Point by point reply

Anthropogenic activity is increasing nitrogen inputs to the oceans particularly downwind of fast growing economies such as in Asia and there is evidence that the deposition of this nitrogen to marine waters may be sufficient to cause a deleterious effect. This paper includes as noted later one very impressive illustration of this. This paper adds further information on deposition in this region and is therefore valuable although I would suggest it needs a few modifications before final publication.

Thanks for reviewer’s appreciation of the merit of our story.

Question 1: One important general point that I think may need to be included in this paper is a discussion of the relationship between fog, aerosol and precipitation. There have now been several papers, at least some of which are referenced here, that illustrate that fogs are relatively regular occurrences in this region and may be important vectors of nitrogen deposition. This paper contributes further to this information. It is clear that fogs can contain high concentrations of many components and I think that has been known for many years from other settings such as the acid rain debate. However, although fogs can be sampled by aerosol collectors, or indeed by specialist fog samplers, I am not really sure if it is appropriate to compare aerosols collected under normal conditions and under fogs, since fog seem to me to be somewhere between rain and aerosol.

Answer: Thanks for this comment. We will add more descriptions into Introduction in Page 25586 Line 5 as below.

“Fog is the intermediate stage between precipitation and aerosol. Fog forms by the activation of particulate with subsequent growth and incorporation of other gases and particles (Cape et al., 2011). Fog droplet is smaller in size when compares to rain drops, however, concentrations of water-soluble species in fog water were not necessarily to be higher or lower than that of precipitation (Sasakawa et al., 2002;

Watanabe et al., 2006; Jung et al., 2013). Fogs can be sampled by specialist fog samplers; however, during aerosol sampling on the sea there is no way to avoid fog once sea fog forms. Fog chemistry was well studied previously on land and its impacts on terrestrial ecosystems were also highlighted (Chang et al., 2002; Lange et al., 2003). Moreover, researchers designed experiments to examine the aerosol chemistry for pre- and post- fog formation periods to explore the inland fog impact on aerosol chemistry (Biswas et al., 2008; Safai et al., 2009). Nevertheless, sea fog impact on aerosol, particularly, in the coastal and marginal seas of China has not yet been studied. ”

Question 2: Gas exchange processes between water (fog) droplets and aerosol particles may be different and hence if the observed differences in composition between fogs and other aerosols (e.g. 3.2, 3.3 Table 2) represent differences in sources, cycling or simply that they are different types of atmospheric particles. It is also not really clear to me how to convert concentrations to fluxes since conventional deposition velocities are not appropriate. This comment does not invalidate any of the information here, but just to caution that any comparison needs to be done carefully.

Answer: Reviewer is right. The chemistry of these aerosols we collected have altered by sea fog due to different addition, removal and cycling processes including gas exchange. Even aerosols with the same property may have changed into entirely different chemistry if aerosols have experienced different flow path with various temperature and humidity (formation history, as mentioned in Introduction), not mentioning after sea fog modification. We did not collect fog; yet, our aerosol collection was under influenced by fog (contamination). The aerosol was sampled by TSP, thus, the concentration unit is ng m^{-3}. We clearly knew that aerosol may act as a precursor for fog formation, but this does not necessarily mean all the aerosols we sampled were directly associated with fog. This is also why we can only defined our sample as “sea-fog modified aerosol”. As reviewer mentioned, the deposition rate of fog may differ from that of aerosol, yet, no technology so far to separate aerosol and fog droplet during aerosol sampling. Nevertheless, we observed distinctive chemistry for this type of aerosol either comparing with aerosols sampled during the same cruise or comparing with "non-foggy" aerosols collected in the ECS in previous study. Meanwhile, we believed the deposition of nitrogen species will be also changed by sea fog formation. As replied below, we will add more descriptions about the uncertainty of deposition velocity in our estimation, particularly, sea-fog modified aerosol deposition.

Question 3: Page 25587 Line 8 Sampling only when "cruising", presumably meaning the ship is moving forward, does not of itself guarantee clean sampling – it is about wind direction in relation to that ship's moment.

Answer: Agree. It is difficult indeed to avoid contamination from the vessel itself.

Based on simultaneous one-second particle number concentration measurements made by Optical Particle Sizer (Tsi, US), we found ship plumes affect the TSP sampling occasionally during the cruising (data will be presented in a separate paper). We calculated the short-period plume contribution to the measured volume particle concentration of PM_{10} during each TSP sampling (self-contamination) and the contribution was less than 3%. According to this comment, we added above descriptions into sampling descriptions to let readers know the degree of self-contamination.

Question 4: Page 25589 Line 9 it is probably worth adding a reference for sea water composition.

Answer: Chester, (1990) has been added.

Question 5: RA calculation – this is really deriving the acidity from an ion balance calculation, which is OK but does ignore other ions such as bicarbonate which may be there at higher pH. It’s also not quite clear why a ratio rather than a cations-anions approach is preferable so I would suggest this approach needs bit of explanation and justification.

Answer: Thanks for this suggestion. Both approaches had been applied previously basing on the same concept of “imbalance of cations and anions”. The imbalance was basically caused by non-detected ions such as H^+ and HCO_3^- and CO_3^{2-}. Thus, both approaches are correct in terms of revealing the imbalance. However, when the amount of measured total ions distribute over a wide range (by a factor of 20 in our case), the ratio measure (the slope of the scatter plot of total anions vs. cations in neq m^{-3}) will be more effective to present the “relative” acidity. By contrast, the absolute value of imbalance (total cations – total anions) represents absolute acidity, which is applicable for a dataset with narrower range of ion concentration. In revision, we added one more reference (Kerminen et al., 2001) as well as explanations for the rationale of using RA.

Question 6: Page 25589 Line 20 I assume the WSON error estimate is an average because it must be vary from sample to sample.

Answer: Thanks for this suggestion. The sentence is now “The standard errors propagated through WSON calculation vary from sample to sample (17% to 1500%). The average standard error is 116% when all samples are considered and is 81% when the extreme value is excluded.”

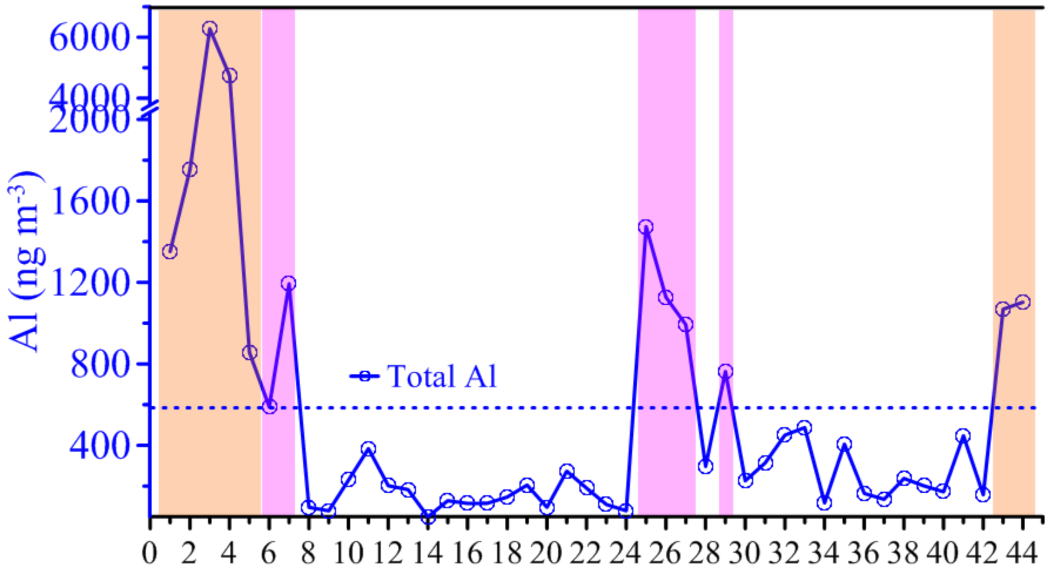
Question 7: Section 2.3 It is important in any calculation of this type to emphasize the uncertainty in deposition velocities, particularly where wind speed and size distribution are not well known as here – a recent paper by Baker et al 2013 (DOI: 10.1002/gbc.20062) illustrates some of the difficulties in this.

Answer: This suggestion is well taken. In the version, we added discussions about uncertainties regarding wind speed changes and unknown grain size distribution.

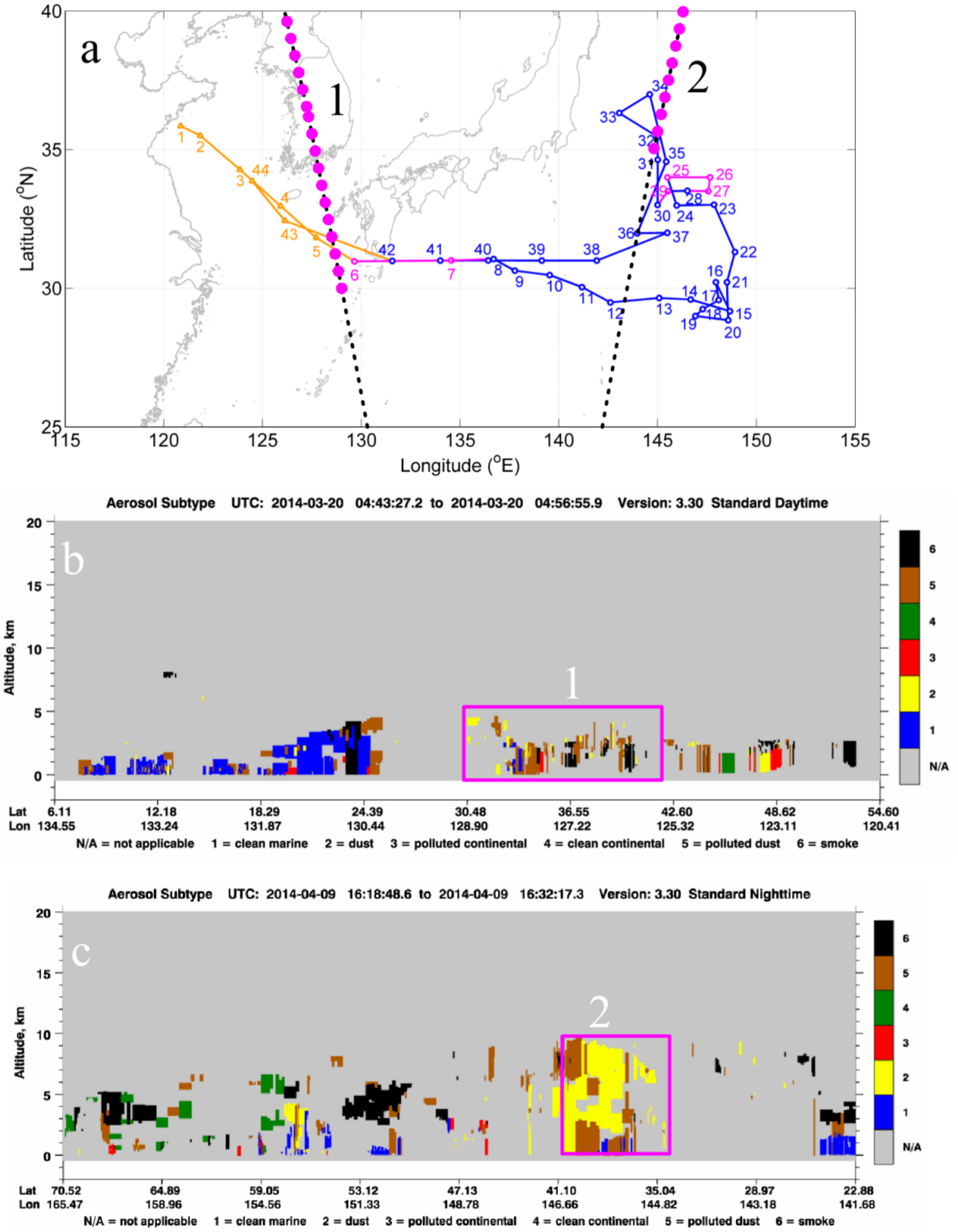
Baker et al. (2013) had been added in to Reference also.

Question 8: Page 25592 Line 11 dust is highly variable as these authors know well, so 5 samples is a small basis for producing average values. The authors seem to be using 1000 ng/m3 as a threshold for dusty samples (see also the end of section 3.1) but I don't think this is stated

Answer: In fact, we did not use a threshold value to define dust aerosol. The dashed line in Fig. 3 was just a reference line for background aerosol, which has concentrations significantly lower than other two types (See panel A with linear y-axis below). Actually, we provided CALIPSO Lidar Browse Images in Supplementary Information in the old version; yet, we missed to mention this criterion in the main text clearly. This is our mistake. In this version, we make a clear CALIPSO images including satellite orbit trajectories into Figure S1 (see panel B below). The consistency between Al-defined dust aerosol and occurrence of dust and polluted dust defined by NASA will be presented in the newer version.



Panel A. Total Al concentration in collected TSP.



Panel B. The spatial coverage of CALIPSO images for dust and polluted dust (brown and yellow) during our cruise period.

Question 9: Page 25592 Line 15-20 the discussion of Al solubility here is difficult to follow partly because Fig3 does not contain an explicit Al solubility and also because of the earlier noted differently of really understanding their RA term.

Answer: Reviewer is correct. We should not mention solubility here in Section 3.1 (Aerosol type classification) and ask readers to "see below".

In this version, we added solubility estimate into Table 2 to help readers to follow our illustrations and discuss this issue latter in Section 3.3.1. rather than in Section 3.1.

Question 10: Page 25594 Line 1-14 There are clearly several sources of Ca and K including seawater and dust but I suspect that beyond stating this, the authors could shorten this section and remove some vague speculation.

Answer: As suggested, we deleted the speculative part associated with fertilized soil and the spatial heterogeneity of seawater major ions.

Question 11: Page 25594 Line 15-20 The tabulated data is in nM/m3 and yet figure 5 is in nequiv/m3 with no explanation. I would do everything in one unit and this affects the statements on ammonium/sulphate ion balances.

