Organic Nitrogen of Atmospheric Aerosols in the Coastal Area of Seto Inland Sea

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ABSTRACT

Chemical compositions and particle number densities of atmospheric aerosols were measured in the coastal area of Seto Inland Sea during the spring of 2015. The mean concentrations of NH_4^+ , NO_3^- , and water-soluble organic nitrogen (ON_{ws}) in the total (fine and coarse) particles were 1.6, 0.85, and $0.28 \mu\text{g N m}^{-3}$, respectively. Although NO_3^- existed in fine and coarse particles, while NH_4^+ and ON_{ws} existed primarily in fine particles. The contribution of ON_{ws} to the total nitrogen was approximately 10%, however, these fractions are comparable to the contribution of fine NO_3^- and coarse NH_4^+ .

The dry deposition fluxes of particulate NH_4 , NO_3^- , and ON_{ws} were 280, 660 and $83 \mu\text{g N m}^{-2} \text{ day}^{-1}$, respectively. The dry deposition flux of NO_3^- was more effective than any other nitrogen compounds, since the deposition rate depends upon the size distribution. The dry deposition flux of ON_{ws} was approximately 8.1% of nitrogen compounds, however, it is found that ON_{ws} should be considered in evaluating the effects of nitrogen compounds on marine ecosystems.

Keywords: Nitrogen compounds; Atmospheric pollutants; Atmospheric deposition of nutrients.

INTRODUCTION

The Seto Inland Sea is recognized as a beautiful scenic area not only in Japan, but also globally, and it is a treasure trove of valuable fishery resources (Ishii and Yanagi, 2006). It is also one of the most industrialized regions in Japan and characterized by frequent occurrence of red tides, therefore, to prevent this problem, chemical oxygen demand (COD) and total amount of nitrogen and phosphorus have been regulated (Hori *et al.*, 2008). As a result, the water quality has continued to improve, the occurrence of red tides has decreased, and the transparency of the seawater has been restored (Tada *et al.*, 2010). However, recently, concerns impacting the fishery industry have been identified, such as the discoloration of laver aquaculture (Tada *et al.*, 2010) and

the reduction in fish caught due to the decrease of nutrients in the seawater (Tanda *et al.*, 2014).

The inflow of atmospheric pollutants such as yellow dust and anthropogenic substances from the East Asian has been actualized (Zhou *et al.*, 1990; Uematsu *et al.*, 1992), and the coastal area of the Seto Inland Sea is also affected by these pollutants (Nakamura *et al.*, 2015). Based on a simulation using the chemical transport model, approximately 48% of the anthropogenic nitrogen compounds transported from China are deposited in the Yellow Sea, the East China Sea, and the Sea of Japan, and the importance of sea salt particles in this deposition process has been indicated (Itahashi *et al.*, 2016). Moreover, these deposits affect marine biological production (Uematsu *et al.*, 2004). Therefore, it is necessary to obtain information on the nitrogen compounds deposited in the ocean from the atmosphere. Previous Studies have indicated that the inflow pathways of nutrients to the Seto Inland Sea are primarily from the open ocean (Pacific) (Ishii and Yanagi, 2006), bottom sediment, and rivers (Tada *et al.*, 2010), but little is understood about the inflow from the atmosphere (Nakamura *et al.*, 2015).

Among the nitrogen compounds present in the atmospheric aerosols, inorganic nitrogen has been generally measured. Although research on organic nitrogen has been increasing in recent years, despite its importance, it has been studied significantly less than inorganic nitrogen (Cornell *et al.*,

This article is an English version of “Organic Nitrogen of Atmospheric Aerosols in the Coastal Area of Seto Inland Sea [Japanese]” published in the *Earozeru Kenkyu* in Mar. 2017.

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1995). Currently, there is limited information regarding the concentration of organic nitrogen, its ratio to total nitrogen, sources, size distribution, behavior in the atmosphere, and deposition; in addition, these findings vary greatly depending on the individual studies (Jickells *et al.*, 2013).

