

Response to All Referees' Comments

We sincerely thank two anonymous referees for providing insightful suggestions for the manuscript. Our responses to the comments are listed below. We also revised the estimate of terrestrial MSA/nss-SO₄²⁻ for the calculation of marine versus terrestrial contributions to aminiums.

Color Code: Referee's comments, [Authors response](#), [Proposed changes in manuscript](#)

1. Response to Referee #1

Abstract: It would be worthwhile to strengthen the abstract to increase the impact of the paper.

[Response: Thanks for the suggestion. We have revised the abstract.](#)

Line 17: What is the reason to group TMA and DEA together?

[Response: TMAH⁺ and DEAH⁺ cannot be completely separated by the Ion Chromatography columns, but the slopes of two calibration curves \(ratios of peak areas to injected mass loading\) are close to each other \(1.00E-02 vs. 1.03E-02 \$\mu\text{S min ng}^{-1}\$ \). Therefore, the sum of TMAH⁺ and DEAH⁺ concentrations \(named as TMDEAH⁺\) are quantified using the calibration curve of TMAH⁺ with errors less than 3%. We have added the explanation in section 2.2 and referred to previously published paper \(Zhou et al., 2018\) for details.](#)

[Lines 133-136: It should be noted that TMAH⁺ and DEAH⁺ could not be completely separated using the IC system \(VandenBoer et al., 2012; VandenBoer et al., 2011; Zhou et al., 2018; Huang et al., 2014\). Therefore, the sum of TMAH⁺ and DEAH⁺ concentrations \(named as TMDEAH⁺\) were quantified using the calibration curve of TMAH⁺ with errors less than 3% \(Zhou et al., 2018\).](#)

Introduction: I understand the authors focused on the aerosol phase aminium only, but it would be useful to discuss some gas phase measurements of amines as well, at least for those measured in the same region (e.g., Shanghai).

Response: Thanks for the suggestion. We have added the gas phase measurement results of amines and discussed the previous studies on gaseous and particulate amines together.

Lines 81-95: Many studies have been done on the gas and/or particle phases of amines over eastern China and adjacent seas (Huang et al., 2012; Hu et al., 2015; Zheng et al., 2015; Huang et al., 2016; Tao et al., 2016; Yu et al., 2016; Shen et al., 2017; Xie et al., 2018; Yao et al., 2018; Yao et al., 2016). For example, C1- to C6-amines over Shanghai were measured during the summer of 2015, of which C1-, C2- and C4-amines were the dominant species with the average concentrations of 15.7, 40.0 and 15.4 ppt, respectively (Yao et al., 2016). Zheng et al. (2015) measured an average concentration 7.2 ppt of total amines in a suburban site of Nanjing during the summer of 2012, derived mainly from industrial emissions in adjacent areas. The aminiums in fine particles over Shanghai in the summer of 2013 were found to exhibited a high concentration (mean 86.4 ng m^{-3}) and played an important role in the new particle formation events (Tao et al., 2016). Previous studies on aminiums over the marginal seas of China indicated that DMAH⁺ and trimethylaminium (TMAH⁺) were overwhelmingly from marine sources (Hu et al., 2015; Yu et al., 2016; Xie et al., 2018). In May 2012, the concentrations of DMAH⁺ and TMAH⁺ over the Yellow Sea (YS) and Bohai Sea even reached 4.4 and 7.2 nmol m⁻³, which was 1–3 orders of magnitude higher than those reported in other oceanic regions (Hu et al., 2015). These extremely high concentrations were thought to be associated with high biological activities. In spite of these field studies, the long-term observation of aminiums over the coastal sea and quantitative estimate of the contribution of marine biogenic source to aerosol aminiums are still lacking.

This is also related to the discussion of the source analysis of aminium and I would wonder how aminium and amines are related to each other. In particular, I would

suggest the authors to look at Yao et al. amine data in Shanghai to see what it the correlation or ratio of each amine vs aminium – roughly (considering different measurement times). See discussions in You, Y., et al. (2014), Atmospheric amines and ammonia measured with a Chemical Ionization Mass Spectrometer (CIMS), Atmos. Chem. Phys., 14, 12181-12194, for example.