Answer: We now apply nM m^{-3} throughout entire paper except the part about ion stoichiometry, which is related to charge balance.

Question 12: It is probably worth noting the importance of ammonia emissions in Asia which supply this neutralising ammonia.

Answer: As suggested, we added one sentence for the importance of ammonia emissions in Asia.

Question 13: Page 25596 Line 15-20 rates of NOx oxidation may also be important

Answer: We added one reference and two sentences as below to discussion the lifetime and oxidation of NOx.

"The lifetime of NOx in boundary layer is generally less than 2 days (Liang et al., 1998). Basing on our back trajectory analysis, the travel time of air mass from China inland to the marginal seas is long enough for oxidation of NOx into HNO_3."

Question 14: Page 25596 Line 23 to Page 25597 Line 2 include references to explain the sources of the Jeju data and as noted before I am not really sure that it is simple to compare fog and aerosol in this way. They are obviously different but there are several possible explanations of why.

Answer: As indicated in Introduction, no data for aerosol collected on the sea or island during foggy day was reported so far. To compare with aerosols collected in non-foggy days is the only way and also meaningful. In fact, we proposed several possibilities for nitrogenous compound enrichment in the paragraph before the comparison (specifically on NH_4^+ and NO_3^-) among datasets. In this new version, we added more discussions about the possible causes and switched the two paragraphs to make the reading smooth.

Question 15: Page 25597 Line 9-11. Without some knowledge of particle size I don't think you can say whether sulphuric or nitric acid is neutralized by ammonium, you simply have the ratio of ammonium to nitrate+2xsulphate on a molar basis.

Answer: Agree with reviewer. We delete the specific sentence and the deletion does not influence the paragraph integrity.

Question 16: Page 25597 Line 20-30 Concentrations differences for WSON between aerosols and fog do not tell you about scavenging I think and the different WSON% of TN suggests different source regions to me.

Answer: According to this comments, we adjust the sentence to "Such high WSON concentration but low WSON% in TDN in sea fog modified aerosol may indicate the lower scavenging efficiency of WSON relative to other nitrogen species or its source region is different or both."

Question 17: Section 3.3.3 As the authors show these aerosols are not at all "background" but quite contaminated so I would suggest changing the naming.

Answer: We added a few lines in Section 3.1, Aerosol type classification, to define the term "background".

"Here in this paper, background aerosol stands for non-dusty and non-foggy aerosol in our classification. It is more like a baseline aerosol collected within the study area during the investigating period. Note that "background" may vary over space and time and it does not necessarily to be pristine."

Question 18: The discussion of WSON sources in section 3.3.3 seems to assume there is one single source and to confuse the reader by arguing for no marine source (line 9) and a marine source (line 26). There are multiple sources of WSON (see for example Cape et al., 2011 review in atmospheric research).

Answer: We did not make a clear point. What we want to state is that we do not have "direct evidence (i.e., biological productivity data)" to support the natural WSON sourced from marine. Nevertheless, we have "indirect evidence", that is, the wind-driven sea spray. In the revision, we will clarify this part and add Cape et al., 2011 into References.

Question 19: The discussion on Page 25600 Line 0-8 about sources of nitrate and ammonium from seawater I think is a bit confusing – it is very hard to see seawater as a significant source of nitrate and ammonium to aerosols, and I do not really understand the reasons for arguing for a source of ammonium and nitrate from photolysed marine DON.

Answer: We rewrote these two paragraphs to avoid confusing. In fact, we indicated that the seawater is impossible to be a source of aerosol nitrate and ammonium due to their low concentrations (a few tens to hundreds nM) in surface ocean. By contrast, DON concentration in the surface ocean is 1 to 2 orders of magnitude higher than ammonium and nitrate, thus, the surface ocean can act as a potential source of WSON. That is also why we emphasized the resemblance among these positive correlations of aerosol WSON, sea salt ions (Na^+, Cl^- and Mg^{2+}) against wind speed. On the contrary, over a wide range of wind speed we observed relatively narrow concentration ranges of aerosol ammonium and nitrate. Since high wind speed implies vigorous exchange on the air-sea interface, during which both sea salt emission and scavenging were supposed to be high. Under efficient scavenging condition, to maintain a relatively uniform nitrate/ammonium concentration (quasi-static) some supply processes are need for compensation. Since the surface ocean is not a possible source for both ammonium and nitrate, therefore, we suggested that the alternative supplies might include deposition from the upper atmosphere and photochemical production. Nevertheless, we will reorganize these two paragraphs to clarify our arguments.

Question 20: Section 3.4 Others have done this kind of comparison of WSON and TN (e.g Jickells et al. DOI: 10.1098/rstb.2013.0115) and argue that it suggests most of the WSON is anthropogenic, do these authors have a different interpretation?

Answer: Follow the Figure 1 (rainwater only) in Jickells et al. (2013), we compiled global data including aerosol and rainwater and made comparisons in terms of WSON/TDN in Section 3.4. Jickells et al. stated that since nitrate and ammonium are mainly anthropogenic, the significantly positive correlation between WSON and TDN may imply WSON’s anthropogenic origin. We agree with their interpretation for this positive trend. However, in old version Section 3.4, we did not mention the source of WSON. According to this question, we added sentences into this part of discussion to emphasize the anthropogenic source of WSON. We believe that anthropogenic WSON dominates in urban area and coastal/marginal seas where aerosol ammonium and nitrate concentrations are high; on the other hand, marine sourced WSON cannot be ignored in the open ocean where polluted components are relatively low such as our case of “background” aerosol in Section 3.3.3.

Question 21: Note that the rain and aerosol data bases are different so the different %WSON may be sampling biases.

Answer: Thanks for reminding us. We added one sentence to remind readers that the sampling bias can be inherited in such comparison.

Question 22: The list of references at the top of p25601 could probably go to the figure caption.

Answer: We re-checked the list and make sure all references go to the specific figure caption now.

Question 23: P25602 the estimation that nitrogen deposition from the atmosphere exceeds river and offshore inputs is a startling illustration of the importance of these inputs in this region and might be highlighted. The comparison of impacts on productivity might best be made with “new” not total primary production rates.

Answer: Reviewer is right, it is better to compare with new production. However, no data about new production in the East China has been reported so far. Since primary production composed of upwelling-, atmospheric deposition-, riverine-induced plus recycled production. Such comparison is still meaningful.

Question 24: Section 4 seems to be a summary not a conclusion.

Answer: We rewrote the Conclusion and the important of sea fog associated N deposition was highlighted

"We presented total dissolved nitrogen species including organic nitrogen in TSP sampled over the ECSs and NWPO during spring and the ECSs samples were collected in sea fog weather. Three types of aerosol, sea fog modified, dust and background aerosols, were classified. We found that sea fog formation significantly altered the aerosol chemistry resulting in the highest concentrations of all nitrogen species among three types of aerosol, accompanying with higher acidity and higher cation deficiency. On daily basis, the nitrogen supply from sea fog associated atmospheric deposition into the ECSs is around 6 times the nitrogen supply from the Yangtze River in spring (total amount of 3.1 Gg DIN d^{-1}) and 2 times the supply from subsurface intrusion of Kuroshio (7.9 Gg NO_3^-- N d^{-1}). Sea fog associated deposition and chemical processes require more attention and need to be considered in future aerosol monitoring especially in the marginal sea during the seasonal transition.

In the open sea, the spring background aerosol ammonium and nitrate were 10 times higher than previous report for summer season indicating an anthropogenic influence and the importance of the seasonality of air mass source. The ammonium and nitrate varied in narrow ranges showing no correlation with wind speed, which may represent the degree of sea salt emission and scavenging. It is likely that nitrate and ammonium in the atmosphere above sea surface had reached a budget balance. Since the supply of nitrate and ammonium from surface ocean (bottom) is not possible, their source might come from upper boundary layer (top) or photochemical production. On the contrary, WSON revealed a similar pattern to sea salt ions (Na^{+}, Mg^{2+} and Cl^{-}), of which concentrations increased as the wind speed increased. Such a similarity indicated that at least a portion of WSON should come from the surface ocean where DON emits with sea salt.

The dust aerosols were significantly enriched in nitrate and ammonium, but not in WSON. Unless WSON-depletion processes had occurred, such disproportionate enrichment suggested that dust aerosols from high latitude and altitude may have less chance to contact WSON during the long range transport.

Except background aerosols, the WSON to TDN ratios of sea fog modified and dust aerosols collected in the ECSs and NWPO fell within the pattern of global aerosols. Since nitrate and ammonium are mainly anthropogenic, the significantly positive correlation between WSON and TDN may imply WSON's anthropogenic origin. When TDN concentrations are low (<100 nmol m^{-3}), the proportions of WSON in TDN are more diffusive indicating factors other than anthropogenic involved. The mean ratio of WSON to TDN in aerosols was only 1/2 of that for precipitation over the world. Such lower proportion of WSON in aerosol TDN suggested that aerosol is less capable of scavenging hydrophilic organic nitrogen when comparing with precipitation. Nevertheless, WSON occupies a significant portion in TDN for both aerosol and precipitation, thus, cannot be overlooked in the atmospheric nitrogen cycle.

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Lists of all the relevant changes

The manuscript had been polished by a native speaker. We did not reveal every single change since correction and changes are minor although numerous. The relevant changes are listed below.

Question 1: we added more descriptions into Introduction (P. 3 Line 21 to P. 4 Line 4) in the new manuscript.

Question 2: More descriptions about the difficulties in estimating deposition fluxes were added into Section 2.3 (P. 8 Lines 8-22).
We also explicitly addressed the possible influence of the sea fog on a fixed deposition velocity for our sampled aerosol (P. 9 Lines 9-13).

Question 3: Based on data of one-second particle number concentration measurements, we added several lines to illustrate the maximum influence of self-contamination from the research vessel (P. 5, Lines 1-7).

Question 4: A requested reference has been added (P. 7, Line 9).

Question 5: More illustrations about the RA have been inserted into Section 2.2 (P. 7, Lines 14-19).

Question 6: The new estimate and descriptions about the standard error were added (P. 7, Lines 24-27).

Question 7: As replied above.

Question 8: A clear CALIPSO images including satellite orbit trajectories had been introduced into Figure S1, and one sentence was presented in Page 11, Lines 6-8.

Question 9: We added Al solubility estimate into Table 2, and mention the term in Section 3.3.1.

Question 10: The vague speculation has been deleted.

Question 12: We added one sentence (P. 13, Lines 5-7) to reveal the importance of ammonia emissions in Asia.

Question 13: We added one reference and two sentences to discussion the lifetime and oxidation of NOx (P. 15, Lines 11-15).

Question 14: We added more statements regarding this issue in various pages (P. 14, Lines 8-9; P. 16, Lines 16-22) and also switched two paragraphs (the bottom paragraph in P. 14 and the first paragraph in P. 15) to make the reading flow more smooth.

Question 15: We delete the specific sentence and the deletion does not influence the paragraph integrity.

Question 16: The sentence was rewritten (P. 16, Lines 12-15).

Question 17: We added more descriptions in Section 3.1 (P. 11, Lines 8-13) to clarify the term “background”.

Question 18: We clarify this point by adding “direct” and “indirect” evidences into proper places (P. 17 Line 28 to P. 18 Lines 1-2 and P. 18 Line 6).

Question 19: We rewrote this paragraph to avoid confusing (P. 18 Line 23 to P. 19 Line 5) and the most recently published paper, Paulot et al. (2015), to support our idea (P. 19, Lines 13-17).

Question 20: We added one sentence to reveal the anthropogenic source of WSON (P. 20, Lines 2-4).

Question 21: We added one sentence in P. 20, Line 16 to remind readers that the sampling bias can be inherited in such comparison.

Question 22: We re-checked the list and make sure all references go to the specific figure caption now.

Question 24: We rewrote the Conclusion. The comparison between sea fog associated N deposition and the Yangtze River N loading was highlighted (P. 22 Line 14 to P. 23 Line 27).

Nitrogen speciation in various types of aerosols in spring over the northwestern Pacific Ocean

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Abstract

The cumulative atmospheric nitrogen deposition has been found to profoundly impact the nutrient stoichiometry of the East China seas (ECSs) and the northwestern Pacific Ocean (NWPO). In spite of the potential significance of dry deposition in those regions, ship-board observations of atmospheric aerosols remain insufficient, particularly regarding the compositions of water-soluble nitrogen species (nitrate, ammonium and water-soluble organic nitrogen – WSON). We conducted a cruise covering the ECSs and the NWPO during the spring of 2014 and observed three types of atmospheric aerosols. Aluminum content, air mass backward trajectories, weather conditions, and ion stoichiometry allowed us to discern dust aerosol patches and sea fog modified aerosols (widespread over the ECSs) from background aerosols (open ocean). Among the three types, sea fog modified aerosols contained the highest concentrations of nitrate (536 ± 300 nmol N m^{-3}), ammonium (442 ± 194 nmol N m^{-3}) and WSON (147 ± 171 nmol N m^{-3}); furthermore, ammonium and nitrate together occupied ~ 65% of the molar fraction of total ions. The dust aerosols also contained significant amounts of nitrate (100 ± 23 nmol N m^{-3}) and ammonium (138 ± 24 nmol N m^{-3}) which were obviously larger than those in the background aerosols (26 ± 32 for nitrate and 54 ± 45 nmol N m^{-3} for ammonium), yet, this was not the case for WSON. It appeared that dust aerosols had less of a chance to contact WSON during their transport. In the open ocean, we found that sea salt (e.g. Na^{+}, Cl^{-}, Mg^{2+}), as well as WSON, correlated positively with wind speed. Apparently, marine dissolved organic nitrogen (DON) was emitted during breaking waves. Regardless of the variable wind speeds from 0.8 to as high as 18 m s^{-1}, nitrate and ammonium, by contrast, remained in narrow ranges implying that some supply and consumption processes of nitrate and ammonium were required to maintain such a quasi-static condition. Mean dry deposition of total dissolved nitrogen (TDN) for sea fog modified aerosols (1090 ± 671 μmol N m^{-2} d^{-1}) was 5 times higher than that for dust aerosols (190 ± 41.6 μmol N m^{-2} d^{-1}) and around 20 times higher than that for background aerosols (56.8 ± 59.1 μmol N m^{-2} d^{-1}). Apparently, spring sea fog on the ECSs played an important role in removing atmospheric reactive nitrogen from the Chinese mainland and depositing it into the ECSs, thus effectively preventing its seaward export to the NWPO.

