

Contribution of Water Soluble Organic Nitrogen to Total Nitrogen in Marine Aerosols over the East China Sea and Western North Pacific

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ABSTRACT

This paper presents information on concentrations, size distributions, geographical distributions and sources of water-soluble organic nitrogen (ON_{ws}) in aerosols over the East China Sea and western North Pacific to understand its impact on the atmospheric processes and the oceanic ecosystems in the autumn and spring in the East Asian region. Results revealed ON_{ws} contributions to the total nitrogen in aerosols to be $\sim 24\%$ and $\sim 10\%$ over the East China Sea in the autumn and the spring, respectively. The particulate ON_{ws} mainly existed in fine sized particles. Gas to particle conversion may be the major formation process for ON_{ws} . Occurrence of particulate ON_{ws} in both fine and coarse modes during the Kosa event suggests gaseous ON adsorption and/ or adhesion to the coarse mode mineral. This behavior of ON_{ws} is unique whereas NH_4^+ occurred dominantly in fine mode and NO_3^- in coarse mode.

Key Words: organic nitrogen; marine atmosphere; nitrogen cycling; atmospheric particulate matter

1. INTRODUCTION

In recent years, the inorganic nitrogen species (i.e., nitrate and ammonium) considered hitherto to assess the transport and deposition of nitrogen in the atmosphere have been extended to organic nitrogen compounds (e.g., Cornell et al., 1995; Seitzinger and Sanders, 1999). The results suggest that organic nitrogen compounds influence atmospheric chemistry and air quality, and contribute to the nutrient budgets of land and marine ecosystems. Deposition of organic nitrogen in seawater from atmosphere can promote primary productivity since a major fraction of the water soluble organic nitrogen (ON_{ws}) supplied by rainwater is found to be biologically available (e.g., Seitzinger and Sanders, 1999). Duce (1998) estimated that inclusion of ON_{ws} increases total N deposition from ~30 to ~40% for coastal areas worldwide. In addition, the air borne organic nitrogen investigations are very important from the cloud chemistry point of view as it is associated with particulate organic carbon (Saxena and Hildemann, 1996).

Currently not much information on the composition and chemistry of organic N in aerosols is available to understand the transport and transformations of atmospheric nitrogen species and their role in the global nitrogen cycle. This is true for ON_{ws} over the remote marine atmosphere, since organic N contributes significantly (~ 31 and ~ 64 % of the total N under clean marine and dirty continentally affected conditions, respectively) in remote atmosphere (Cornell et al., 2001). The western North Pacific region is affected by continental air masses from East Asia (e.g. Uematsu et al., 1983; Tsunogai et al., 1985). The East China Sea is one of the largest marginal seas in the world and is situated between the east coast of China and the western North Pacific (Lin et al., 2000). Nakamura et al. (2005) reported that the East China Sea receives a large influx of atmospheric pollutants from the East Asia in the autumn and that atmospheric nutrients supply to the East China Sea is comparable to the outflow from the Chanjiang River. However, there have been no measurements of organic nitrogen in Asian aerosols yet.

This study presents our results on concentrations, size and geographical distributions and sources of ON_{ws} in aerosols over the East China Sea and western North Pacific to enable understanding its impact of atmosphere processes on the oceanic ecosystems in the autumn, a low dust season, and the spring, a high dust season. Through this study we attempted to elucidate the human impact on the regional atmosphere with implications to surface ocean processes.

2. METHODS

Figure 1 shows the observation areas of Leg 2 of the KH02-3 cruise conducted on board the vessel R/V *Hakuho-maru* between 26 September 2002 and 9 October 2002, and KH04-1 cruise conducted between 4 and 22 March 2004 (Leg1; 4-13 March, Leg2; 14-22 March). These cruises represent the observations in the autumn and spring, respectively. A high volume virtual impactor air sampler (Kimoto Electric Co., Ltd., AS-9) was used to collect atmospheric aerosols on pre-combusted (4 hours at 850 °C) Quartz fiber filter papers (PALLFLEX Products Co., 2500QAT-UP, 90 mm in diameter). The sampler used an inertial force to separate atmospheric aerosols according to their aerodynamic diameters, which were segregated into fine (<2.5 µm) and coarse modes (>2.5 µm) on the same filter. The sample collection was continuous for approximately 3-4 days during the KH02-3 cruise in the autumn and 4 (during the Kosa event) or 12 (during the non-Kosa event) hours for KH04-1 cruise in the spring at a flow rate of about 220 L min⁻¹. A wind-sector controller was used to avoid contamination from ship's exhaust.

