Western Pacific Air-Sea Interaction Study,
Eds. M. Uematsu, Y. Yokouchi, Y. W. Watanabe, S. Takeda, and Y. Yamanaka, pp. 33–36.
© by TERRAPUB 2014.
doi:10.5047/w-pass.a01.003

Phase Partitioning of NH_3 and Gas to Particle Conversion

K. Osada

Graduate School of Environmental Sciences, Nagoya University,
Chikusa-ku, Furo-cho, Aichi 464-8601, Japan
E-mail: kosada@nagoya-u.jp

Keywords: Ammonia; Nitric Acid; Phase Partitioning; New Particle Formation; Precursor Gas

Phase Partitioning of Ammonia

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. Furthermore, NH_3 can enhance new particle formation on a regional scale and on a laboratory scale, although NH_3 enhancement of ternary nucleation processes (H_2SO_4–H_2O–NH_3) is controversial. The NH_3 concentrations in the atmosphere, near the ground, range from <0.01 μmol/m^3 in remote regions to >4 μmol/m^3 near emission sources, such as a bird colony. Phase partitioning, that occurs between gaseous NH_3 and particulate NH_4^+, varies with environmental conditions (temperature and humidity), concentrations of relating species, and acidity of the counteracting aerosols. 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 a precise simulation of their temporal and spatial distributions in chemical transport models. 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 a low NH_3 concentration, are difficult. To obtain reliable data, a semi-continuous microflow analytical system (MF system) using a simple diffusion denuder was developed for measuring gaseous NH_3 and particulate NH_4^+ in the atmosphere (Osada *et al*. 2011).

Measurement System

Two inlet lines were used to differentiate between the total amounts of NH_x and particulate NH_4^+ after gaseous NH_3 was removed by a phosphoric acid coated denuder from the sample air stream. Small water droplets were mixed with the 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^{-1} with stripping water at a flow rate of 100 μl min^{-1}, 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.

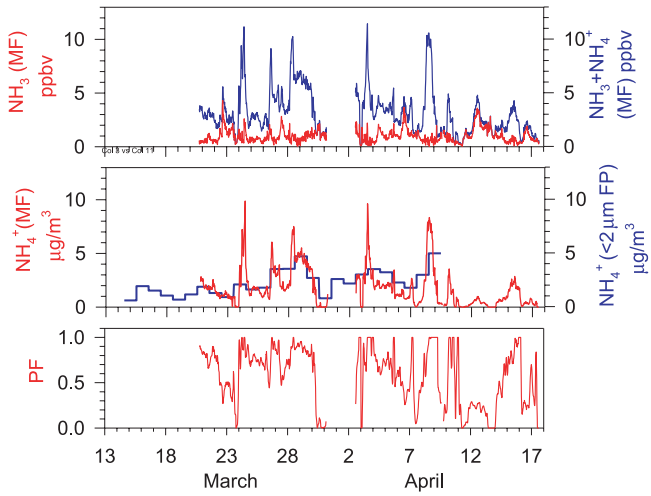

Fig. 1. Results of field measurements at Cape Hedo, Okinawa, Japan obtained during March–April, 2008. No data were obtained during 31 March–2 April because of malfunctions. The blue and red lines in the upper panel show total ($NH_4^+ + NH_3$) and NH_3 concentrations, respectively. The blue and red lines in the middle panel show NH_4^+ concentrations in fine (<1.5 μm) particles obtained by stacked filter packs, and data from the MF system, respectively. PF in the lower panel shows the NH_4^+ fraction to the total NH_x concentration.

Observation at Cape Hedo

The MF system was used for a field campaign from mid-March to mid-April, 2008, 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*. 2011). The station is located at the northern end of Okinawa Island, far away from populated areas of the island. Westerly winds prevail during winter to spring. Therefore, this station has been used to study the outflow of pollution from continental Asia. Figure 1 shows the results of the MF system with the NH_4^+ concentration 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.

A large variation was also found for NH_3 concentrations, but most large spikes in the NH_3 concentrations were out of phase with peaks of NH_4^+ concentrations, possibly because of local NH_3 emission from fertilized farmland. The drastic change of PF from nearly 0 to almost 1 during March 23–24 was attributed to a rapid and large variation of NH_4^+. The NH_3 concentrations were almost constant at about 1 ppbv during this period. 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 duration. For that reason, the MF system is useful for observing short-term variations of NH_4^+/NH_x.

Observation near the Sea Ice Edge in the Antarctic Ocean

Measurements of atmospheric NH_3 concentration over the remote ocean were very limited, especially for the Antarctic (Southern Indian) Ocean. We made meas-