1 Introduction

Anthropogenic reactive nitrogen (N_r) emissions have dramatically increased in the last few decades owing to rapidly growing populations and industry (Galloway et al., 2008). China is one of the largest producers and emitters of Nr in the world (N_r emission of 12.18 Tg y^{-1}; Reis et al., 2009). Inevitably, large amounts of Nr emanate into the adjacent seas through various pathways. Through the atmosphere, annual nitrogen depositions into the east China seas (ECSs; the Yellow Sea and East China Sea) had been reported to be the same order of magnitude carried by the Yangtze River discharge (Nakamura et al., 2005; Zhang et al., 2007). Besides observational data, global models revealed that both of the Chinese marginal seas and the northwestern Pacific Ocean (NWPO) are under the atmospheric influence of the Asian continent, which supplied significant amounts of anthropogenic Nr (Duce et al., 2008) and terrigenous materials (Jickells et al., 2005). The cumulative effect of atmospheric input in the past decades even altered the nutrient stoichiometry on a regional scale, including the Chinese marginal seas and the North Pacific Ocean (T. W. Kim et al., 2011; I. N. Kim et al., 2014).

To better constrain atmospheric deposition of Nr into the ocean over large spatial and temporal scales, modeling the transport and deposition of air pollutants is essential. Models of atmospheric nitrogen deposition include abundant parameters, such as local emission densities, particle size, deposition velocity, chemical processes and meteorological conditions (Liu et al., 2005; Guenther et al., 2006; Kanakidou et al., 2012). However, model accuracy strongly relies on the validation by observational data. Unfortunately, ship-board observations, particularly for an offshore gradient from marginal seas to the open sea, are still limited.

In the marginal seas of China, dust and fog storms are two common intermittent weather events during the transition period from a cold to a warm season (Sun et al., 2001; Zhang et al., 2009). Dust aerosols may serve as a carrier bringing significant amounts of terrigenous and anthropogenic fingerprints including trace elements (Duce et al., 1980) and Nr (Chen and Chen, 2008) from inland into the open sea via long-range transport. By contrast, sea fog is relatively stagnant and restricted on a spatial scale. *Fog is the intermediate stage between precipitation and aerosol. Fog forms by the activation of particulate with subsequent growth and incorporation of other gases and particles (Cape et al., 2011). Fog droplets are smaller in size when compared to rain drops; however, concentrations of water-soluble species in fog water were not necessarily higher or lower than those of precipitation because of complicated chemical processes (Sasakawa et al., 2002; Watanabe et al., 2006; Jung et al., 2013). Inland fog chemistry was well studied and its impacts on terrestrial ecosystems were highlighted (Chang et al., 2002; Lange et al., 2003). Researchers even designed experiments to investigate the differences in aerosol chemistry for pre-*

and post- fog formation periods to explore the inland fog impact on aerosol chemistry (Biswas et al., 2008; Safai et al., 2009). Fog, in fact, can be sampled only by specialist fog samplers; however, during aerosol sampling at sea there is no way to avoid fog once sea fog forms. Nevertheless, the effect of sea fog on aerosol chemistry has not yet been well studied, not mentioning in the coastal and marginal seas of China where air pollution is serious. Therefore, compared with inland fog and dust aerosols, we have less knowledge about sea fog chemistry and the aerosol chemistry under sea fog influence. This is the first investigation of Nr speciation and deposition of sea fog modified aerosols (aerosol collected under sea fog influence) on the marginal seas off a continent producing strong emissions.

Different types of aerosols may be composed of different amounts of nitrogen species based on their formation history (e.g. origin, flow path, reactions during transport). In this study, we sampled total suspended particulate (TSP) marine aerosols on a cruise crossing over the ECSs and NWPO during spring 2014. Water-soluble nitrogen species and ion characteristics among different aerosol types, including dust, background and sea fog modified aerosols, were investigated. These observational data promoted our understanding of the type-specific concentration and deposition of various nitrogen species and the role of sea fog on nitrogen scavenging. The data may aid in validating model outputs for the Asian region and potentially evaluate the framework of nitrogen and aerosol interactions in current models.

2 Materials and Methods

2.1 Aerosol sample collection and chemical analyses

A total of 44 TSP samples were collected using a high-volume TSP aerosol sampler (TE–5170D; Tisch Environmental Inc.) during a research cruise on the R/V *Dongfanghong* II from 17 March to 22 April 2014. The cruise tracks (Fig. 1) covered the ECSs and the NWPO. The samples were taken at ~ 12 h intervals. To avoid self-contamination from the research vessel, we sampled only when the vessel was cruising; thus, the sampling interval was not exactly 12 h. *Based on simultaneous one-second particle number concentration measurements made using an Optical Particle Sizer (Tsi, US), we found that ship plumes affected the TSP sampling occasionally during cruising (these data will be presented in a separate paper). We calculated the plume contribution to the measured volume particle concentration of* PM_{10} *during each TSP sampling (self-contamination) and the short-period contribution was less than 3%.* Detailed sampling information including date, time period and locations for each sample are listed in Table S1. Meteorological data (Fig. 2) including wind speed and direction, relative humidity (RH) and temperature were recorded on-board.

The cruise encountered sea fog in the first few days (orange shadow in Fig. 2 for 17–19 March) and five samples (nos. 1–5) were collected. Surprisingly, sea fog occurred again on 21–22 April while approaching land (samples nos. 43 and 44). During the fog events, high RH and slow wind speed were recorded (see orange shadow in Fig. 2). The strong temperature gradient indicated that the sea fog formed owing to a cold air mass from land confronting warm air from the sea. Since these samples were collected on fog days (see orange tracks in Fig. 1) when we could collect aerosols, the sea fog modified the aerosols as well as sea fog droplets. Since we could not separate them from each other through our method, we classified these samples as “sea fog modified aerosol”.

Whatman 41 cellulose filters (Whatman Limited, Maidstone, UK) were used for filtration. The analytical procedures were described by Hsu et al. (2010b and 2014). Briefly, one-eighth of the filter was extracted using 15 mL of Milli-Q water on a reciprocating shaker for 0.5 h and at rest for an additional 0.5 h at room temperature. Then, the extract was filtered through a polycarbonate membrane filter (0.4 μm pore size and 47 mm in diameter from Nuclepore). The filter was leached three times with Milli-Q water, and then 5 mL Milli-Q water was used to rinse the filter. The extract 45 mL solution was mixed with the rinsing 5 mL, poured into a 50 mL clean plastic centrifuge tube and used for the determination of the ion species and water-soluble aluminum (Al).

The water soluble and total concentrations of Al in the TSPs were analyzed using an inductively coupled plasma mass spectrometers (ICP-MS). For total Al, briefly, one-eighth of the filter was digested with an acid mixture (4 mL HNO_3 + 2 mL HF) using an ultra-high throughput microwave digestion system (MARSXpress, CEM; Corporation, Matthews, NC), and the efficiency of the digestion scheme was checked by subjecting a certain amount of a standard reference material (SRM1648, urban particulate matter, National Institute of Standards and Technology, USA) to the same treatment. The recoveries of Al in the SRM 1648 through digestion with the HNO_3-HF mixture fell within ±10% (n = 5) of the certified values. Details regarding the ICP-MS analysis were described by Hsu et al. (2008).

The major ionic species ($\mathrm{Na^+}$, $\mathrm{NH_4^+}$, $\mathrm{K^+}$, $\mathrm{Mg^{2+}}$, $\mathrm{Ca^{2+}}$, $\mathrm{Cl^-}$, $\mathrm{NO_3^-}$, $\mathrm{NO_2^-}$ and $\mathrm{SO_4^{2-}}$) in the extract were analyzed using ion chromatography (model ICS-1100 for anions and model ICS-900 for cations) equipped with a conductivity detector (ASRS-ULTRA) and suppressor (ASRS-300 for the ICS-1100 and CSRS-300 for the ICS-900). Separator columns (AS11-HC for anions, and CS12A for cations) and guard columns (AG11-HC for anions and CG12A for cations) were used in the analyses. The precision for all ionic species was better than 5%. Details of the analytical processes can be found in Hsu et al. (2014). Only five samples contained $\mathrm{NO_2^-}$ (1.39 nmol m^{-3} for no. 2, 2.32 nmol m^{-3} for no. 4, 3.69 nmol m^{-3} for no. 5, 5.96 nmol m^{-3} for no. 43 and 3.76 nmol m^{-3} for no. 44), which accounted for < 1% of the total dissolved nitrogen (TDN).

The TDN was analyzed using the wet oxidation method to convert all nitrogen species into nitrate with re-crystallized potassium persulfate, and then the concentration of nitrate was measured using chemiluminescence (Knapp et al., 2005). Monitoring with laboratory stock ($\mathrm{NO_3^-}$ + $\mathrm{NH_4^+}$ + Glycine + EDTA) showed that the recoveries of TDN by the persulfate oxidizing reagent (POR) digestion fell within 95–105% (n = 6) over the range of detection.

2.2 Data analysis

The amount of non-sea-salt Ca^{2+} (nss-Ca^{2+}) and non-sea-salt SO_4^{2-} (nss-SO_4^{2-}) in the aerosol, and the $Ca^{2+}$and SO_4^{2-} fractions in excess over that expected from sea salt, were calculated using the unit of equivalent concentration (neq m^{-3}) in the following equations

$$[\text{nss-}Ca^{2+}] = [Ca^{2+}] – [\text{ss-}Ca^{2+}], \text{ where } [\text{ss-}Ca^{2+}] = 0.044 \times [Na^{+}], \quad (1)$$

$$[\text{nss-}SO_4^{2-}] = [SO_4^{2-}] – [\text{ss-}SO_4^{2-}], \text{ where } [\text{ss-}SO_4^{2-}] = 0.121 \times [Na^{+}], \quad (2)$$

where the factors 0.044 and 0.121 used above are the typical calcium-to-sodium and sulfate-to-sodium equivalent molar ratios in seawater *(Chester, 1990)*.

Relative acidity (RA) was calculated using all the observed ion species in their equivalent concentrations following Yao and Zhang (2012):

$$RA = ([Na^{+}] + [Mg^{2+}] + [K^{+}] + [Ca^{2+}] + [NH_4^{+}]) / ([Cl^{-}] + [NO_3^{-}] + [SO_4^{2-}]), \quad (3)$$

where $[Na^{+}]$, $[Mg^{2+}]$, $[K^{+}]$, $[Ca^{2+}]$, $[NH_4^{+}]$, $[Cl^{-}]$, $[NO_3^{-}]$ and $[SO_4^{2-}]$ are the equivalent concentrations of those water extracted ions. *The relative acidity is based on the imbalance of cations and anions, which caused by the non-detected ions such as H^{+}, HCO_3^{-} and CO_3^{2-} (Kerminen et al., 2001). When the total ions were distributed over a wide range (by a factor of 20 in our case), the ratio of total anions to cations in neq m^{-3} is more effective in presenting the relative acidity than the absolute value of imbalance (total cations – total anions).*

The concentration of water-soluble organic nitrogen (WSON) was calculated using the following equation:

$$[WSON] = [TDN] – [NO_3^{-}] – [NH_4^{+}] – [NO_2^{-}], \quad (4)$$

where [TDN], $[NO_3^{-}]$, $[NH_4^{+}]$ and $[NO_2^{-}]$ are molar concentrations (nmol N m^{-3}) of those water-soluble nitrogen species in TSPs. *The standard errors propagated through WSON calculation varied from sample to sample (17 to 1500%). The average standard error was 116% when all samples were considered and when the extreme value was excluded the average standard error was reduced to 81%.*

2.3 Flux calculation

The dry deposition flux (F) was calculated by multiplying the aerosol concentrations of water-soluble nitrogen speciation (C) by the dry deposition velocity (V):

$$F = C \times V, \tag{5}$$

where V is a primarily function of particle size and meteorological parameters, such as wind speed, RH and sea surface roughness (Duce et al., 1991). According to previous reports, dry deposition velocity varies by more than 3 orders of magnitude at a particle size ranging from 0.1 to 100 μm (Hoppel et al., 2002). *In general, ammonium appears in submicron mode from 0.1 to 1 μm with a small fraction residing in the coarser mode; on the contrary, nitrate is mainly distributed in a supermicron size ranging from 1 to 10 μm (Nakamura et al., 2005; Baker et al., 2010; Yao and Zhang, 2012; Hsu et al., 2014). The non-single-mode size distribution appears not just in nitrogenous elements but also metals including aluminum and iron (e.g., Baker et al., 2013). Thus, for any compound or elements by using a fixed deposition velocity to calculate dry deposition flux might cause under- or overestimation as discussed by Baker et al. (2013). Unfortunately, we collected TSPs with no information for size distributions. Not mentioning when the highly variable meteorological parameters were considered. In our observation wind speed ranging from 0.8 to 18 m s^{-1} under a RH ranging from 40 to 100% (Fig. 2). Thus, it is very difficult to provide variable dry deposition velocities under a wide range of environmental conditions (Hoppel et al., 2002; Baker et al., 2013); thus, assumptions were made based on existing knowledge.* Based on the model and experimental results for aerosols deposition to the sea surface (Duce et al., 1991; Hoppel et al., 2002) and the size distribution of nitrate and ammonium in particles as reported above, deposition velocity of 2 cm s^{-1} was applied for nitrate and 0.1 cm s^{-1} for ammonium. Both deposition velocities were often used in calculating the specific nitrogen deposition fluxes, especially for the maritime aerosols, though uncertainties were involved (de Leeuw et al., 2003; Nakamura et al., 2005; Chen et al., 2010; Jung et al., 2013). As for WSON, the size distribution of WSON in previous studies showed that

WSON appears in a wide size spectrum (Chen et al., 2010; Lesworth et al., 2010; Srinivas et al., 2011). In previous studies, different orders of magnitude of deposition velocity were employed for WSON deposition (1.2 cm s^{-1} by He et al., 2011; 0.1 cm s^{-1} for fine and 1.0 cm s^{-1} for coarse by Srinivas et al., 2011; 0.075 cm s^{-1} for fine and 1.25 cm s^{-1} for coarse by Violaki et al., 2010). Our TSP aerosols covered the entire size distribution; thus, 1.0 cm s^{-1} was applied for WSON deposition. Since 1.0 cm s^{-1} is near the upper boundary of velocities previously applied for WSON deposition, our calculation of WSON deposition may represent the upper boundary.