Response: We compared our data with the gaseous amines measurement results by Yao et al. (2016) in Section 3.1. Besides, we added a short discussion about TEA's industrial source in Section 3.4.1.

Lines 184-192: According to previous measurement results for gaseous amines in the same site from July 25 to August 25 in 2015, the average mass concentrations of C2-, C3- plus C4-, and C6-amines were 80.4, 53.1 and 15.8 ng m⁻³, respectively (Yao et al., 2016). The order of concentrations was consistent with that of the corresponding aerosol aminiums in the summer of 2013 which was DMAH⁺ > TMDEAH⁺ > TEAH⁺ (9.1, 1.7 and 0.9 ng m⁻³, respectively) in this study. Based on these concentrations, the ratios of each amine vs. aminium were roughly calculated and C2-amines/DMAH⁺, (C3- plus C4-amines)/TMDEAH⁺ and C6-amines/TEAH⁺ were 8.8, 30.1 and 17.9, respectively. These values were comparable to the ratio of total amines to total aminiums (14.9) over a mountain site in southern China (Liu et al., 2018). Except for the three aminiums commonly detected in this study, MMAH⁺ and MEAH⁺ (Liu et al., 2018a; Ho et al., 2015; Shen et al., 2017) were other abundant aminiums detected in the urban site.

Lines 309-310: It was consistent with the observation result in a suburban site that gaseous C4- to C6-amines had some abrupt and frequent increase in the night and may be caused by some local emissions (You et al., 2014).

Related to this, it seems that we should not ignore the direction emissions of aminiums (rather than only focusing on those converted from the gas phase amines). The authors mentioned one example in the text but I am curious what is the status of the field.

Response: In general, there are very few studies about the aerosol aminiums contributed by primary marine source, and their conclusions are different. Over the North Atlantic, the size distributions of DMAH⁺ and DEA⁺ were analogy with those of nss-SO₄²⁻ and NH₄⁺ and the concentrations of aminiums and water soluble organic nitrogen (WSO_N) in the sea spray aerosols artificially generated by bubble bursting were below the detection limits, suggesting that secondary formation should be a dominant source of aminiums in marine aerosols (Facchini et al., 2008; Rinaldi et al., 2010). However, primary amines measured by Fourier Transform Infrared (FTIR) spectroscopy accounted for about 8% of PMF-derived marine factor of submicron aerosols over the southeastern Pacific, and the origin of marine factor was bubble bursting according to the characteristics of organic functional groups (Hawkins et al., 2010). Besides, FTIR measurements demonstrated that the submicron organic carbon was composed of 50% hydroxyl, 33% alkane and 14% amine in nascent sea spray aerosols artificially generated off the California coast (Bates et al., 2012) and of 55% hydroxyl, 32% alkane and 13% amine over the open ocean (Frossard et al., 2014). Recently, Aerosol Time-of-Flight Mass Spectrometry (ATOFMS) was used to investigate the composition and mixing state of submicron aerosols in the Antarctic sympagic environment and the contribution of primary marine source to alkylamines in ambient aerosols were estimated to be 11 – 25% (Dall'Osto et al., 2019). We have added the discussion on primary source of aerosol aminiums in the marine boundary layer.

Lines 63-70: In addition to gas-to-particle conversion which has been generally considered to be the major formation pathways (Facchini et al., 2008; Rinaldi et al., 2010), aminiums in marine boundary layer may also be generated with primary marine aerosols. For example, Fourier Transform Infrared (FTIR) spectroscopy measurements demonstrated that the submicron organic carbon was composed of 50% hydroxyl, 33% alkane and 14% amine in nascent sea spray aerosols artificially generated off the California coast (Bates et al., 2012) and of 55% hydroxyl, 32% alkane and 13% amine over the open ocean (Frossard et al., 2014). Aerosol Time-of-Flight Mass Spectrometry (ATOFMS) analyses of ambient aerosols in the Antarctic sympagic environment also

indicated that 11–25% of aminiums were contributed by primary marine source (Dall'Osto et al., 2019).