After the deposition of organic nitrogen in the ecosystems, some forms can be used as nutrients directly (Murphy *et al.*, 2000) or after decomposition (Smidt, 1994) by microorganisms. However, some forms are toxic to organisms (Paumen *et al.*, 2009). As mentioned above, organic nitrogen has various chemical forms, however, it needs to be considered to prevent the underestimation of the deposition of nitrogen compounds (Jickells *et al.*, 2013). To date, there have been no studies on organic nitrogen in atmospheric aerosols in the coastal area of the Seto Inland Sea.

In this study, we focused on the nitrogen compounds in aerosols that are utilized as nutrients in the ecosystems. The purpose of this study was to determine the chemical forms of the nitrogen compounds (organic and inorganic) based on their particle size, importance and sources of organic nitrogen, and the deposition of nutrients by atmospheric aerosols in the coastal area of the Seto Inland Sea.

METHODS

Atmospheric aerosols were measured on a rooftop (approximately 15 m above the ground) at the National Institute of Technology, Kagawa College (Mitoyo City, Kagawa Prefecture), between February 15 and March 20, 2015 (Fig. 1).

An automated sequential air sampler (Tokyo Dylec Co., Ltd., GS-10) was used to collect the atmospheric aerosols on pre-combusted (4 h at 450°C) quartz fiber filters (Pallflex Products Co., Model 2500QAT-UP). The samples were collected at 24 h intervals at a flow rate of 20 L min⁻¹. The inline 2-stage filter folders (Nilu, NL-I-02) equipped with a multi-nozzle cascade impactor (Tokyo Dylec Co., Ltd., NL-2.5A) were used to separate the atmospheric aerosols

according to their aerodynamic diameters, which were segregated into fine (< 2.5 µm) and coarse (> 2.5 µm) particles. The air sampler can hold a maximum of 10 filter holders, and the samples can be automatically changed every 24 h. In this study, the period of sample attachment to the air sampler, including the sampling time, was set to 4 days to prevent deterioration of the samples. The filters were stored at approximately -20°C until the analysis.

The atmospheric aerosols collected on the filters were extracted by shaking with 50 mL ultra-pure water (specific resistivity: approximately 18 M in a polyethylene container for 30 min. The water-extracted aerosol samples were filtered through a glass fiber filter (Whatman GF/F). The filtrates were analyzed for Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, NO₃⁻, and SO₄²⁻ with ion chromatography (DIONEX, DX-320), and the water-soluble total nitrogen (TN_{ws}). The TN_{ws} was analyzed using high-temperature catalytic oxidation at a furnace temperature of 720°C (Shimadzu Co., TNM-1) with a chemiluminescence gas analyzer (Shimadzu Co., TNM-1).

The blank for each component was determined using six blank filters, and the mean value was subtracted from the values obtained for actual samples. The detection limits of each component were determined to be three times the standard deviation of the measured values of the six blank filters. For the fine particles (< 2.5 µm), the blank values for NH₄⁺, K⁺, Cl⁻, NO₃⁻, and SO₄²⁻ were 0.038, 0.018, 0.025, 0.044, and 0.037 mg L⁻¹, respectively, and the other components were within 0.010 mg L⁻¹. The detection limits were 0.014 mg L⁻¹ for NH₄⁺ and within 0.010 mg L⁻¹ for the other components. For the coarse particles (> 2.5 µm), the blank values for NH₄⁺, K⁺, Cl⁻, NO₃⁻, and SO₄²⁻ were 0.019, 0.016, 0.024, 0.042, and 0.032 mg L⁻¹, respectively, and the other components were within 0.010 mg L⁻¹. The detection limits were within 0.010 mg L⁻¹ for all ion components. The blank values for TN_{ws} were 0.037 and 0.026 mg L⁻¹, whereas the detection limits were 0.013 and 0.016 mg L⁻¹, for fine and coarse particles, respectively.