Note that, a period of our aerosol sampling was influenced by sea fog, which we could not avoid as mentioned earlier in the Introduction. Apparently, the deposition velocity for sea fog modified aerosol differs from that of common aerosol, thus, the deposition velocity needs to be revised once we have sufficient knowledge about the influence of sea fog on aerosol deposition.

2.4 Air mass backward trajectories analysis

In order to investigate the likely origins of aerosols in the transporting air masses, 3 days with three heights of above sea level air mass backward trajectories were calculated using the National Oceanic and Atmospheric Administration (NOAA) Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model with a 1 °×1 °latitude–longitude grid and the final meteorological database. Details about the HYSPLIT model can be found at https://ready.arl.noaa.gov/HYSPLIT.php, as prepared by the NOAA Air Resources Laboratory. The time period of 3 days was suggested to be sufficient for dust transport from dust source to the NWPO (Husar et al., 2001). The three heights (100, 500 and 1000 m) were selected because 1000 m can be taken as one of the typical atmospheric boundary layers (Hennemuth and Lammert, 2006).

3 Results and discussion

Using the Al content, air mass backward trajectories, weather conditions, and ion stoichiometry, we classified aerosols into three types and then discussed the speciation and concentrations of Nr for each aerosol type as well as the potential processes involved. We compared the chemical characteristics of dust aerosols collected in the ECSs with ours under sea fog influence. Global aerosol and precipitation WSON data were also compiled to reveal the significance of WSON. Finally, we estimated the deposition of individual nitrogen species for the three types of aerosol and highlighted the importance of atmospheric nitrogen deposition in different regions.

3.1 Aerosol type classification

Total Al content in aerosol samples is an often used index to identify dust events (Hsu et al., 2008). As shown in Fig. 3, the total Al concentrations in aerosols ranged from 52 to 6293 ng m^{-3} during our entire cruise. For the first three samples (from nos. 1to 3 collected in the Yellow Sea), total Al increased from 1353 to 6293 ng m^{-3}, and then rapidly decreased (nos. 4 and 5 in the East China Sea) as the cruise moved eastward to the NWPO (orange shadow in Fig. 3). When the cruise returned to the ECSs, the total Al concentrations in the aerosols (nos. 43 and 44) increased once again. Apparently, an abundance of dust is frequently present in the low atmosphere over the Chinese marginal seas in spring. The air mass backward trajectories by HYSPLIT (Fig. 4a) revealed that the air masses for these fog samples mainly hovered over the ECSs at an altitude of < 500 m and the air masses for nos. 1–5 originated from the east coast of China. The air masses for the samples of nos. 43–44 were from south of Korea. The water-soluble Al followed the same pattern as total Al (Fig. 3) but the *leachable concentrations* were significantly higher when compared with dust aerosols reported for the same area. The relative acidity of aerosols showed that the values of sea fog modified aerosols were all below 0.9 (Fig. 3) indicating an enhanced acidification relative to those aerosols with sea fog influence. The low RA values explained the higher *concentrations* of water-soluble Al.

As for sample nos. 6, 7, 25–27 and 29 collected in the NWPO (see pink tracks in Fig. 1), the total Al concentrations ranged from 590 to 1480 ng m^{-3} with an average of

1025 ± 316 ng m^{-3} (pink shadow in Fig. 3), which were significantly higher than the remaining samples (212 ± 120 ng m^{-3}) from the NWPO. Although most of the air mass backward trajectories of these samples collected in the NWPO originated from 25° N to 40° N (and beyond) as well as high altitude (Fig. 4b), the lidar browse images from NASA (Fig. S1) clearly indicated that the air masses of these aerosol samples pass through dusty regions. *The consistency between high total Al concentration and the occurrence of dust and polluted dust defined by the lidar browse images from the NASA allowed us to separate dust aerosols from background aerosols. In this paper, background aerosols stand for non-dusty and non-foggy aerosol in our classification. It is more like a baseline aerosol collected within this study region during the investigating period, thus, the "background" may vary over space and time and it does not necessarily have to be pristine. Below we can also see a discernable ion stoichiometry among the three types.*

3.2 Ion stoichiometry in three types of aerosol

Excluding sea fog modified aerosols, all the ratios of total anions and total cations followed close to a 1:1 linear relationship (Fig. 5a). Such a well-defined positive relationship indicated the charge balance and further emphasized the validity of our measurements. The sea fog modified aerosols in the ECSs contained higher contents of anions than cations, which was consistent with previous observations for fog water (Chang et al., 2002; Lange et al., 2003; Yue et al., 2014). The non-measured H^+ ion should be the dominant cation for charge compensation as indicated previously (Chang et al., 2002; Lange et al., 2003). The low RA values for sea fog modified aerosols also supported this notion (Fig. 3). Below we set out the characteristics of the three types of aerosol with ion stoichiometry.

Since the Cl^-/Na^+ ratios of all samples including sea fog modified aerosols (Fig. 5b) were near 1.17, this indicated that almost all the Na and Cl for our aerosols originated from sea salt. The relationship between Mg^{2+} vs. Na^+ (Fig. 5c) indicated that almost all Mg^{2+} also originated from sea salt sources (Mg/Na_{ss} = 0.23) except sea fog modified aerosols, which held a deviated correlation due to Mg enrichment ($y = 0.32x + 8.7$, $R^2 = 0.88$) because of terrestrial mineral sources of Mg. Such Mg enrichment was not observed in summer sea fog in the subarctic North Pacific Ocean (Jung et al., 2013).

As for Ca^{2+} (Fig. 5d), all types of aerosol were enriched in Ca^{2+} but at different levels, indicating various degrees of terrestrial mineral influence on the marine aerosols. For background aerosols, a strong correlation between Ca^{2+} and Na^{+} ($y = 0.044x + 6.6$, $R^2 = 0.92$) was observed. The slope was identical to that of sea water ($Ca/Na_{ss} = 0.044$) suggesting that most Ca^{2+} and Na^{+} in background aerosols were sourced from sea salt. An unusually high regression slope (20 × the sea salt) observed between Ca^{2+} and Na^{+} in sea fog modified aerosols ($y = 0.90x - 1.8$, $R^2 = 0.71$) was attributable to the reaction between mineral $CaCO_3$ and H^+ in fog droplets during the formation of sea fog (Yue et al., 2012). The more excessive Ca^{2+} observed in dust aerosols implied that stronger heterogeneous reactions between the acid gas and dust minerals had occurred during long-range transport (Hsu et al., 2014). Similar to Ca^{2+}, patterns between K^{+} and Na^{+} can also be seen in Fig. 5e. However, besides the contribution from inland dust (Savoie and Prospero, 1980) excess K^{+} may also originate from biomass burning in China (Hsu et al., 2009). Note that statistically significant intercepts could be seen in Ca^{2+} against Na_{ss} and K^{+} against Na_{ss} scatter plots for background aerosols. Although small, such excesses in Ca^{2+} and K^{+} relative to Na^{+} in widespread background aerosols warrant explanation.

As shown in Fig. 5f, a correlation was found between NH_4^+ and nss-SO_4^{2-}. Except for three sea fog samples, all ratios fell close to the 1:1 regression line suggesting the dominance of $(NH_4)_2SO_4$ rather than NH_4HSO_4. Complete neutralization of NH_4^+ by nss-SO_4^{2-} had likely occurred, and a similar phenomenon was found elsewhere (Zhang et al., 2013; Hsu et al., 2014).

The ratio of [NO_3^- + nss-SO_4^{2-}] / [NH_4^+ + nss-Ca^{2+}] for background aerosols (Fig. 5g) closely followed unity, thus suggesting that NH_4^+ + nss-Ca^{2+} was neutralized by the acidic ions NO_3^- and nss-SO_4^{2-}. However, for the dust and foggy aerosols, [NO_3^- + nss-SO_4^{2-}] / [NH_4^+ + nss-Ca^{2+}] ratios located between 1:1 and 2:1 indicated that the excessive anthropogenic acidic ions that originated from coal fossil fuel combustion and vehicle exhaust had been transported to the ECSs and NWPO by the Asian winter monsoon as previously indicated (Hsu et al., 2010a). *On the other hand, Liu et al. (2013) suggested that NHx emission in China is important and may play a major role in neutralizing the acidic ions.* As shown in Fig. 5h, the scatter plot of NH_4^+ against NO_3^-, revealed that almost all dust and background aerosols sampled in the NWPO had NH_4^+/NO_3^- ratios larger than 1, which is common in aerosol observation. However, significantly enriched NO_3^- in sea fog modified aerosols drew the ratio down to < 1. Nevertheless, such relatively enriched nitrate to ammonium was consistent with a previous study of sea fog water collected from the South China Sea (Yue et al., 2012). In summary, the three types of aerosol had distinctive features in nitrogen speciation and ion stoichiometry including relative acidity (Fig. 6a) further supporting our aerosol type classification.

3.3 Nitrogen speciation and associated processes in different types of aerosol

3.3.1 Sea fog modified aerosols

Only a few studies concerning water-soluble nitrogen species in sea fog water were reported (Sasakawa and Uematsu, 2002; Yue et al., 2012; Jung et al., 2013). To the best of our knowledge, ours is the first first-hand data from the Chinese marginal seas (the ECSs) in spring concerning water-soluble nitrogen species in aerosols collected under the influence of sea fog. As shown in Table 1 and Fig. 6a, in sea fog modified aerosols the concentrations of nitrate ranged from 160 to 1118 nmol N m^{-3} with a mean of 536 ± 300 nmol N m^{-3} and ammonium was slightly lower than nitrate ranging from 228 to 777 nmol N m^{-3} with a mean of 442 ± 194 nmol N m^{-3}. WSON in sea fog modified aerosols was the lowest nitrogen species ranging from 23 to 517 nmol N m^{-3} with a mean of 147 ± 171 nmol N m^{-3} (Table 1 and Fig. 6a). The sea fog modified aerosols contained 2–11 times higher concentration of nitrate, 2–6 times higher ammonium and 3–6 times higher WSON when compared with aerosols in the ECSs and other regions (Table 1). Such high concentrations of Nr not only highlighted the seriousness of the nitrogen air pollution in Chinese marginal seas, but also underscored that water-soluble nitrogen species can be scavenged efficiently during sea fog formation.

Since none chemistry data of sea fog modified aerosols had been reported before, we can only compare with the dust aerosols from the same regions in spring. The concentrations of leachable ions, water-soluble and total Al and RA for dust aerosols and sea fog modified aerosols sampled in the ECSs were listed in Table 2. The seven sea fog modified aerosols were distinctive in chemical characteristics. For all except $\mathrm{NH_4^+}$, $\mathrm{NO_3^-}$ and $\mathrm{SO_4^{2-}}$, sea fog modified aerosols had lower or similar molar concentrations relative to dust aerosols. The anthropogenic species, particularly $\mathrm{NO_3^-}$ and $\mathrm{NH_4^+}$, were the most abundant ions in the sea fog modified aerosols. On the contrary, $\mathrm{Na^+}$ and $\mathrm{Cl^-}$ were the highest among all the ions in dust aerosols from the island of Jeju and the East China Sea. Taking Jeju as an example, the concentration levels of $\mathrm{Na^+}$ and $\mathrm{Cl^-}$ were similar to those of our sea fog modified aerosols, yet both $\mathrm{NO_3^-}$ and $\mathrm{NH_4^+}$ in sea fog modified aerosols were > 6 times higher than those from the island of Jeju.

The pie charts for ion fractions of aerosols from the ECSs were shown in Fig. 7. Note that the fraction distribution of ions for the dust aerosols from a previous cruise in the ECS (n = 8, Fig. 7b, Hsu et al., 2010b) resembled that collected from the island of Jeju (n = 49, Fig. 7c, Kang et al., 2009) despite the fact that their sampling were in different spaces and at different times. Such consistency in the ion pie chart indicated the representativeness of these dust aerosols. However, the pie chart for sea fog modified aerosols revealed that $\mathrm{NH_4^+}$ and $\mathrm{NO_3^-}$ occupied approximately 30 and 36% of the total ionic concentration (Fig. 7a). Such an overwhelmingly high occupation of nitrogenous ions emphasized the role of sea fog in modifying the chemistry of non-foggy dust aerosols.

In a previous study in the Po Valley, the average scavenging efficiency for aerosol nitrate and ammonium were reported to be at similar levels (70 and 68%; Gilardoni et al., 2014), while in our case the concentrations of nitrate in sea fog modified aerosols were higher than those of ammonium (Table 1 and Fig. 6a). Since the gas phase HNO_3 is rapidly dissolved in liquid water particles during the early stages of fog formation (Fahey et al., 2005; Moore et al., 2004), it was reasonable to infer that the enriched nitrate in sea fog was attributed to gaseous HNO_3 owing to the gas–liquid equilibrium between NO_3^- and HNO_3 in fog droplets. Moreover, our sea fog modified aerosols were collected from the air masses roaming around east China and the ECSs, where the NO_x emission is the highest in China (Gu et al., 2012). *The lifetime of NOx in the boundary layer is generally less than 2 days (Liang et al., 1998). Based on our air mass backward trajectories analysis, the travel time of air masses from inland China to the marginal seas is long enough for oxidation of NOx into HNO_3.* Thus, nitrate enrichment in the sea fog modified aerosol was likely a synergistic consequence due to the sea fog formation and gas–liquid equilibrium of gaseous HNO_3.