The particulate matter collected on filter was ultrasonically extracted with deionized water. The deionized water was made from a Milli-Q Plus system (specific resistivity > 18 MΩcm, Millipore Co.). The water extracted aerosol samples were filtered through a pre-combusted glass fiber filter (Whatman GF/F). The filtrates were used in the inorganic nitrogen (IN) species and water soluble total nitrogen (TN_{ws}) analyses. A portion of the filtrate was frozen in sealed glass ampoules at -20 °C for total nitrogen analyses.

The concentrations of IN was determined using DX-320 Ion Chromatograph. For TN_{ws} analysis a high temperature catalytic oxidation (HTCO) system consisting of a commercial unit, the Shimadzu TOC-5000 (Ogawa and Ogura, 1992), was used together with the total nitrogen micro analyzer, Yanaco TN-7 fitted with a chemiluminescence (CLS) detector (Maita and Yanada, 1990; Koike and Tupas, 1993). The measurement followed the generation of nitrogen monoxide (NO) from the TN_{ws} compounds decomposition during the HTCO process (temperature: 680°C, catalyst: 0.5% Pt-Al₂O₃) in the TOC-5000 and its detection with the TN-7-CLS combination (Ogawa et al., 1999).

All sample and standard solutions were handled in a clean chamber throughout the analyses. The concentration of ON_{ws} was obtained by subtracting IN (NO₃⁻ + NH₄⁺) from TN_{ws}. The filter and the instrument derived (from the column packing materials) blank

value range for TN_{ws} was approximately 0.05 - 4.6 % of the extracted TN_{ws} in aerosol samples. In this study, negative values of ON_{ws} were set to zero. We measured TN_{ws} in all fine mode samples in the autumn and the spring, measured the coarse mode samples in all samples in the autumn, and before, during and after Kosa event in the spring, based on the measurement results in the autumn.

The particle number densities were measured continuously using an optical particle counter (Rion Co., Ltd., KC01D) in 5 size fractions of 0.30-0.50, 0.50-1.0, 1.0-2.0, 2.0-5.0 and $>5.0 \mu m$.

3. RESULTS AND DISCUSSION

3.1. Autumn

Figure 2 shows the variations in concentrations of ON_{ws} , NO_3^- and NH_4^+ in fine and coarse mode aerosols in the autumn. The total aerosol (fine and coarse modes) samples collected in the autumn over the East China Sea and Japanese waters contained $170 \pm 87 \text{ nmol N m}^{-3}$ (mean with standard deviation) as inorganic nitrogen (IN; of which about 20% was NO_3^- and 80% was NH_4^+) and $54 \pm 36 \text{ nmol N m}^{-3}$ of ON_{ws} . The ON_{ws} contributed to ~24 % of total nitrogen. These concentrations of IN and ON_{ws} were higher than those reported (11 ± 5.4 and $28.5 \pm 25 \text{ nmol N m}^{-3}$, respectively) in Hawaii affected by land (Cornell et al., 2001). The present ratio of ON_{ws} to water soluble total nitrogen (TN_{ws}) was much lower than in Hawaii (0.64) samples. The concentrations of ON_{ws} were much higher than $3.6 \text{ nmol N m}^{-3}$ (~21 % of total N) on average found in Southern Hemisphere at Cape Grim, Tasmania, in samples affected locally (Mace et al., 2003a). Furthermore, the concentrations obtained for ON_{ws} were similar to those reported 61 nmol N m^{-3} (~ 43 % of total N) on average in Amazon Basin aerosols during the dry season (Mace et al., 2003b). In an oceanic region strongly affected by the anthropogenic substances, such as the East China Sea (e.g., Nakamura et al., 2005), the contribution of IN appears to be more important than ON_{ws} , although the latter is also important. As shown in Figure 2, the major inorganic nitrogen species was NH_4^+ in fine mode and NO_3^- in coarse mode. Most of the ON_{ws} was found in fine mode, with only one sample containing very low amount in coarse mode fraction. The fine mode ON_{ws} may be formed from anthropogenic gaseous ON to particle conversions in the atmosphere (Heintzenberg, 1989), and/or formed in the atmosphere through reactions of anthropogenic volatile organic compounds and NO_x (Atkinson, 2000).