The concentrations of non-sea-salt sulfate (nss-SO₄²⁻) and nss-calcium (nss-Ca²⁺) were calculated from the weight ratios of SO₄²⁻/Na⁺ (0.251) and Ca²⁺/Na⁺ (0.038) in the seawater.

The concentration of water-soluble organic nitrogen (ON_{ws}) in the atmospheric aerosols was obtained by subtracting the water-soluble inorganic nitrogen IN_{ws} (NO₃⁻-N + NH₄⁺-N) from TN_{ws} (ON_{ws} = TN_{ws} - IN_{ws}). In this study, negative values of ON_{ws} were set to zero. However, when calculating the concentrations of ON_{ws}, the measurement errors of IN_{ws} and TN_{ws} were propagated, and the errors were significant when the concentrations of IN_{ws} were high and those of ON_{ws} were low (Cornell *et al.*, 2003). When ON_{ws} was 50% of TN_{ws}, the coefficient of variation was approximately 10%, whereas, when ON_{ws} was 10% of TN_{ws}, the coefficient of variation was approximately 80% (Hansell, 1993; Cornell *et al.*, 2003). Additionally, when measuring TN_{ws}, ON_{ws} potentially was not completely oxidized to NO_x (Scudlark *et al.*, 1998), and ON_{ws} volatilized during the aerosol sampling (Matsumoto and Yamato, 2016). Given that the ON_{ws} values in this study were partly negative, it is assumed that the ON_{ws} values may have been underestimated.

Fig. 1. Observation station (Kagawa prefecture).

Simultaneously, the mass concentration of the atmospheric aerosols with aerodynamic diameters smaller than $2.5\ \mu\text{m}$ ($\text{PM}_{2.5}$) (Thermo, FH62C14) was measured at 30 min intervals, and the particle number density was measured using an optical particle counter (Rion Co., Ltd., KC01D) in five size fractions of > 0.3 , > 0.5 , > 1 , > 2 , and $> 5\ \mu\text{m}$ at 15 min intervals.

A backward trajectory analysis was conducted to estimate the air mass history that reached the observation station using the NOAA HYSPLIT4 model (Draxler and Rolph, 2016) with a tracking time of 72 h at an altitude of 500 m. The meteorological field was also estimated using weather maps provided by Japan Meteorological Agency.

RESULTS AND DISCUSSION

Overviews of the Observation Results

The variations in the particle number densities (> 0.3 , $> 2\ \mu\text{m}$) are shown in Fig. 2. These particle sizes indicate the distinction between the fine and coarse classifications. The variations of nss-SO_4^{2-} and nss-Ca^{2+} in the aerosols are shown in Fig. 3. Periods A–F are treated as high-concentration events, which demonstrated continuous rapid increases. In particular, the daily averages of $\text{PM}_{2.5}$ were $27\text{--}35\ \mu\text{g m}^{-3}$ in Period B (2/23–2/26) and $28\text{--}34\ \mu\text{g m}^{-3}$ in Period F (3/16–3/18), near the environmental standard value of $35\ \mu\text{g m}^{-3}$. On February 23 and 24 (Period B), the Japan Meteorological Agency reported the observation of a Kosa (aeolian dust) event in Takamatsu (http://www.data.jma.go.jp/gmd/env/kosahp/kosa_table_2015.html; accessed 17 April 2016). In this study, a rapid increase in the $> 2\ \mu\text{m}$ particle number densities and the concentration of nss-Ca^{2+} , which is an indicator of mineral particles, were also observed (Fig. 3).

The representative weather charts are shown in Fig. 4 to estimate the causes of the increase in pollutants for each period. In Periods A, B, C, and E, high concentrations of pollutants were observed due to their transport to the observation station by high-pressure systems near the continent with the development and passage of cold fronts. In Period D, the atmospheric pollutants were transported by

Fig. 3. Variations in particulate nss-SO_4^{2-} and nss-Ca^{2+} .

a migratory high-pressure system, and in Period F, the observation area was covered with a high-pressure system, rising temperatures, and minimal air mass movement. The Period F atmospheric conditions were thought to have been primarily affected by the industrial area of the Seto Inland Sea and were supported by 72-hour backward trajectories (Fig. 5).