As for SO_4^{2-}, both the concentration and percentage occupation were comparable in sea fog modified aerosols and dust aerosols (Table 2 and Fig. 7). However, the concentrations of nss-SO_4^{2-} in sea fog modified aerosols was 60% higher than those of dust aerosols (Table 2), suggesting the addition of anthropogenic SOx emission during sea fog formation as indicated by Gilardoni et al. (2014). In the marginal seas adjacent to the anthropogenic emission source, acidified sea fog induced by additional sulfuric and nitric acid was common (Sasakawa and Uematsu, 2005; Yue et al., 2014).

In general, Al in marine aerosols originated from terrestrial minerals (Uematsu et al., 2010). The mean concentrations of total Al in our seven sea fog samples were the lowest among those in dust aerosols from the ECSs (Table 2). However, the concentrations *as well as the fractions* of water-soluble Al in sea fog modified aerosols were significantly higher than those of dust aerosols. Because of the high acidity (low RA values) for sea fog modified aerosols (Fig. 6a), we suspected that during the seasonal transition period the formation of sea fog at the land–ocean boundary may acidify the aerosol to effectively promote the solubility of metals in aerosol minerals.

Finally, it has been shown that dissolved organic matter can be scavenged by fog, but its scavenging efficiency was lower than those of nitrate and ammonium due to hydrophobic organic species were more difficult to be scavenged than hydrophilic ones (Maria and Russell, 2005; Gilardoni et al., 2014). In our case, although concentrations of WSON in sea fog modified aerosols (147 ± 171 nmol N m^{-3}) were significantly higher than those of background aerosols, the ratio of WSON to TDN in sea fog modified aerosols (10 ± 6%) was similar to those (ranging from 10 to 24%) of background aerosols sampled in the ECSs (Table 1). *Such high WSON concentration but low WSON% in TDN in sea fog modified aerosols may indicate the lower scavenging efficiency of WSON relative to other nitrogen species or that its source region is different or both*.

Note that all these aerosols in our study were sampled by TSP. Conventional knowledge indicates that aerosol may act as a precursor for fog formation, but this does not necessarily mean all the aerosols we sampled were directly associated with fog. Nevertheless, we observed distinctive chemistry for this type of aerosol either comparing with aerosols sampled during the same cruise or comparing with "non-foggy" aerosols collected in the ECS in previous study. More studies are needed to explore the effect of sea fog formation on aerosol chemistry.

3.3.2 **Dust aerosols**

For dust aerosols collected in the NWPO, nitrate ranged from 79 to 145 nmol N m^{-3} with an average of 100 ± 23 nmol N m^{-3}, and ammonium ranged from 94 to 163 nmol N m^{-3} with an average of 138 ± 24 nmol N m^{-3} (Table 1 and Fig. 6a). Relative to background aerosols, both nitrate and ammonium were significantly higher in dust aerosols revealing the anthropogenic nitrogen fingerprint carried by the Asian dust outflow along with westerlies (Chen and Chen, 2008). Interestingly, dust aerosols contained a low concentration of WSON (11.2 ± 4.0 nmol N m^{-3}) resembling that of background aerosols (Table 1 and Fig. 6a). Moreover, dust aerosols held the lowest WSON fraction in total dissolved nitrogen among the three types (Table 1 and Fig. 6b). Based on the good correlation between nss-Ca^{2+} and WSON, previous studies demonstrated that dust can carry anthropogenic "nitrogen" activity into remote oceans and simultaneously promote the ratio of WSON /TDN in aerosol (Mace et al., 2003b; Lesworth et al., 2010; Violaki et al., 2010). However, in our case there was no correlation between WSON and nss-Ca^{2+} (not shown), likely illustrating that these aerosols had less chance to contact WSON along their pathway from a high altitude, or that WSON had been scavenged during transport. However, the latter was less likely.

3.3.3 Background aerosols

For the 31 background aerosol samples, the mean concentrations of NO_3^- and NH_4^+ were 26 ± 32 and 54 ± 45 nmol N m^{-3} (Table 1). Both were 10 times higher than those collected in the same region during summer (2.5 ± 1.0 nmol N m^{-3} for nitrate and 5.9 ± 2.9 nmol N m^{-3} for ammonium; Jung et al., 2011). The 10 times higher Nr for springtime background aerosols indicated that the "spring background" was not pristine at all. Such distinctive seasonality was ascribed to the origins of air mass, since in summer the air masses in our study area were mainly from the open ocean while in spring the air masses came from the northeast of China through the Japanese Sea and Japan (Fig. 4c), where they were strongly influenced by anthropogenic nitrogen emission (Kang et al., 2010). The concentration of WSON in background aerosols was 10.9 ± 6.8 nmol N m^{-3}, which fell within the wide range reported previously (~1 to 76 nmol N m^{-3}; Table 1). In the open ocean, the WSON in aerosols may come from natural and anthropogenic sources. For example, the highest percentage of WSON in TDN in the southern Atlantic (84%) was attributed to high biological productivity (Violaki et al., 2015). *Unfortunately, no marine biological* *data (i.e. special amines or amino acids as summarized by Cape et al., 2011) existed in our case to directly support marine sourced aerosol WSON.*

Nevertheless, our sampling cruise experienced a wide range of wind speed with variable sea salt contents during the collection of background aerosols. The correlations between ion content and wind speed may reveal some useful information *as indirect evidence*. Higher sea salt, e.g. Na^+, Cl^-, Mg^{2+}, appeared with higher wind speed conditions (Fig. 8a-c). Positive correlations can be seen although r square values were small possibly due to time-integrated sampling (~12 h) and averaged wind speed over the sampling period. The positive correlation illustrated that the emission of sea salt aerosols was driven by wind intensity as indicated by Shi et al. (2012). Except for WSON (Fig. 8d), which was consistent with sea salt associated ions, no statistically significant relationships can be derived from scatter plots of nitrate and ammonium against wind speed (Fig. 8e and f). An analogous tendency between WSON and sea salt ions suggested that WSON might come from the surface ocean. Since the concentration of dissolved organic nitrogen (DON) in surface sea water was less variable, ranging from 4.5 to 5.0 μM in the Pacific Ocean (Knapp et al., 2011), DON can be taken as a relatively constant component in surface sea water similar to Na^+, Cl^- and Mg^{2+}. Very likely, breaking waves and sea spray brought DON into the atmosphere under higher wind speed. In fact, using free amino acids and urea compositions in the maritime aerosol, Mace et al. (2003a) indicated that live species in the sea surface microlayer may serve as a source of atmospheric organic nitrogen.

Compared with DON in the surface ocean, it is not possible that nitrate and ammonium in the surface seawater are a source of atmospheric aerosol nitrate and ammonium since the concentrations of nitrate and ammonium are very low (a few tens to hundreds of nM) in the surface ocean. However, under a wide range of wind speed, we observed relatively narrow concentration ranges of aerosol ammonium and nitrate. This was strange, given that high wind speed implied vigorous exchange on the air-sea interface, during which both sea salt emission and scavenging were supposed *to be high. Under efficient scavenging conditions, to maintain a relatively uniform aerosol nitrate or ammonium concentration (quasi-static), some supply processes are needed for compensation. Since the surface ocean is not a possible source for both aerosol ammonium and nitrate, we suggested alternative supplies which included deposition from the upper atmosphere and photochemical production/consumption.*

Based on $\delta^{15}N–NH_4^+$ in aerosol (Jickells et al., 2003) and rainwater (Altieri et al., 2014) collected in the Atlantic, the ocean was suggested to be one of the ammonium sources for the atmosphere. Because of the low concentration of ammonium in the ocean surface, direct ammonium emission via sea spray was less likely. Based on our observation, we hypothesized that the emitted marine WSON in the atmosphere may serve as a precursor for ammonium and/or nitrate via the photo-degradation and photo-oxidation processes reported previously (Spokes and Liss, 1996; Vione et al., 2005; Xie et al., 2012). *A most recent study by Paulot et al. (2015) supported our hypothesis. By modeling global inventories of ammonia emissions, they found that the ammonia source from the ocean cannot neutralize the sulfate aerosol acidity, thus photolysis of marine DON at the ocean surface or in the atmosphere was suggested to be a source of atmospheric ammonia.* More studies about the exchange processes among nitrogen species through the ocean–atmosphere boundary layer are needed.

3.4 WSON in aerosol and rainwater: a global comparison

Organic nitrogen, distributed in the gas, particulate and dissolved phases, is an important component in the atmospheric nitrogen cycle. In our case, mean fractions of WSON in aerosol TDN were 10 ± 6, 5 ± 2 and 14 ± 8% for modified sea fog, dust and background aerosols. All values fell within the wide range reported previously (also in Table 1). Here we synthesized a published data set about aerosol WSON from around the world for comparison (Fig. 9a). The synthesized data revealed that aerosol WSON concentrations varied over 3 orders of magnitude and the fraction of WSON in TDN ranged from 1% to as high as 85%. Additionally, the fraction of WSON was the less variable towards high WSON concentrations. The slope of the linear regression between WSON and TDN indicated that WSON accounted for 18% of aerosol TDN. *Although the positive correlation between WSON and TDN may imply WSON's anthropogenic origin (Jickells et al., 2013), the marine sourced WSON cannot be ignored in the open ocean as discussed in Section 3.3.3.*

In Fig. 9b, we made a comparison between the distribution of the WSON fraction in rainwater TDN and that in aerosol. The distribution pattern of WSON fractions in aerosols (Fig. 9b, grey bar) was relatively concentrated revealing a tendency towards lower fractions. Its peak frequency appeared at the category of 10–20% and at least 80% of the observed WSON fractions fell within the range < 25%. However, for WSON/TDN in rainwater (Fig. 9b, blue bar), the distribution pattern was relatively diffusive shifting towards a higher percentage and peaking at around categories of 25–40% with a mean value of 33% (n = 332), which is slightly higher than that (24%, n = 115) obtained by Jickells et al. (2013). Although values of the coefficient of variation for both aerosol and rainwater were high, the results were still statistically meaningful. *The mean WSON fraction for rainwater was around 2 times that for aerosol (18%), but the sampling bias inherited in such comparison should be noted.* In a previous study, Mace et al. (2003a) reported that the fractional contribution of dissolved free amino acids to organic nitrogen in rainwater was 4 times higher than that in aerosol. The higher fractional contribution of WSON to TDN for rainwater may imply that precipitation washed out hydrophilic organic matter or WSON from the atmosphere more effectively (Maria and Russell, 2005).

3.5 Dry deposition of TDN and the implications

As shown in Fig. 10, the atmospheric nitrogen dry deposition over the cruise revealed a large spatial variance under different weather conditions. In the ECSs, the mean DIN (NH_4^+ + NO_3^-) deposition on fog days was estimated to be ~ 960 μmol N m^{-2} d^{-1} (926 ± 518 and 38 ± 17 μmol N m^{-2} d^{-1} for nitrate and ammonium), which was around 6 times higher than the average values for ordinary aerosols derived from literature reports (153 μmol N m^{-2} d^{-1} for aerosol nitrate and 12.3 μmol N m^{-2} d^{-1} for aerosol ammonium; see Table 3). The WSON deposition ranged from 20 to 446 μmol N m^{-2} d^{-1} with an average of 127 ± 148 μmol N m^{-2} d^{-1}. Since the bioavailability of aerosol WSON to phytoplankton was reported to be high (12–80%; Bronk et al., 2007; Wedyan et al., 2007), by adding WSON into consideration, the deposition of TDN will be ~ 1100 μmol N m^{-2} d^{-1}.

Taking 1150 $\times 10^3$ km^2 for the total area cover by the ECSs, we calculated the daily nitrogen supply from atmospheric deposition associated with sea fog to be 18 ± 11 Gg TDN d^{-1}, which is around 6 times the nitrogen input from the Yangtze River in spring (total amount of 3.1 Gg DIN d^{-1}; Li et al., 2011) and 2 times the supply from the subsurface intrusion of the Kuroshio (7.9 Gg NO_3^--N d^{-1}; Chen, 1996). In the ECSs, the sea fog occurrence was around 3–5 days in March and 8–10 days in April (Zhang et al., 2009). Given such high TDN deposition per day, the contribution of foggy weather should really be taken into account on a monthly estimate even though the occurrence of sea fog is limited in time and space. Moreover, the atmospheric influence is more widespread than the river focusing on the plume area.

Assuming that nitrogen was the limiting nutrient and that all the total dissolved nitrogen deposited from atmosphere into the sea was bioavailable and would be utilized for carbon fixation, we obtained a C-fixation rate of ~ 87 mg C m^{-2} d^{-1} in spring for the ECSs based on the Redfield C/N ratio of 6.6. Since atmospheric nitrogen deposition is an external source, such a conversion represents new production. When compared with the primary productivity in the East China Sea (292–549 mg C m^{-2} d^{-1}; Gong et al., 2000), the new production associated with sea fog nitrogen deposition may account for 16–30% of the primary production in the ECSs on foggy days in spring.

