions. The blue line shows NH_4^+ concentrations in fine (< 1.5 μm) particles obtained by stacked filter packs. Wind data were obtained at the station.
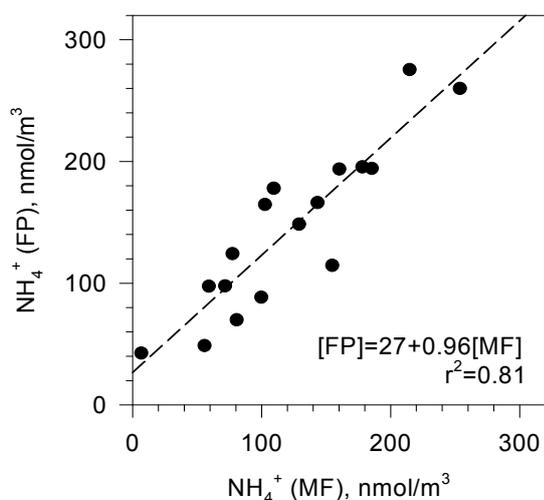

Fig. 9. Relation of NH_4^+ concentrations between MF and FP. Data of MF were averaged for the sampling duration of FP samples.

Potential Effects of Bacterial Activity in the MF System

After several field and laboratory tests of the MF system, responses of gaseous standards, especially for inlet line 1 (NH_3 denuded line coated with phosphoric acid and glycerol), decreased gradually. After washing the sampling line with methanol, the response reverted to its earlier level. Some aerobic microorganisms such as *Nitrosomonas* and *Nitrococcus* can convert ammonia to nitrate. Gradual growth and accumulation of these microorganisms might decrease NH_4^+ concentrations in the sampling line, especially in the air–liquid separator. It is particularly interesting that the degree of NH_4^+ suppression for the

other line without the coating reagent was not so much and slower, which implies that combined activities might enhance nitrification from NH_4^+ such as *Nitrosomonas* associated with *Nitrobacter* (Spieck and Bock, 2005). Considering this potential activity of nitrifying microorganisms at the inside walls of the PTFE tubes and the air–liquid separators, methanol was added as 2.5% by volume to the ultrapure sampling water. Addition of methanol to the water provides good system performance for long-term operations.

CONCLUSIONS

A semi-continuous microflow analytical system (MF system) was developed for measuring gaseous NH_3 and particulate NH_4^+ in the atmosphere. The MF system can quantify concentrations as low as 3 nmol/m³ of atmospheric NH_3 using an air sampling rate of 1 L/min. Comparison with annular denuder data for gaseous NH_3 and particulate NH_4^+ concentrations agreed reasonably well with the MF data. One month of field testing of the MF system proved the long-term capability of semi-continuous monitoring. Data on gaseous NH_3 and particulate NH_4^+ concentrations at 30 min interval provide short-term partitioning data to elucidate the NH_x cycle in the atmosphere and to evaluate the performance of chemical transport models.

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