Nitrogen Components in Atmospheric Aerosols

The variations of water-soluble inorganic nitrogen (NH_4^+ , NO_3^-) and water-soluble organic nitrogen (ON_{ws}) are shown in Fig. 6. The aerosol samples corresponding to the high-concentration events in Periods A–F (shown in Fig. 2) were

Fig. 2. Variations in particle number densities (> 0.3 , $> 2\ \mu\text{m}$).

Fig. 4. Weather charts at 0900 JST on (A) February 17, (B) 24. (C) March 2, (D) 7, (E) 12 and (F) 17, 2015 provided by Japan Metrological Agency (<http://www.data.jma.go.jp/fcd/yoko/hibiten>; accessed 17 Apr. 2016).

defined as polluted atmospheric conditions, and all the other samples were defined as normal atmospheric conditions. The mean concentrations and the ratios of each nitrogen component classified by particle size and categorized into normal or polluted atmospheric conditions are shown in Fig. 7.

Inorganic Nitrogen Components

The variation of NH_4^+ in the fine particles (Fig. 6) was similar to that of the nss-SO_4^{2-} in the fine particles (Fig. 3), and the $>0.3 \mu\text{m}$ particle number density (Fig. 2). The mean concentrations and standard deviations of the total (fine and coarse) NH_4^+ in the normal and polluted conditions were 1.0 ± 0.46 and $2.1 \pm 0.80 \mu\text{g N m}^{-3}$, respectively, indicating that the concentration level was approximately 2.1 times higher in the polluted conditions than in the normal conditions. The proportions of fine particles in the normal and polluted conditions were 97% and 92%, respectively. Although the proportion of fine particles decreased slightly during the dust event, the size distribution did not change significantly.

The variation of NO_3^- in Periods A and B was similar to that of the $>2 \mu\text{m}$ particle number density (Fig. 2) and the coarse nss-Ca^{2+} (Fig. 3). In Period F, that potentially had been affected by the industrial area of the Seto Inland Sea, NO_3^- primarily existed as fine particles. As indicated here, the size distribution of NO_3^- shifted significantly by atmospheric conditions. The mean concentrations and standard deviations of NO_3^- in the normal and polluted conditions were 0.47 ± 0.23 and $1.2 \pm 0.41 \mu\text{g N m}^{-3}$, respectively; thus, the concentration level was approximately 2.6 times higher in the polluted conditions than in the normal conditions. Coarse particles have a high deposition velocity, which affects the amount of deposition. Therefore, the formation of coarse NO_3^- was investigated. The correlation between the nss-Ca^{2+} and NO_3^- coarse particles is very high ($R^2 = 0.94$) (Fig. 8(a)) at equivalent concentrations (neq m^{-3}); this implies that the formation of coarse NO_3^- is correlated with nss-Ca^{2+} . Furthermore, the chlorine loss (Cl-loss) estimated from

Fig. 5. 72 hours backward trajectories during the Period F at every 2 hours starting from 0900. JST on 15 March to 0900 on 17 March (NOAA ARL HYSPLITS4 Model).

Fig. 6. Variations in particulate nitrogen compounds (NH_4^+ , NO_3^- and ON_{ws}).

Eq. (1) from the Cl^- concentration, with Na^+ entirely from sea salt. By adding this value to nss-Ca^{2+} , the relationship between NO_3^- and $\text{nss-Ca}^{2+} + \text{Cl-loss}$ is almost 1:1 (Fig. 8(b)). Here, the concentration unit is equivalent concentrations (neq m^{-3}).

$$\text{Cl-loss} = 1.174 \times \text{Na}^+ - \text{Cl}^- \quad (1)$$

Despite the slight existence of coarse nss-SO_4^{2-} , approximately 65% of NO_3^- is combined with nss-Ca^{2+} as evidenced by the slope value of 0.65 in Fig. 8(a). Based on the relationship between NO_3^- (x) and Cl-loss (y) ($y = 0.28x + 3.8$, coefficient of determination $R^2 = 0.64$), it is estimated that approximately 28% of NO_3^- has combined with sea salt. It can be assumed that the remaining 7.0% of NO_3^- has combined with other cations except nss-Ca^{2+} and Na^+ . This assumption also can be supported by the slope value of 0.93 in Fig. 8(b). Based on these findings, coarse NO_3^- has a relationship with mineral and sea salt particles, affecting the deposition rate of NO_3^- .