Similar to sea fog on the ECSs, sporadic dust events are frequently observed from March to May in the NWPO (Shao and Dong, 2006). In our spring case, the average deposition of dust aerosol nitrate and ammonium (172 ± 40 μmol N m^{-2} d^{-1} for nitrate and 11.9 ± 2.1 μmol N m^{-2} d^{-1} for ammonium) were significantly higher than that of background aerosols (44.6 ± 55.3 μmol N m^{-2} d^{-1} for nitrate and 4.7 ± 4.0 μmol N m^{-2}

d^{-1} for ammonium; see Table 3). However, both dust and background aerosols depositions were significantly higher in spring when compared to summer dry deposition in the subtropical western North Pacific (3.0 ± 1.5 for nitrate and 2.7 ± 2.1 μmol N m^{-2} d^{-1} for ammonium) and the subarctic western North Pacific (3.3 ± 2.3 for nitrate and 1.9 ± 0.63 μmol N m^{-2} d^{-1} for ammonium) (Jung et al., 2011). Likewise, the C-fixation rate in the NWPO during spring was estimated to be 4.5–15 mg C m^{-2} d^{-1} based on the above assumptions and observations. The minimal level of C-fixation induced by dry deposition, in fact, equals to the maximum carbon uptake (3.6 mg C m^{-2} d^{-1}; Jung et al., 2013) in summer by the total atmospheric DIN deposition (wet + dry + sea fog) in the western North Pacific Ocean. Thus, the contribution of atmospheric nitrogen deposition to primary production in the NWPO could be significantly different between seasons.

4 Conclusions

We presented the total dissolved nitrogen species including water-soluble organic nitrogen in TSP sampled over the ECSs and NWPO during spring and the samples of the ECSs were collected under sea fog influence. Three types of aerosol, the sea fog modified, the dust and the background aerosols, were classified. We found that sea fog formation significantly altered the aerosol chemistry resulting in the highest concentrations of all nitrogen species among the three types of aerosol, accompanied with higher acidity and higher cation deficiency. On a daily basis, the nitrogen supply from sea fog associated atmospheric deposition into the ECSs was around 6 times the nitrogen supply from the Yangtze River in spring (total amount of 3.1 Gg DIN d^{-1}*) and 2 times the supply from the subsurface intrusion of Kuroshio (7.9 Gg* NO_3^-*-N* d^{-1}*). Sea fog associated deposition and chemical processes require more attention and need to be considered in future aerosol monitoring and modeling works especially in marginal seas during seasonal transition.*

In the open sea, the spring background aerosol ammonium and nitrate were 10 times higher than previous report for summer indicating an anthropogenic influence and the importance of the seasonality of the air mass source. The ammonium and *nitrate varied in narrow ranges showing no correlation with wind speed, which may represent the degree of sea salt emission and scavenging. It is likely that nitrate and ammonium in the atmosphere above sea surface had reached a budget balance. Since the supply of nitrate and ammonium from surface ocean (bottom) is not possible, their sources might come from upper atmospheric boundary layer (top) or photochemical production of nitrogenous compounds. On the contrary, WSON revealed a similar pattern to the sea salt ions (*Na^{+}*,* Mg^{2+} *and* Cl^{-}*), in which concentrations increased as the wind speed increased. Such a similarity indicated that at least a portion of the WSON should come from the surface ocean where DON emitted with sea salt. Future studies of nitrogen isotopic compositions of aerosol WSON and marine DON may shed light on the role of marine DON in nitrogen cycling of the air-sea interface.*

The dust aerosols were significantly enriched in nitrate and ammonium, but not in WSON. Unless WSON-depletion processes had occurred, such a disproportionate enrichment suggested that dust aerosols from high latitude and altitude may have less chance to contact WSON during long range transport.

The WSON to TDN ratios of aerosols collected in the ECSs and NWPO fell within that of the global pattern of aerosols. Since nitrate and ammonium are mainly anthropogenic, the significantly positive correlation between WSON and TDN may imply WSON's anthropogenic origin. When TDN concentrations were low (<100 nmol m^{-3}*), the proportions of WSON in TDN were more diffusive indicating that factors other than anthropogenic ones were involved. The mean ratio of WSON to TDN in aerosols was only 1/2 of that for precipitation over the world. Such a low proportion of WSON in aerosol TDN suggested that the aerosol was less capable of scavenging hydrophilic organic nitrogen when compared with precipitation. Nevertheless, WSON occupies a significant portion of the TDN for both aerosol and precipitation and, thus, cannot be overlooked in the atmospheric nitrogen cycle.*

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Table 1. Nitrogen speciation in various aerosols reported from different regions.

Sample type	Date	Location		NO_3^- nmol m^{-3}	NH_4^+ nmol m^{-3}	WSON nmol m^{-3}	NO_3^- %[a]	NH_4^+ %[a]	WSON %[a]	Reference
TSP (Fog)	Mar–Apr 2014	ECSs	Shelf	536 ± 300	442 ± 194	147 ± 171	48 ± 7	42 ± 9	10 ± 6	This study
TSP (Dust)	Mar–Apr 2014	NWPO	Remote ocean	100 ± 23	138 ± 24	11.2 ± 4.0	41 ± 5	56 ± 7	5 ± 2	This study
TSP (Bgd.)	Mar–Apr 2014	NWPO	Remote ocean	26 ± 32	54 ± 45	10.9 ± 6.8	27 ± 9	60 ± 11	14 ± 8	This study
TSP (Dust)	Aug–Sep 2007, 2008	Barbados, Atlantic	Island	101 ± 4	11 ± 7	1.4 ± 1.3	45[c]	49[c]	6[c]	Zamora et al. (2011)
TSP (Dust)	May 2007–July 2009	Miami, FL, Atlantic	Coast city	28 ± 9	26 ± 10	3.0 ± 2.0	50[c]	45[c]	5[c]	
$PM_{>2}$ (Dust)		Tropic Atlantic Ocean							14	Violaki et al. (2015)
TSP (Dust）	Mar 2005–Apr 2007	Southwest ECS	Shelf	84 ± 98	177 ± 151	—	—	—	—	Hsu et al. (2010b)
TSP (Dust）	Feb 1992–May 2004	Island of Jeju	Island	71 ± 44	72 ± 48	—	—	—	—	Kang et al. (2009)
TSP	Feb–Mar 2007	Northwest ECS	Shelf	68[c]	193[c]	—	—	—	—	Shi et al. (2010)
TSP	Mar 2005–Apr 2007	Southwest ECS	Shelf	38 ± 45	89 ± 76	—	—	—	—	Hsu et al. (2010b)
TSP	Sep–Oct 2002	ECS	Shelf	34[c]	136[c]	54 ± 36	15[c]	61[c]	24	Nakamura et al. (2006)
TSP	Mar 2004	ECS	Shelf	39[c]	91[c]	16 ± 19	27[c]	62[c]	10	
TSP	Mar 2005, Apr 2006	Yellow Sea	Shelf	—	—	—	—	—	20	Shi et al. (2010)
TSP	Apr 2010	Northwest ECS	Island	111[c]	76[c]	—	—	—	—	Zhu et al. (2013)
TSP	Mar 2011	Northwest ECS	Island	137[c]	202[c]	—	—	—	—	Zhu et al. (2013)
TSP	Spring 2003–2004	Northeast ECS	Island	85 ± 47[c]	133 ± 78[c]	—	—	—	—	Kundu et al. (2010)
TSP	Jul–Aug 2008	NWPO	Remote ocean	2.5	5.6	—	—	—	—	Jung et al. (2013)
TSP	Aug 2003–Sep 2005	Gulf of Aqaba	Coast	39 ± 19	25 ± 14	8 ± 5	53[c]	34[c]	11[c]	Chen et al. (2007)
TSP	Nov – Dec 2000	Island of Tasmania	Island	11 ± 7	2.6 ± 3.0	3.6 ± 5.7	63	15	21	Mace et al. (2003a)
TSP	Aug–Sep 2008	NWP	Remote ocean	1.8 ± 1.5	1.2 ± 1.1	1.1 ± 0.93	43[c]	30[c]	28[c]	Miyazaki et al. (2011)
TSP	Apr 2007–Mar 2008	Marina, Singapore	urban	50 ± 31	14 ± 8	56 ± 22	40 ± 15	11 ± 6	49 ± 17	He et al. (2011)
TSP	Jan–Dec 2006	Keelong, Taiwan	Coast city			76 ± 28			26[c]	Chen et al. (2010)

TSP (Sea-spray)				6.7 ±2.7	4.2 ±1.7	0.5 ±0.3	59[c]	37[c]	4[c]	Zamora et al. (2011)
TSP (Bb)[b]				11 ±11	18 ±13	3.3 ±2.0	34[c]	56[c]	10[c]	
TSP (Bb)[b]				28 ±16	48 ±48	6.2 ±6.4	34[c]	58[c]	8[c]	Zamora et al. (2011)
TSP (Pollution)				22 ±11	23 ±24	3.7 ±2.8	45[c]	48[c]	8[c]	
PM$_{1.3-10}$	2005, 2006	Crete, Greece	Island	26 ±9	8.9 ±4.0	5.5 ±3.9	64	23	13	Violaki et al. (2010)
PM$_{1.3}$	2005, 2006	Crete, Greece		1.5 ±1.3	70 ±35	12 ±14	2	85	13	
PM$_{2.5}$	Jan–Dec 2005	Indian Ocean	Remote ocean	0.3 ±0.2	1.3 ±1.0	0.8 ±1.4	14	53	32	Violaki et al. (2015)
PM$_{2.5-10}$				0.2 ±0.1	0.3 ±0.1	0.2 ±0.4	26	39	35	
PM$_{2.5}$	Jan 2007	Middle S. Atlantic	Remote ocean			1.3 ±0.8			51	

[a] Percentage in total dissolved nitrogen

[b] Bb indicated Biomass burning

[c] Calculated value from the original data

Table 2. Mean molar concentrations (nmol m^{-3}) of major ionic species together with Al (ng m^{-3}) in sea fog modified aerosols and dust aerosols in the ECSs.

	Sea fog[a]	Dust[b]	Dust[c]
	mean ± SD	mean ± SD	mean ± SD
Na^+	123.2 ± 97.5	294.8 ± 238.3	130.4 ± 85.2
NH_4^+	441.5 ± 193.9	177.6 ± 150.7	72.2 ± 47.7
Mg^{2+}	24.1 ± 16.5	41.2 ± 32.4	25.0 ± 12.9
K^+	17.5 ± 9.9	21.8 ± 19.1	17.9 ± 9.2
Ca^{2+}	54.7 ± 52.2	61.7 ± 39.5	76.9 ± 58.5
Cl^-	125.2 ± 111.3	280.9 ± 349.1	121.3 ± 101.6
NO_3^-	535.9 ± 299.7	83.6 ± 98.4	71.0 ± 43.5
SO_4^{2-}	172.5 ± 54.1	145.2 ± 103.2	104.0 ± 47.2
nss-SO_4^{2-}	165.1 ± 50.3	94.9 ± 89.0	96.1 ± 47.3
Total Al	2460 ± 2160	3470 ± 2730	4900 ± 6500
Soluble Al	124 ± 36	38 ± 45	nd.
Al Solubility	5.0 ± 1.7 %	1.1 ± 1.6%	nd.
Relative acidity	0.73 ± 0.13	1.07	1.06

[a] This study; [b] Hsu et al. (2010b); [c] Kang et al. (2009); nd.: no data

Table 3. The depositional fluxes reported or calculated for the Asian region and Pacific Ocean based on assumed deposition velocity.

Locations	Collection type	Date	NO_3^-[a]	NH_4^+[a]	WSON[a]	Total[a]	Reference
ECSs (Sea fog)	Cruise	Mar–Apr 2014	926 ± 518	38 ± 17	127 ± 148	1090 ± 671	This study
NWPO (Dust)	Cruise	Mar–Apr 2014	172 ± 40	11.9 ± 2.1	6.5 ± 5.7	190 ± 41.6	This study
NWPO (Bgd.)	Cruise	Mar–Apr 2014	44.6 ± 55.3	4.7 ± 3.9	7.6 ± 6.5	56.8 ± 59.1	This study
Subarctic western North Pacific	Cruise	Jul–Aug 2008	3.3 ± 2.3	1.9 ± 0.63	--	5.3 ± 2.6	Jung et al. (2011)
Subtropical western North Pacific	Cruise	Aug–Sep 2008	3.0 ± 1.5	2.7 ± 2.1	--	5.7 ± 3.5	Jung et al. (2011)
Central North Pacific	Cruise	Jan 2009	1.6 ± 0.44	1.4 ± 0.96	--	3.1 ± 1.4	Jung et al. (2011)
Northwest ECS*	Cruise	Feb–Mar 2007	117	17	--	134	Shi et al.(2010)
Southwest ECS*	Cruise	Spring 2005–2007	66	8	--	74	Hsu et al. (2010b)
Northwest ECS*	Coastal island	Apr 2010	192	6.6	--	198.6	Zhu et al. (2013)
Northwest ECS*	Coastal island	Mar 2011	237	17.5	--	254.5	Zhu et al. (2013)

* recalculated fluxes based on assumed deposition velocity

[a] in μmol N m^{-2} d^{-1}

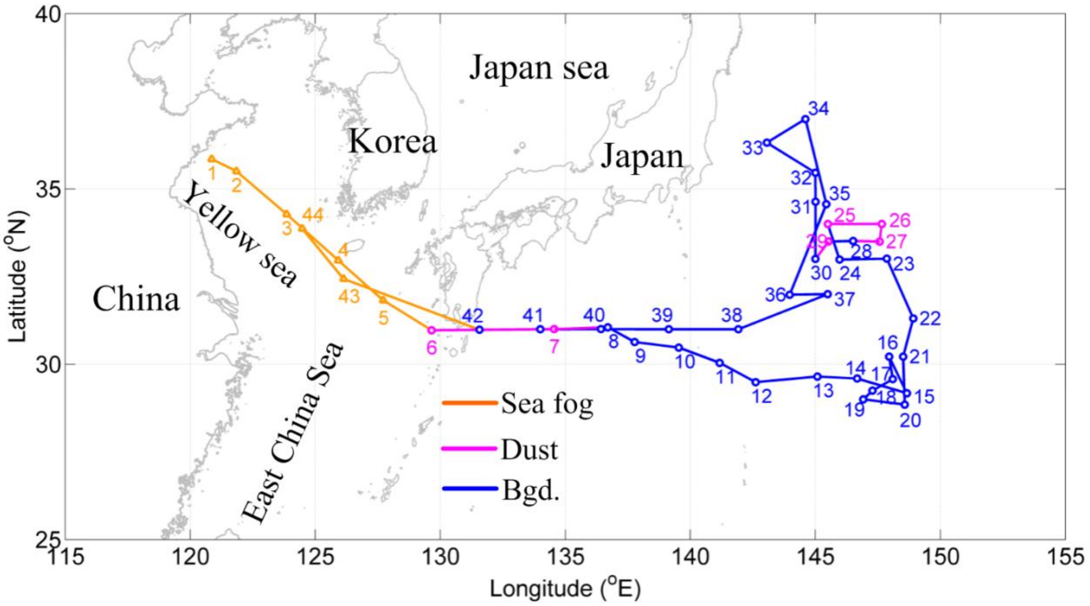


Figure 1. Map of the cruise track. Orange, pink and blue indicate sea fog, dust and background days during the cruise. Sample number and the collection range were shown.