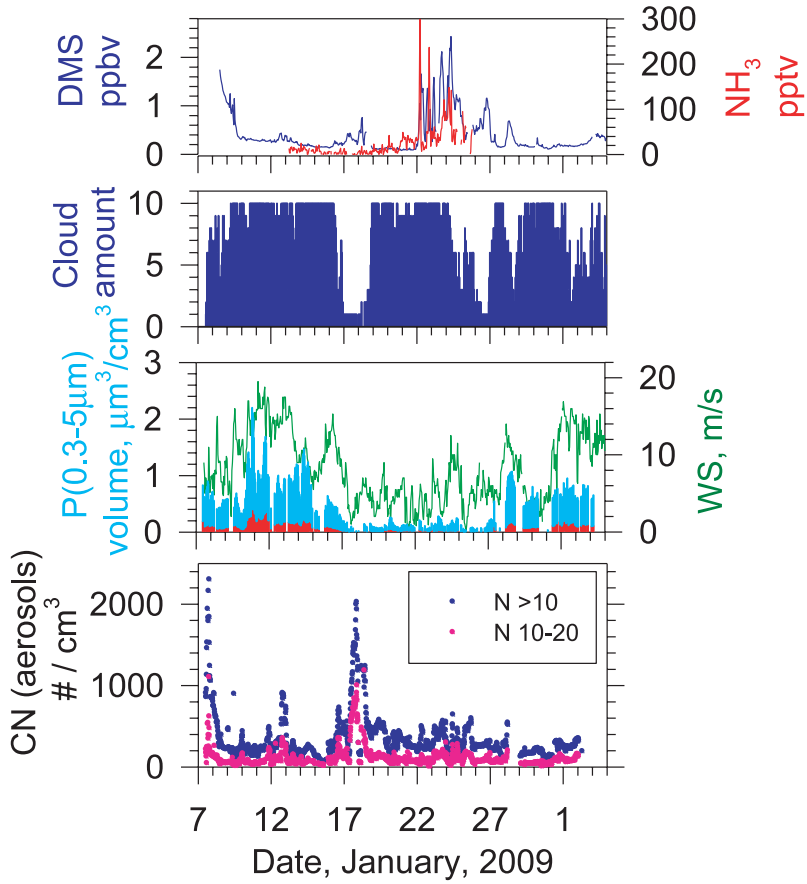

Fig. 2. Results of measurements during the 27th Umitaka-maru cruise, 2009. DMS data are from Wada *et al*. (2011). Volume concentrations of aerosol particles were estimated from OPC (Rion, KC-01D) data. Number concentrations of condensation nuclei were segregated by 2 size ranges.

urements of gaseous NH_3, using the MF system and acid impregnated filter packs, during the 27th Umitaka-maru cruse (January 7–February 6, 2009) from Cape Town, South Africa, via the Antarctic Ocean to Fremantle, Australia. Figure 2 shows the results of various measurements taken onboard (Osada *et al*. 2010). Concentrations of NH_3 and DMS in the air were occasionally high in the marginal sea ice area where sea ice was melting and thinning. A remarkable new particle formation (NPF) event was observed on Jan. 17–18, which coincided with a moderate peak of DMS concentration, very low pre-existing aerosol concentration, and high solar radiation under a clear sky condition. However, during Jan. 23–24, with of high NH_3 and DMS concentrations, CN concentration did not increase, presumably because pre-existing aerosols were relatively high and the weather was not suitable for NPF. Thus, not only the source strength of precursor gases, but also a condensation sink is important for an NPF event, especially in the atmospheric marine boundary layer because of abundant sea salt aerosol particles.

Dry Deposition of Nitrate via Modification of Giant Sea Salt Particles

Modification of sea salt aerosol (SSA) particles by HNO_3 and SO_2 is an important process for changing the phase partitioning of acidic gases from industrial regions to the ocean. During 12–29 September, 2005, size-segregated (>8, 8–2, 2–0.2, and <0.2 μm) aerosol particles and acidic gases were sampled around the western part of the Japanese Islands to elucidate the controlling factors of the modification of SSA particles by acidic gases, and to estimate the dry deposition flux of HNO_3 and SO_2 over the ocean (Kawakami *et al*. 2008). Under high (low) wind conditions, the NO_3^- concentration per unit surface area of coarse SSA particles was lower (higher) for particles >8 μm than for those of 2–8 μm diameter. The respective dry deposition fluxes (F_{dry}) of NO_3^-, nss-SO_4^{2-}, HNO_3, and SO_2 were estimated according to the wind speed and size of the aerosol particles. On average, the F_{dry} of particulate NO_3^- was 10 times larger than that of HNO_3, but F_{dry} of nss-SO_4^{2-} was almost equal to that of SO_2.

Acknowledgements

We are indebted to Mr. Y. Takeda, Dr. S. Ueda and Dr. C. Nishita for assisting our work at CHAAMS, Okinawa. We thank Professor Y. Katayama of Tokyo University of Agriculture and Technology for discussion on nitrification microorganisms. We are grateful to Professor J. Kanda and Dr. F. Hashihama of Tokyo University of Marine Science and Technology, Professor M. Wada and Dr. M. Shiobara of the National Institute of Polar Research, and the researchers and crews of the R/V Umitaka Maru and the R/V Shirase for their help.

References

Kawakami N, Osada K, Nishita C, Yabuki M, Kobayashi H, Hara K, Shiobara M (2008) Factors controlling sea salt modification and dry deposition of non-sea-salt components to the ocean. J. Geophys. Res. **113**: D14216, doi:10.1029/2007JD009410.

Osada K, Hara K, Yabuki M, Nishita C, Kobayashi H, Miura K, Ueda S, Hayashi M, Hashida G, Shiobara M, Wada M, Yamanouchi Y (2010) Observations of atmospheric aerosol particles over the Antarctic Ocean by ocean research vessels. Antarctic Record **54**: 449–464 (in Japanese).

Osada K, Ueda S, Egashira T, Takami A, Kaneyasu N (2011) Measurements of gaseous NH_3 and particulate NH_4^+ in the atmosphere by fluorescent detection after continuous air-water droplet sampling. AAQR **11**: 170–178.

Takami A, Osada K, Sadanaga Y, Bandow H (2011) Variation and distribution of ammonia/ammonium concentration at the Cape Hedo, Okinawa in the ambient air. Earozoru Kenkyu **26**: 42–46 (in Japanese).

Wada M, Nakaoka S, Kasamatsu N (2011) Observations of atmospheric dimethyl sulfide in the Southern Ocean during a cruise on the research vessel Umitakamaru in 2008–2009. Antarctic Record **55**: 82–91 (in Japanese).