Water-soluble Organic Nitrogen

The mean concentrations of the total water-soluble organic nitrogen (ON_{ws}) were 0.24 and $0.31 \mu\text{g N m}^{-3}$ in the normal and polluted conditions, respectively. The concentration level was approximately 1.3 times higher in the polluted conditions than in the normal conditions, indicating a small difference between normal and polluted conditions. During all observation periods, approximately 87% of ON_{ws} existed as fine particles, and the size distribution was similar to that of NH_4^+ . However, although the size distribution of NH_4^+ did not shift during the dust event (Period B), it has been reported that ON_{ws} related to mineral particles increased during a dust event in the eastern Mediterranean region (Mace *et al.*, 2003). In the East China Sea in spring, the concentration of coarse ON_{ws} increased during a dust event, which suggests that this increase is also related to mineral dust (Nakamura *et al.*, 2006). On the other hand, in the Yellow Sea and Qingdao, the concentrations of both IN_{ws} and ON_{ws} increased during a dust event; the rate of increase for IN_{ws} was the higher of the two, resulting in a decreased overall proportion of ON_{ws} (Shi *et al.*, 2010). In the coastal area of the Seto Inland Sea in this study, almost no coarse ON_{ws} was detected in Period B during the dust event. This is because the source of the ON_{ws} was not soil, and the concentration of IN_{ws} had increased, especially with the notable increase in coarse NO_3^- during Period B (Fig. 6), affecting the calculated value of ON_{ws} . A portion of the ON_{ws} could be lost during the long-distance transport between the observation station in this study and the significant pollutant sources, compared with that in the eastern Mediterranean region and the East China Sea.

The contribution of ON_{ws} to the total nitrogen in the aerosol samples classified as the normal condition was 14% in both the fine and coarse particles, as shown in Fig. 7. These fractions are comparable to the contribution of fine NO_3^- and coarse NH_4^+ . The ON_{ws} contribution to total nitrogen in the aerosol samples, classified as polluted air, was 9.3% for the fine and 5.0% for the coarse particles. These results indicated that ON_{ws} cannot be ignored as a nitrogen compound at this observation station.

Table 1 shows the comparison of the mean concentration of ON_{ws} (total) and its contribution to total nitrogen in this study and other regions. The mean concentration of ON_{ws} in the coastal region of the Seto Inland Sea was similar to that in an urban area, Kofu (Matsumoto *et al.*, 2014), lower than in the coastal area strongly affected by continental pollutants (Shi *et al.*, 2010), and higher than in the open ocean (Luo *et al.*, 2016). The contribution of ON_{ws} was high in the East China Sea and the South China Sea and was comparable to that in the other regions.

A correlation analysis between ON_{ws} and the origins of combustion (nss-SO_4^{2-} and NO_3^-), sea salt (Na^+), and soil (nss-Ca^{2+}) was conducted for each particle size to determine the sources of the ON_{ws} in the aerosols (Fig. 9). However, samples with IN_{ws} concentrations higher than TN_{ws} potentially contain measurement errors, so these were excluded from the graphed data. Significant correlations were seen with the fine particles, though not with the coarse particles. Because ON_{ws} is not a single component, it is assumed that the size

Fig. 7. Fractions of nitrogen compounds in (a) Normal and (b) Polluted conditions.