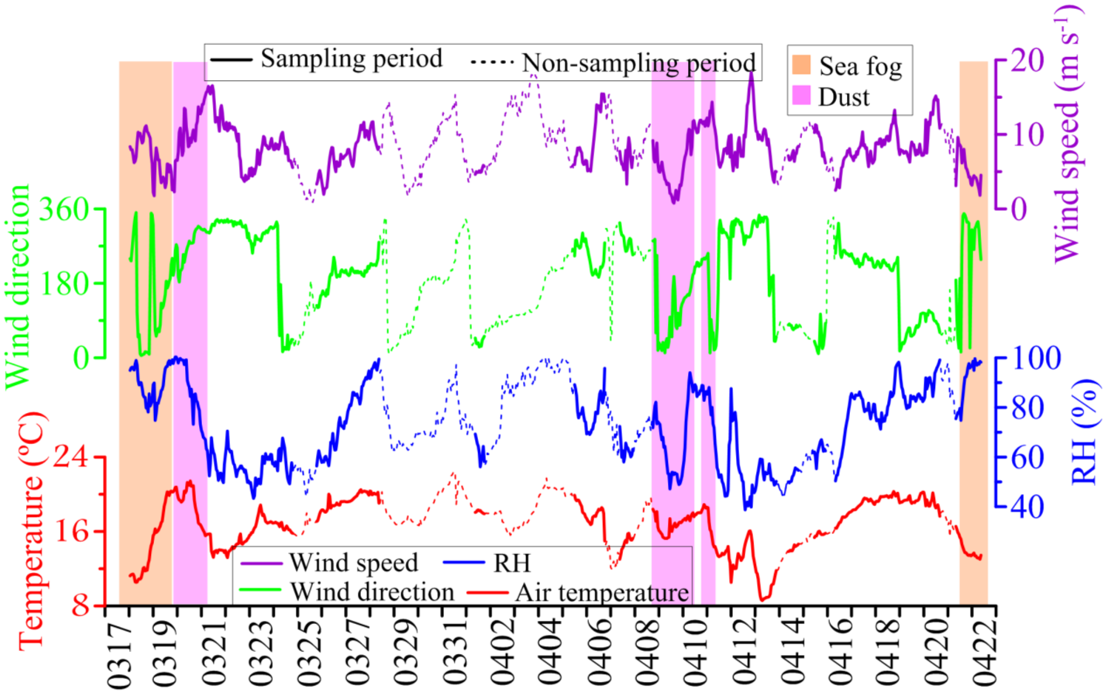


Figure 2. The meteorological parameters collected during the sampling period (solid line). Wind speed is in purple, wind direction in green, RH in blue and temperature in red. The orange shading indicates the period of sea fog contact and pink indicates the dust period. Non-sampling period is in dashed curves.

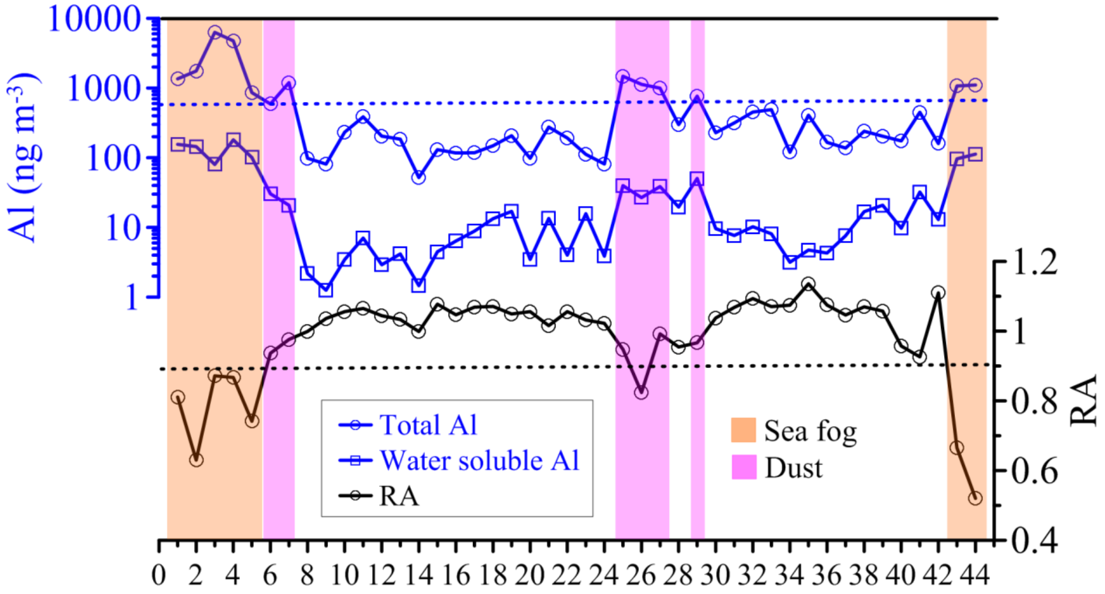


Figure 3. Total and water soluble Al concentrations and relative acidity (RA) for TSP. The orange bars indicate the sea fog period, the pink bars indicate the dust period. Sample identifications are shown on the x-axis (see Table S1). The horizontal blue dashed line (590 ng m^{-3}) stands for the reference to define background aerosols, and black dashed line indicates the criterion of 0.9 for relative acidity.

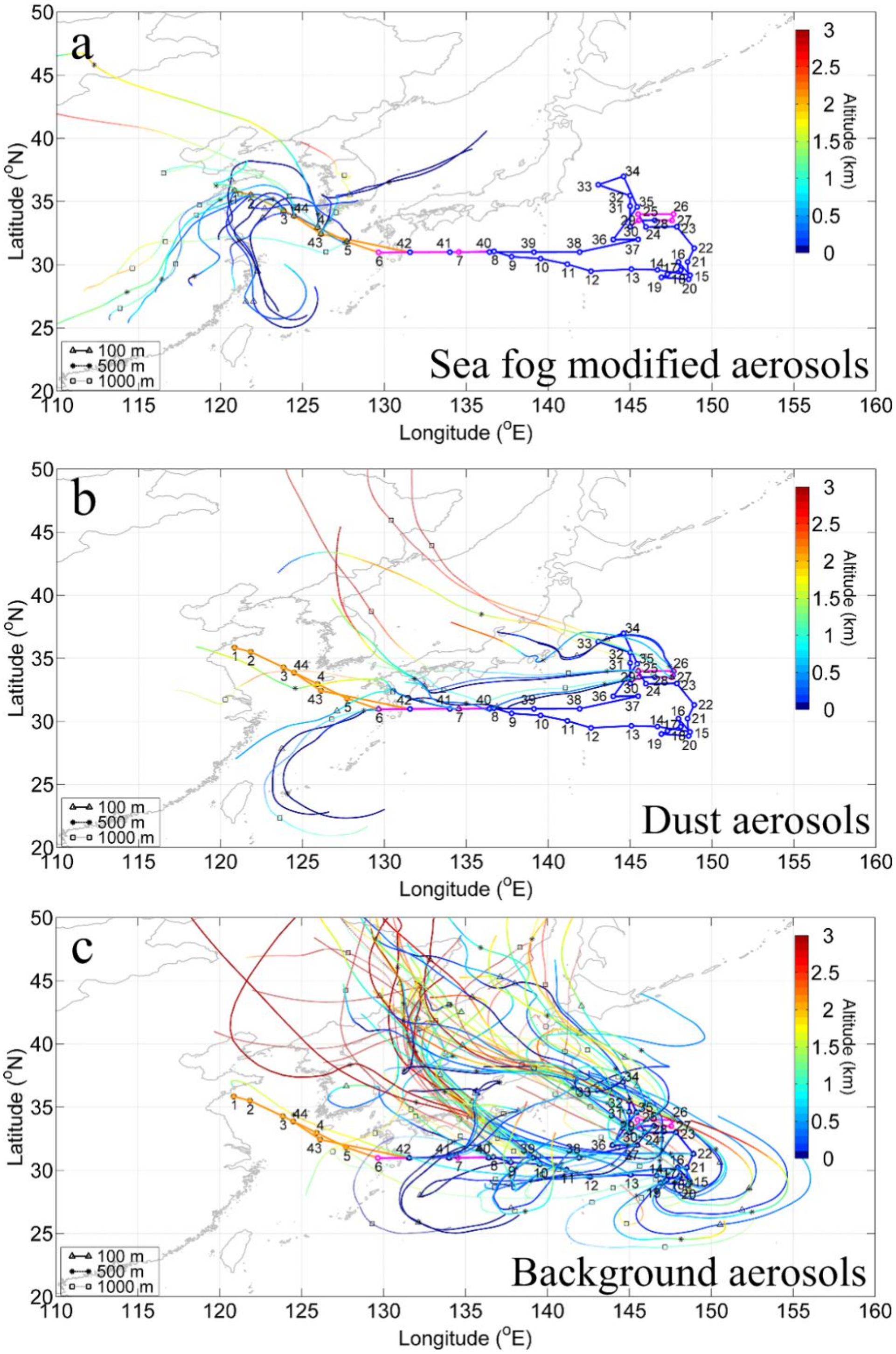


Figure 4. Map and cruise track superimposed on 3-days air mass backword trajectories corresponding to each sample. Altitudes of 100 m a.s.l. (triangles), 500 m a.s.l. (asterisks) and 1000 m a.s.l. (squares) are above sea levels during the collecteion of (a) sea fog modified aerosols, (b) dust aerosols and (c) background aerosols. The colour bar represents the altitude (in km).

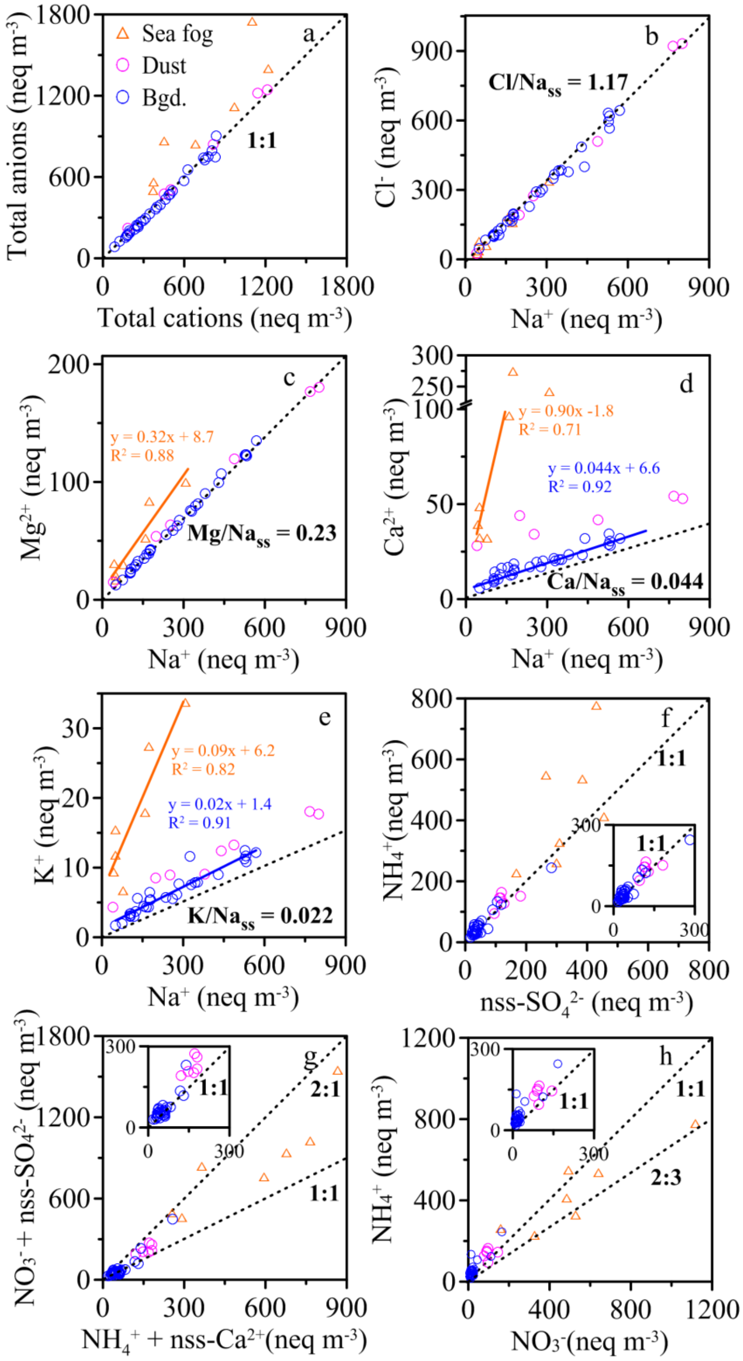


Figure 5. Scatter plots for equivalent concentrations of specific ions. (a) total anions vs. total cations, (b) chloride vs. sodium, (c) magnesium vs. sodium, (d) calcium vs. sodium, (e) potassium vs. sodium, (f) ammonium vs. nss-sulfate, (g) Σ(nitrate + nss-sulfate) vs. Σ(nss-calcium + ammonium) and (h) nitrate vs. ammonium. Orange, pink and blue are for sea fog modified, dust and background aerosols.