Lines 292-297: In addition, some studies have demonstrated that artificially generated sea spray aerosols and actual primary marine aerosol both contained amines/aminiums (Bates et al., 2012; Frossard et al., 2014; Dall'Osto et al., 2019). So we speculate that the elevated concentrations of aminiums at 0.32–0.56 μm over the eastern China seas may be also associated with the increased concentration of sea-spray aerosols which contain substantial primary aminiums. In other hand, the heterogeneous formation of secondary aminiums on the surface of sea spray aerosols cannot be ruled out (Yu et al., 2016).

Line 48: what is emission factor? Please check the unit?

Response: Emission factor means the mass of aminiums produced by unit mass of coal combustion and this term was adopted by Shen et al. (2017). We have changed the unit from mg kg^{-1} to mg (kg coal)^{-1} in Line 57.

Section 2.1: Table 1 shows the measurement periods at each site but it would be helpful if those dates are mentioned in the section as well.

Response: Thanks for the suggestion. We have added the sampling periods in this section.

Lines 109-111: A total of 131 samples were collected within four seasons with the sampling duration around 24 hours (spring: 25 Mar. – 26 Apr., 2013; summer: 16 Jul. – 17 Aug., 2013; autumn: 30 Oct. – 30 Nov., 2013; winter: 1 Dec., 2013 – 23 Jan., 2014) (Table 1).

Lines 114-118: $\text{PM}_{2.5}$ samples were collected in the summer of 2016 (4 Aug. – 18 Aug.) and size-segregated samples were obtained using a 10-stage Micro-Orifice Uniform Deposit Impactor (30 L min^{-1} , MOUDI, MSP Model 110-NR) and 47 mm PTFE filters

(Zeflour, PALL) between in the autumn of 2016 fall (12 Nov. – 3 Dec.), the spring of 2017 (11 Mar. – 19 Mar.) and 2017 the early and late summer of 2017 (22 Jun. – 9 Jul. and 27 Aug. – 12 Sep., respectively) (Table 1).

Line 117: How close were the sampling location of those trace gases (used here) to the Fudan measurement site?

Response: The data of trace gases used in this manuscript are average concentrations of 9 real-time monitoring stations in Shanghai (Figure C1), and Fudan sampling site is located in the northern part of these stations. The average distance of these 9 stations from Fudan site is 11.51 km and the farthest station (Chuansha) is only 23.52 km away. The historical data for single monitoring site are not available in official website. We obtained the monitoring data of 8 stations except Putuo during January–April 2015, and the time series of daily concentrations of gaseous pollutants for each station varied consistently (Figure C2). Therefore, it is reasonable to use the average concentrations of trace gases to represent Fudan site.