Fig. 8. Relationships between (a) NO_3^- and nss-Ca^{2+} , and (b) NO_3^- and $\text{nss-Ca}^{2+} + \text{Cl-loss}$ in the coarse particles ($> 2.5 \mu\text{m}$).

distribution and behavior differ depending on each component. However, based on the correlations between ON_{ws} with nss-SO_4^{2-} and NO_3^- , combustion could be considered as a source of ON_{ws} (Figs. 9(a) and 9(b)). Fine ON_{ws} could be generated by combustion, the reactions between gaseous organic compounds and NO_2 , and secondary photochemical processes such as the photooxidation of gaseous organic nitrogen (Matsumoto *et al.*, 2014). The increasing trend of the ON_{ws} concentrations with higher pollutant concentrations is consistent with that reported in previous studies (Scudlark *et al.*, 1998; Mace *et al.*, 2003; Nakamura *et al.*, 2006; Shi *et al.*, 2010; Matsumoto *et al.*, 2014; Luo *et al.*, 2016;

Matsumoto and Yamato, 2016). The ON_{ws} was not detected during Period F, which was thought to have been strongly affected by the local industries, and the concentration of nss-SO_4^{2-} was high. The relationship between the ON_{ws} and local atmospheric pollutants could not be identified because of the possibility of measurement errors due to high concentrations of IN_{ws} .

Interestingly, a significant correlation between nss-Ca^{2+} and ON_{ws} in fine particles was observed (Fig. 9(d)), probably owing to the formation of secondary particles that are formed when gaseous organic nitrogen and other acidic substances react with mineral particles. However, because

Table 1. Comparison of ON_{ws} in total (fine and coarse) aerosols in different regions.

Location	Date	ON _{ws} μg N m ⁻³	ON _{ws} /TN %	References
Seto Inland Sea (Normal)	Feb.–Mar. 2015	0.24	14	This study
Seto Inland Sea (Polluted)	Feb.–Mar. 2015	0.31	8.6	This study
Pacific Ocean and East China Sea (Autumn)	Sep.–Oct. 2002	0.76	24	Nakamura <i>et al.</i> , 2006*
Pacific Ocean and East China Sea (Spring)	Mar. 2004	0.22	10	Nakamura <i>et al.</i> , 2006*
Yellow Sea	Mar. 2005	2.9	17	Shi <i>et al.</i> , 2010*
Yellow Sea	Apr. 2006	1.2	17	Shi <i>et al.</i> , 2010*
Qingdao	Mar.–Apr. 2006	2.5	20	Shi <i>et al.</i> , 2010*
South China Sea	Apr. 2005	0.91	34	Shi <i>et al.</i> , 2010*
Urban site, Kofu	Aug. 2009–Jan. 2013	0.22	14	Matsumoto <i>et al.</i> , 2014*
North Western Pacific Ocean (dust)	Mar.–Apr. 2014	0.16	5	Luo <i>et al.</i> , 2016*
North Western Pacific Ocean (Background)	Mar.–Apr. 2014	0.15	14	Luo <i>et al.</i> , 2016*

* Calculated value from the origin data.

no correlation was seen with the coarse particles (Fig. 9(h)), the ON_{ws} was not considered to be originated soil itself. These results suggest that some components of organic nitrogen in anthropogenic substances are adsorbed onto or react with mineral particles and exist stably in relatively aged air masses. Further research is necessary, including research on the ON_{ws} relationship with coarse particles.

Dry Deposition Flux of Nitrogen Compounds by Aerosols

The dry deposition flux (F) of particulate nitrogen compounds was calculated using Eq. (2) to estimate the effect of nitrogen components on the biota of the sea surface.

$$F = V_d \cdot C_a \quad (2)$$

Here, V_d represents the deposition velocity (cm s⁻¹), and C_a represents the concentration of each nitrogen component in the atmosphere (μg N m⁻³). The dry deposition velocity is a critical factor in estimating the deposition flux, but the velocity differs substantially due to the particle size distribution.