Ammonium concentrations showed similar variations as ON_{ws} concentrations (Figure 2). The highest concentrations of NH_4^+ and ON_{ws} occurred in the first week of October. Similarly, the lower concentrations of ON_{ws} in aerosol samples from 26 to 30 September and from 6 to 9 October coincided with lower concentrations of NH_4^+ . Nakamura et al. (2005) reported that high concentrations of non-sea-salt SO_4^{2-} (nss-SO_4^{2-}), NH_4^+ , and elemental carbon were observed in air mass passed over the continent (example days: October 1, 2 and 7), and particulate NH_4^+ mainly combined with anthropogenic SO_4^{2-} , while low concentrations were observed in the case of clean marine condition (example day: October 6) over the East China Sea during Leg 2 of the KH02-3 cruise. The size distributions of NH_4^+ were also similar to those of ON_{ws} .

3.2. Spring

To compare with the data in the autumn, the measurement results during the observation over the East China Sea (10- 16 March) are shown in Figure 3. An obvious Kosa event reached the study region on 11 March, after the rain passed as a cold front, when fine and coarse modes aerosols dramatically increased. From 11 to 13 March, the particles number densities larger than $5 \mu\text{m}$ frequently exceeded 100 L^{-1} with the highest value of about 600 L^{-1} . We defined this period as a Kosa event. In the spring, total aerosol samples over the East China Sea and Japanese waters contained $130 \pm 98 \text{ nmol N m}^{-3}$ of IN (with about 30 % as NO_3^- and about 70% as NH_4^+) and $16 \pm 19 \text{ nmol N m}^{-3}$ of ON_{ws} . In these samples ON_{ws} represented ~ 10 % of TN_{ws} . The concentrations of ON_{ws} may be underestimated because we did not measure all the coarse mode samples in the spring. The size distributions of NH_4^+ and NO_3^- in the spring were similar to those in the autumn. Much of the ON_{ws} was found in fine mode during the non-Kosa event while it also occurred in coarse mode during the Kosa event (Figure 4). Cornell et al. (2001) found a significant fraction of the organic N in the polluted coarse mode aerosols ($>1 \mu\text{m}$) and suggested that the organic material is derived from nearby soils or sea salt.

The differences in size distribution of N species between Kosa event and non-Kosa in the spring and autumn, respectively, as shown in Figure 4 arise from two potential reasons:

(1) The reactivity of NO_x with mineral particles is more than ON_{ws} ; possibly excess mineral surfaces reacted with ON_{ws} ; Mineral particles occurred in the autumn and spring during the non-Kosa event and hence a large fraction of NO_3^- existed in coarse mode but ON_{ws} was

hardly detected.

(2) The reaction between ON_{ws} and sea salt particles is not favored near the source regions.

One of the ON_{ws} formation processes in aerosols may be the adsorption of gas-phase organics onto dust particles and/ or particulate ON_{ws} in fine mode adheres to dust particles. Occurrence of ON_{ws} and NO_3^- in both the size fractions of aerosols during the Kosa event (Figure 3) is clearly due to higher particle abundance in both modes and surface reactions as compared to that in the autumn.

