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$_2$SO$_4$–H$_2$O–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$_x$ 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.
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 (<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$_3$ concentration.

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$_3$ within a short duration. For that reason, the MF system is useful for observing short-term variations of NH$_3$/NH$_4^+$.

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-
measurements of gaseous NH$_3$, using the MF system and acid impregnated filter packs, during the 27th Umitaka-maru cruise (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$_2$.

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