In this study, because the atmospheric aerosols were collected in two stages based on their size, we used 0.1 cm s⁻¹ as the dry deposition velocity for fine particles and 2.0 cm s⁻¹ for coarse particles (Duce *et al.*, 1991; Nakamura *et al.*, 2005, Uematsu *et al.*, 2010), although the dry deposition velocity differed depending on weather conditions (such as wind speed, humidity, and air temperature). By calculating the deposition velocity based on the proportion of fine and coarse particles of each nitrogen component, we found the velocities for NO₃⁻, NH₄⁺, and ON_{ws} to be 0.90, 0.21, and 0.34 cm s⁻¹, respectively. Nakamura *et al.* (2005) and Kang *et al.* (2010) estimated the deposition fluxes using 1.7 cm s⁻¹ for NO₃⁻ and 0.22 cm s⁻¹ for NH₄⁺ as the deposition velocities in the East China Sea and the Sea of Japan. Chen *et al.* (2008) used 1.2 cm s⁻¹ for NO₃⁻ and 0.1 cm s⁻¹ for NH₄⁺ as the velocities in the coastal area of northeastern Taiwan. Zhang *et al.* (2008) used 1.15 cm s⁻¹ for NO₃⁻ and 0.6 cm s⁻¹ for NH₄⁺ as the velocities in the Yellow Sea and the East China Sea. Therefore, errors occur in the estimations of deposition flux due to the differences in the deposition velocities. In this study, the deposition velocity of NO₃⁻ was lower than that reported in previous studies because the

proportion of fine particles of NO₃⁻ was relatively large (on average, approximately 60%).

The atmospheric aerosol concentrations and dry deposition fluxes of each nitrogen compound in this study and other regions (coastal waters) previously reported are shown in Table 2. In the East China Sea, the estimation of the NO₃⁻ dry deposition flux was 720 μg N m⁻² day⁻¹ for 0.48 μg N m⁻³ of atmospheric concentration (Nakamura *et al.*, 2005). Although the NO₃⁻ atmospheric concentration was 0.85 μg N m⁻³ in this study, which is higher than that in the East China Sea, the dry deposition flux was 660 μg N m⁻² day⁻¹, which was equivalent to the East China Sea. These differences reported can be attributed to the high proportion of NO₃⁻ existing as fine particles, and the low deposition velocity in the coastal area of the Seto Inland Sea. The atmospheric concentration and dry deposition flux of NH₄⁺ in the East China Sea were 2.3 μg N m⁻³ and 450 μg N m⁻² day⁻¹, respectively (Nakamura *et al.*, 2005), while in the coastal region of the Seto Inland Sea, these concentrations were 1.6 μg N m⁻³ and 280 μg N m⁻² day⁻¹, respectively. This is because the size distributions are comparable, which means that the deposition flux is roughly proportional to the concentration in the atmosphere. The NO₃⁻ deposition flux from the atmosphere is the largest among the nitrogen compounds, accounting for 64% of the total, because the size distribution is mostly biased toward the coarse sizes.

In this study, the dry deposition of gaseous substances (HNO₃ and NH₃) and wet deposition (NO₃⁻ and NH₄⁺) were not measured; however, the deposition flux of inorganic nitrogen (dry and wet) was estimated with reference to the observation results from the Oki Islands, located in the Sea of Japan (Ban *et al.*, 2016). In the Oki Islands, of the total deposition flux of approximately 3,500 μg N m⁻² day⁻¹, dry deposition flux of aerosols and gaseous substances was approximately 990 and 710 μg N m⁻² day⁻¹, while the wet deposition flux was approximately 1,800 μg N m⁻² day⁻¹, respectively, indicating that the dry deposition flux from particulate matter accounts for approximately 28% of the total. The annual rainfall in the Oki Islands was 1,339 mm (Ban *et al.*, 2016), while for the same period at a location approximately 15 km from the observation station in this study, it was 1,108 mm, as calculated from rainfall data by

Fig. 9. Relationships between nss-SO_4^{2-} , NO_3^- , Na^+ , and nss-Ca^{2+} and ON_{ws} , in fine (a)–(d) and coarse (e)–(h) particles.

the Japan Meteorological Agency (<http://www.data.jma.go.jp/gmd/risk/obsdl/index.php>; accessed 02 Dec. 2016). The amount of rainfall at the observation point in this study was slightly less, but the wet deposition flux was similar at both locations; therefore, the total deposition flux would be expected to be approximately four times the dry deposition

flux. Therefore, it is also necessary to consider both gaseous substances and wet deposition to estimate the total deposition flux of nitrogen compounds.