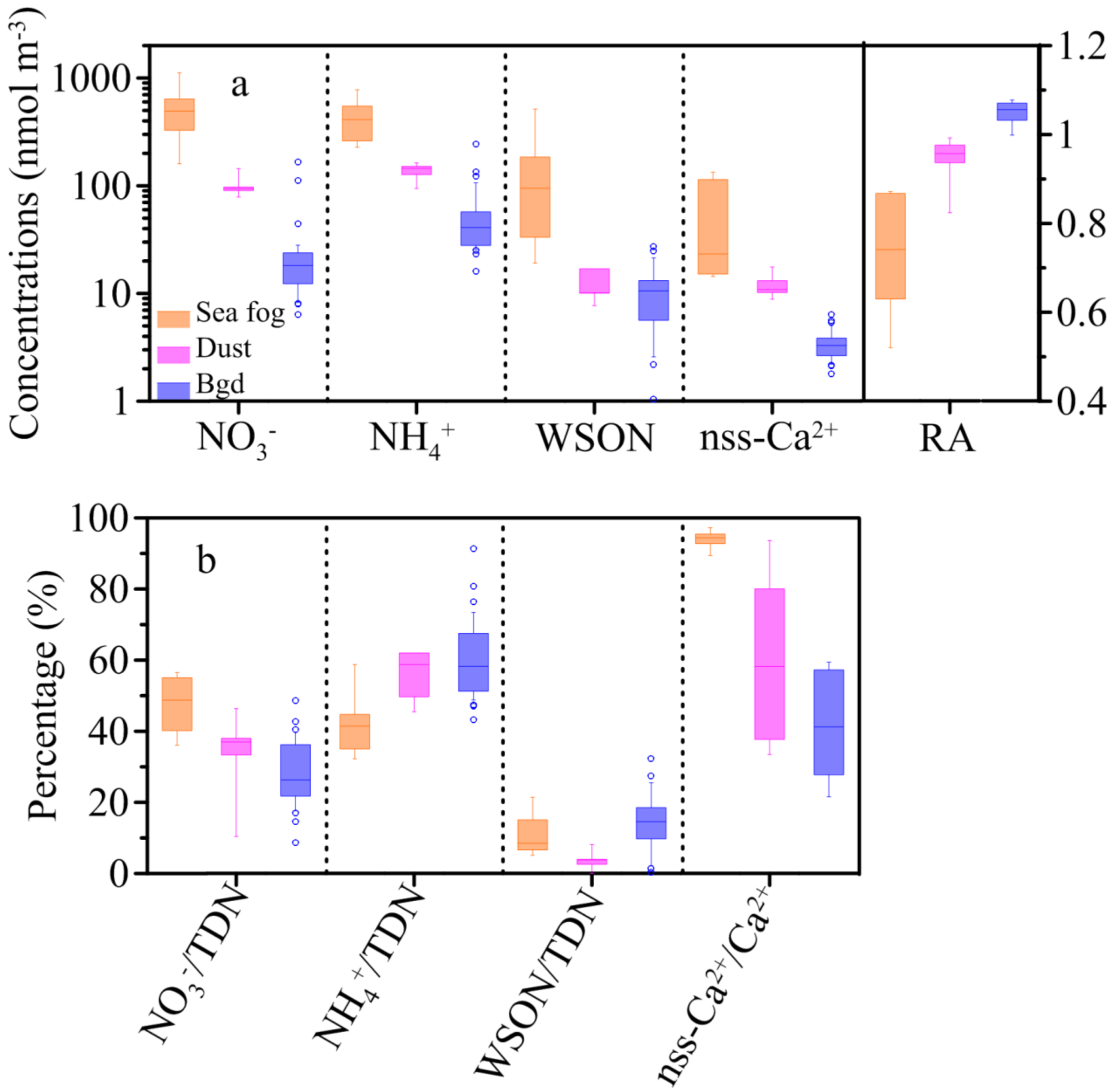
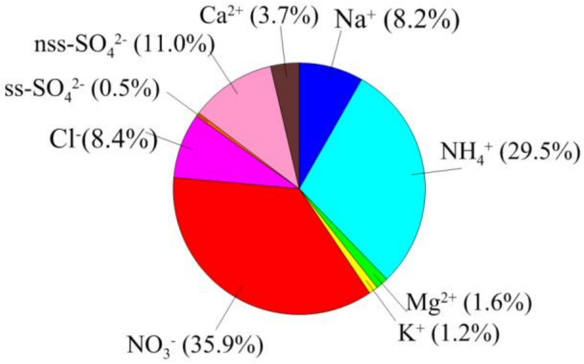
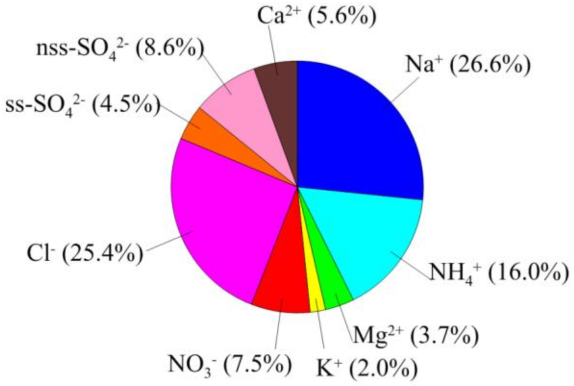


Figure 6. Box plots for (a) concentrations of NO_3^-, NH_4^+, WSON and nss-Ca^{2+}, and RA, and (b) fractions of nitrogen species in total dissolved nitrogen and proportion of nss-Ca^{2+} in Ca^{2+}, in sea fog modified, dust and background aerosols. The large boxes represent the inter-quartile range from the 25th to 75th percentile. The line inside the box indicates the median value. The whiskers extend upward to the 90th and downward to the 10th percentile.

(a) Sea fog in ECSs



(b) Dust in ECS



(c) Dust in Jeju

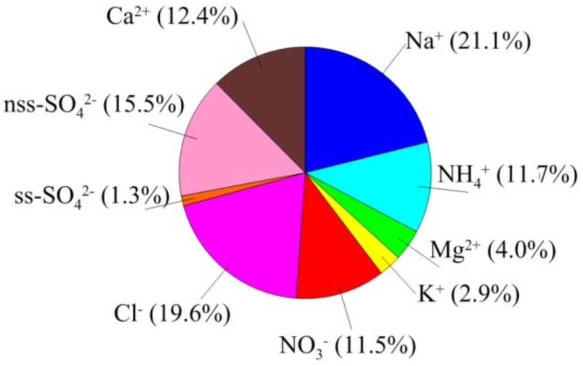


Figure 7. Pie charts of ion distribution for (a) sea fog modified aerosols (this study), (b) dust aerosols collected over the East China Sea (n = 8) (Hsu et al., 2010b), and (c) dust aerosols collected on the island of Jeju (n = 49) (Kang et al., 2009).

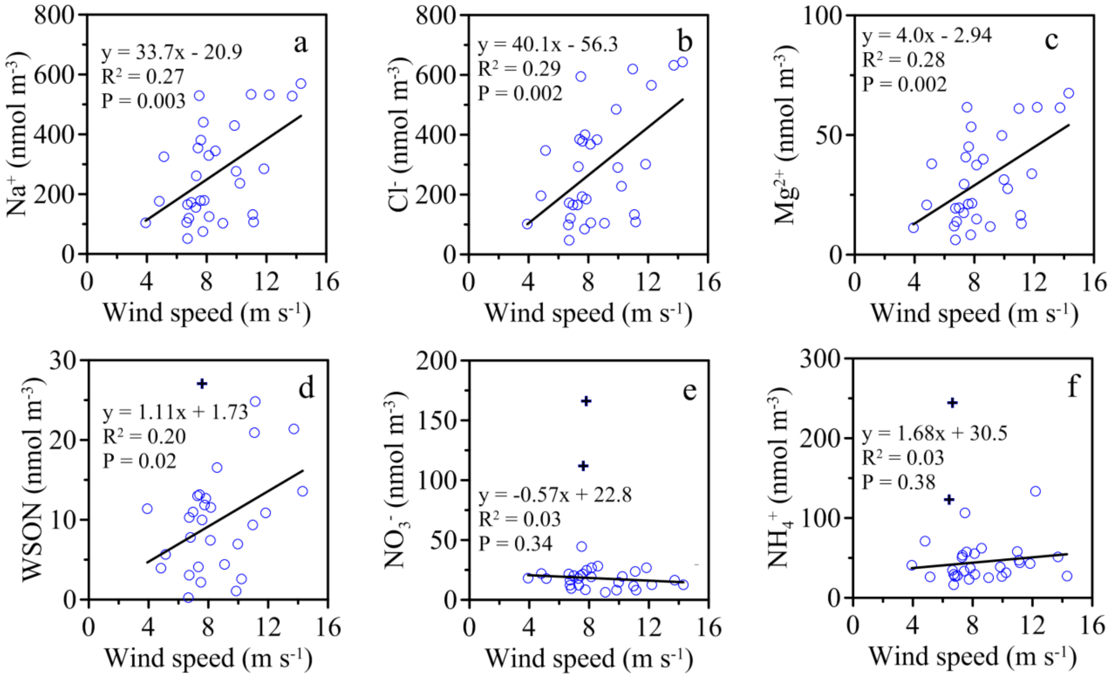


Figure 8. Scatter plots of concentrations of (a) Na^+, (b) Cl^-, (c) Mg^{2+}, (d) WSON, (e) NO_3^-, and (f) NH_4^+ against corresponding wind speed for background aerosols. Wind speed was derived by averaging wind speed (5 min average) in corresponding sampling intervals. Crosses in (d), (e) and (f) were not considered during the linear regression.

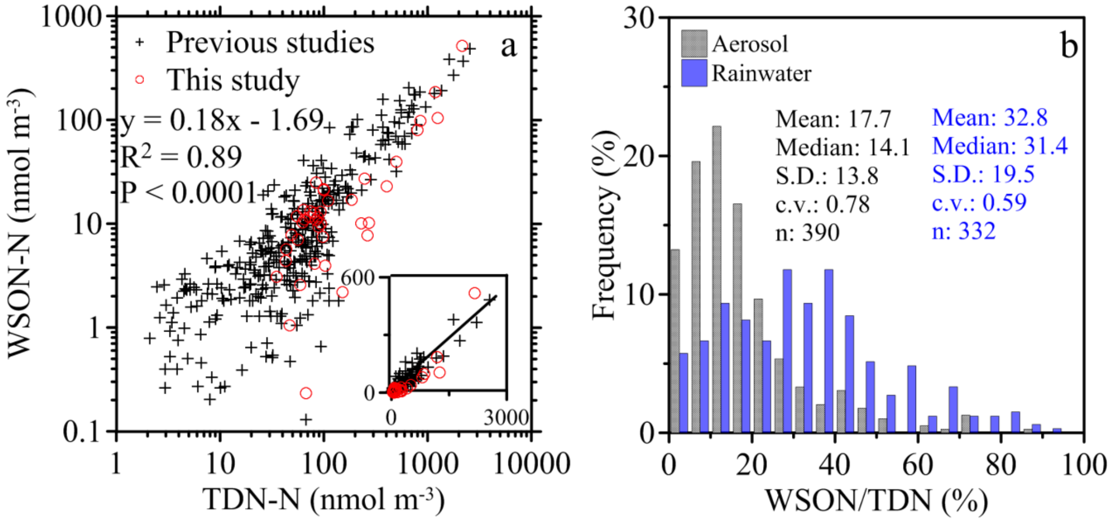


Figure 9. (a) Scatter plot of published aerosol WSON and TDN concentrations from the world (red circles for this study, black crosses from Lesworth et al., 2010; Chen et al., 2007; Mace et al., 2003; Miyazaki et al., 2011; Shi et al., 2010; Srinivas et al., 2011; Zamora et al., 2011; and Violaki et al., 2015). (b) Frequency histograms for percentage WSON in aerosol TDN (grey bars, data from Fig. 9a) and in rainwater (blue bars, data from Cornell, 2011; Zhang et al., 2012; Altieri et al., 2012; Cui et al., 2014; Chen et al., 2015; and Yan and Kim, 2015).

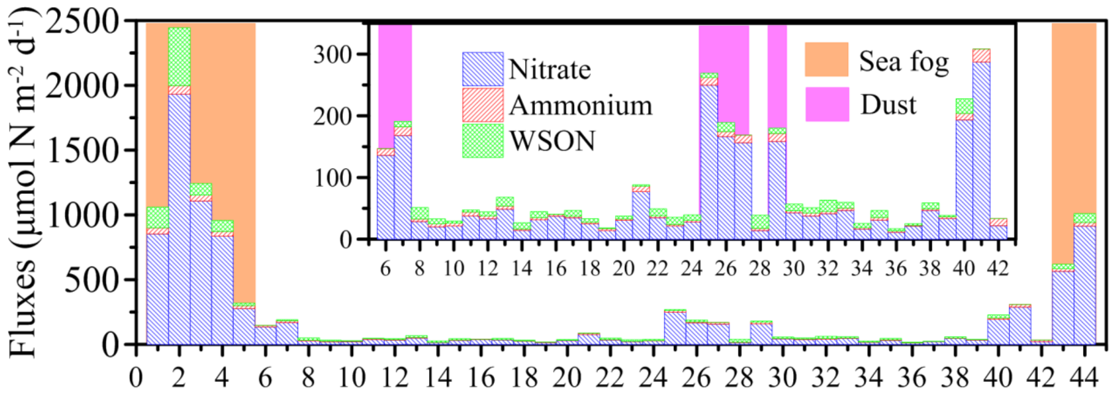


Figure 10. Dry deposition of aerosol nitrogen against sample identification. Nitrate is in blue, ammonium in red and WSON in green. Sample identifications, which matched with Table S1, are shown on the x axis.