In agreement with that in the autumn, ON_{ws} concentrations in aerosols linearly correlated with NH_4^+ in the spring as well (slope = 2.4; intercept = 50; $r^2 = 0.62$; $n = 29$). Association of ON_{ws} with continental materials (anthropogenic substances, particularly NH_4^+ in fine particles) and its size fractionation suggest that the organic nitrogen compounds seem to be mainly of anthropogenic origin.

3.3. Fractions of nitrogen compounds in aerosols

The percent contributions of nitrogen compounds in the autumn are different from that in the spring. Ammonium was the most abundant nitrogen compound in both seasons. Significantly, the percentage contribution of NH_4^+ was the same in both seasons (62 %) in spite of large differences in its average concentrations (140 and 91 nmol N m^{-3} in the autumn and spring, respectively). The percentage of NO_3^- autumn (14 %) was lower in the spring (27 %). This is probably because particulate NO_3^- was composed in the spring due to low temperature (14 ± 3.6 °C on average) but existed as gaseous HNO_3 in the autumn due to high temperature (24 ± 2.4 °C on average). The higher ON_{ws} percentage in the autumn is apparently due to anthropogenic substances and probable generation of organic nitrogen compounds by reactions induced by high temperature and intense light conditions during the season.

4. CONCLUSIONS

We made measurements of inorganic and organic nitrogen compounds in atmospheric aerosols over the western North Pacific and the East China Sea. The conclusions of this study are:

(1) One of the sources of ON_{ws} was suggested to be human activities that contributed ~ 24% and ~ 10% to total nitrogen over the East China Sea and western North Pacific in the autumn

and spring, respectively. It is suggested that ON_{ws} transported from the East Asia is an important nitrogen component over the oceanic region.

(2) The main formation mechanism of particulate ON_{ws} seems to be gas-to-particle conversion since particulate ON_{ws} mainly existed in the fine mode. Particulate ON_{ws} occurred both in fine and coarse modes during the Kosa event over the East China Sea suggesting the gaseous and particulate ON adsorption onto coarse mineral.

(3) Each nitrogen compound (ON_{ws} , NH_4^+ , NO_3^-) has its own size distribution pattern. In particular, during the Kosa-event, the size distribution of ON_{ws} is very different (abundant in both modes) whereas NH_4^+ occurred dominantly in fine mode and NO_3^- in coarse mode.

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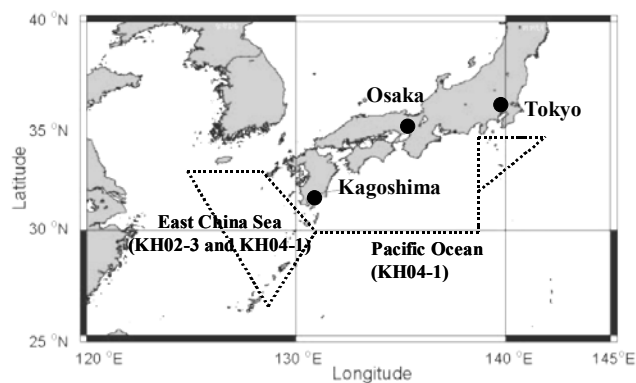


Figure 1. Map of the sampling locations of Leg2 during the KH02-3 and the KH04-1 cruises of the R/V *Hakuho maru*.