The dry deposition flux of ON_{ws} was small, accounting for approximately 8.1% of nitrogen compounds, but the behavior of ON_{ws} was different from that of NH_4^+ and NO_3^-

Table 2. Comparison of average ambient concentrations of nitrogen compounds and deposition flux in different coastal regions.

Location	Seto Inland Sea			Pacific Ocean		East China Sea	
	NO ₃ ⁻	NH ₄ ⁺	ON _{ws}	NO ₃ ⁻	NH ₄ ⁺	NO ₃ ⁻	NH ₄ ⁺
Ambient concentration (μg N m ⁻³)	0.85	1.6	0.28	0.17	0.30	0.48	2.3
Deposition flux (μg N m ⁻² day ⁻¹)	660	280	83	250	66	720	450
Deposition flux Ratio (%)	65	27	8.1	79	21	62	38
Reference	This study			Nakamura et al., 2006			

in some samples; in addition, the atmospheric concentrations of ON_{ws} may account for up to 40% of TN_{ws}. Therefore, ON_{ws} should be considered in evaluating the effects of nitrogen compounds on marine ecosystems.

CONCLUSIONS

The chemical compositions of atmospheric aerosols were measured in the coastal area of Seto Inland Sea between February 15 and March 20, 2015. In this study, we focused on the nitrogen compounds by the chemical forms (organic and inorganic) in aerosols that are utilized as nutrients in the ecosystems.

During all observation periods, the mean concentrations of NH₄⁺, NO₃⁻ and ON_{ws} in the total (fine and coarse) particles were 1.6, 0.85, 0.28 μg N m⁻³, respectively. The contribution of ON_{ws} to the total nitrogen was approximately 10%, however, these fractions are comparable to the contribution of fine NO₃⁻ and coarse NH₄⁺.

A correlation analysis between ON_{ws} and nss-SO₄²⁻, NO₃⁻, Na⁺ and soil nss-Ca²⁺ was conducted for each particle size to determine the sources of ON_{ws} in the aerosols. Significant correlations were seen with the fine particles, though not with the coarse particles. Based on the correlations between ON_{ws} with nss-SO₄²⁻ and NO₃⁻, combustion could be considered as a source of ON_{ws}. But it could not be identified whether ON_{ws} was from long distance transport or locally derived.

The dry deposition flux of particulate nitrogen compounds was estimated. The NO₃⁻ deposition flux from the atmosphere is the largest among the nitrogen compounds, accounting for 64% of the total, because the size distribution is mostly biased toward the coarse sizes. The dry deposition flux of ON_{ws} was small, accounting for approximately 8.1% of nitrogen compounds, but the behavior of ON_{ws} was different from that of NH₄⁺ and NO₃⁻ in some samples; in addition, the atmospheric concentrations of ON_{ws} may account for up to 40% of TN_{ws}. Therefore, ON_{ws} should be considered in evaluating the effects of nitrogen compounds on marine ecosystems.

Further research is necessary, including observations of other seasons and the measurements of ON_{ws} in wet deposits and gaseous matter to understand the sources and formation of ON_{ws}, and the nitrogen cycle in this study area.

ACKNOWLEDGMENTS

This research was supported by the Cooperative Program (No. 148, 2016; No. 146, 2015) of Atmosphere and Ocean

Research Institute, The University of Tokyo.

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Received for review, January 2, 2020

Revised, January 2, 2020

Accepted, March 5, 2020