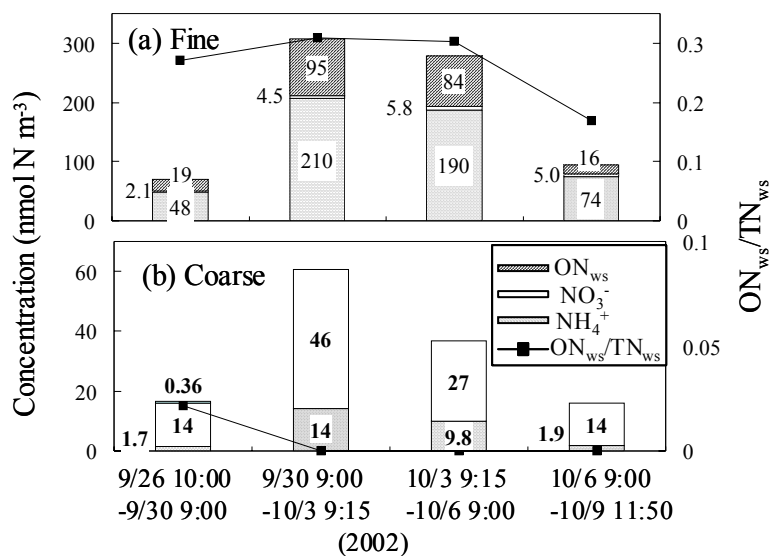


Figure 2. Variations of ON_{ws} , NO_3^- and NH_4^+ over the East China Sea and Japanese waters in the autumn 2002 in (a) fine and (b) coarse modes.

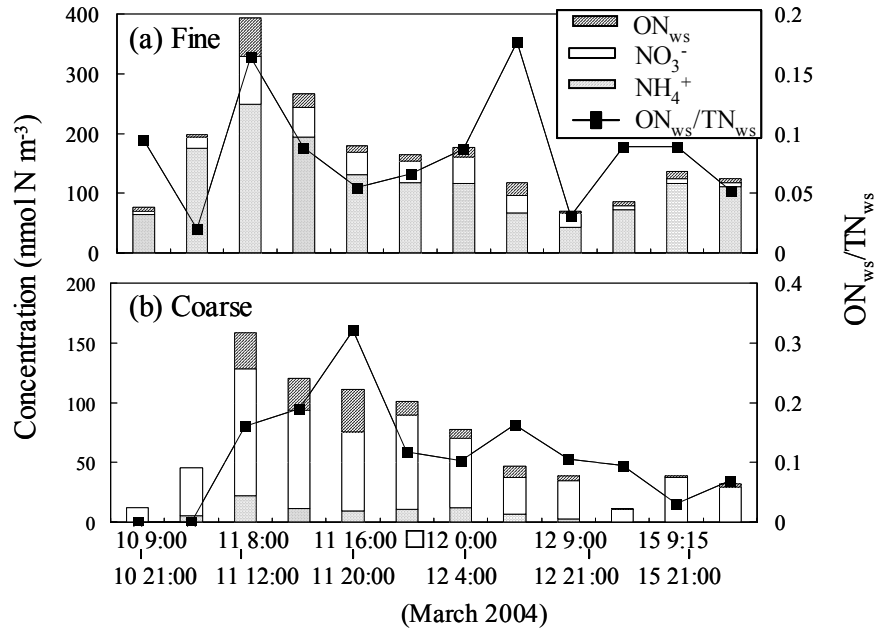


Figure 3. Variations of ON_{ws} , NO_3^- and NH_4^+ in the spring 2004 in (a) fine, and (b) coarse modes during the observation over the East China Sea.

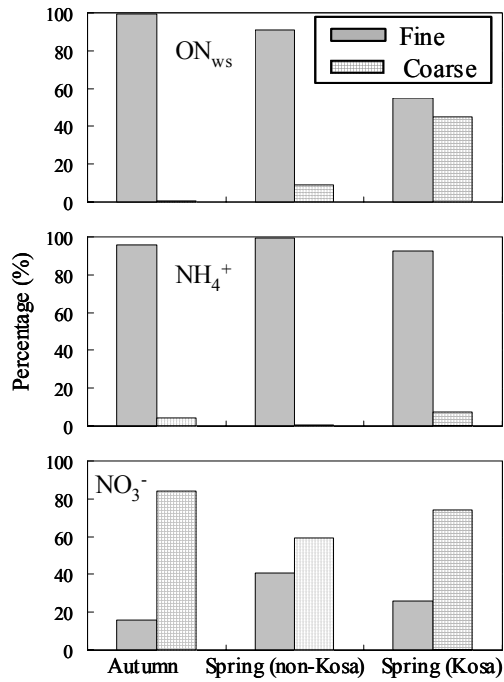


Figure 4. Particle size fractionation of ON_{ws} , NH_4^+ and NO_3^- in the spring (Kosa and non-Kosa events) and the autumn over the East China Sea and Japanese waters.