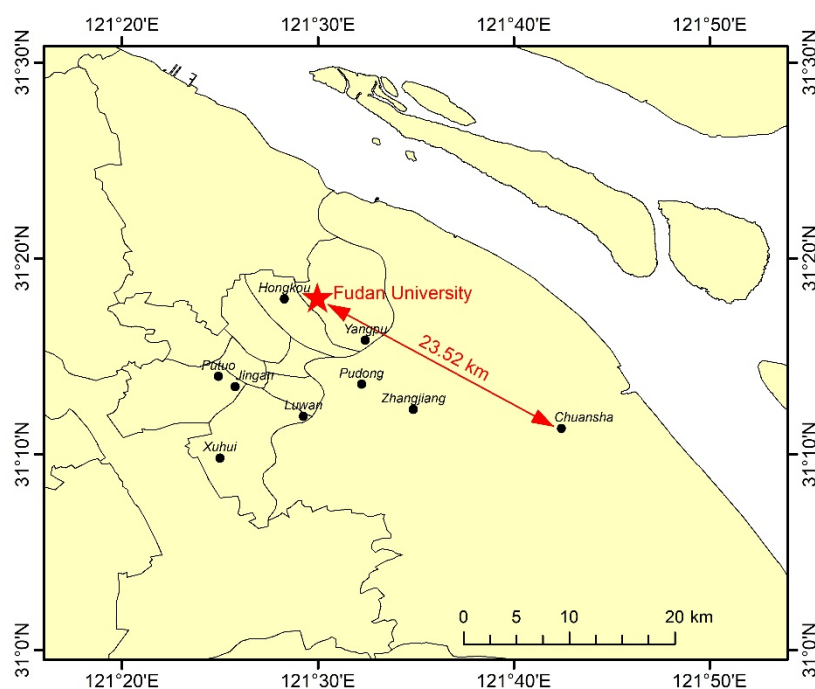


Figure C1. The locations of Fudan site and 9 real-time monitoring stations in Shanghai.

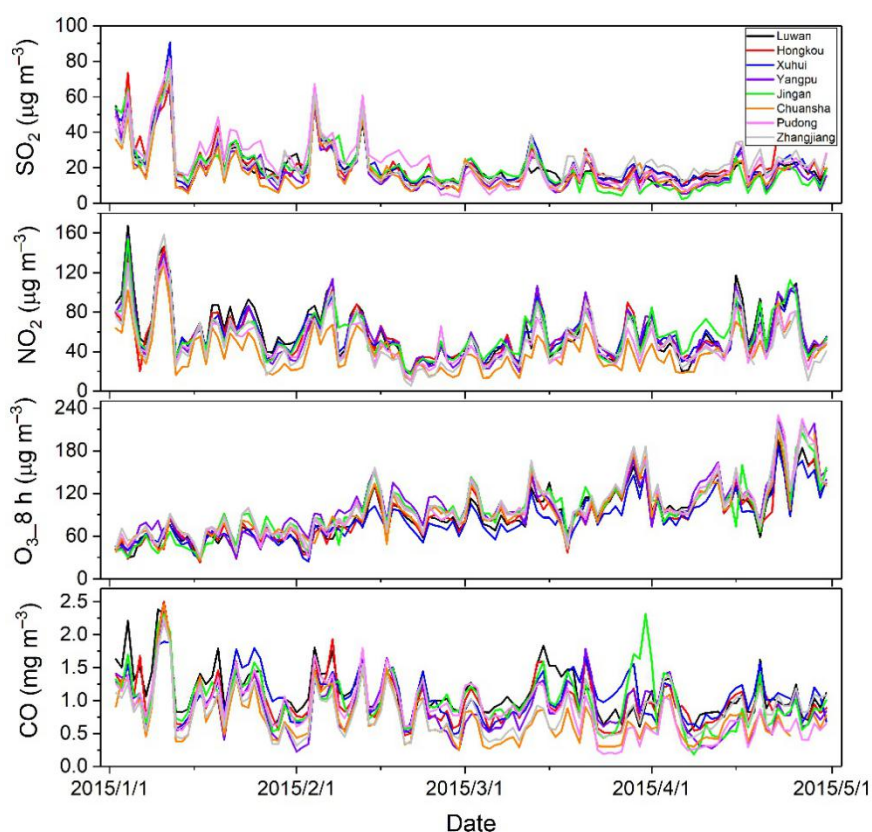


Figure C2. Time series of daily concentrations of gaseous pollutants in 8 monitoring stations during January – April 2015.

Section 3.2.2: You et al. ACP also found that gas-to-particle conversion is an important contribution to the aminiums in the aerosol phase. Please include the results shown Figure 6 in You et al. in Table 2.

Response: Thanks for the suggestion. We have added the measurements of aerosol aminiums by You et al. (2014) in Table 2.

Section 3.2: So, the emerging picture is that the winter time is favorable for higher aminium due to lower BLH, colder temperatures and less oxidation reactions. This is very interesting.

Lines 184-185: Need a ref at the end of the sentence?

Response: Previous discussion about the relationships between O₃ and aminiums was

too speculative (also indicated by referee#2), and therefore we have rewritten this part and the sentence has been deleted.

Lines 232-242: Negative correlations were found between aminiums/ NH_4^+ and O_3 concentrations in Shanghai during the summer of 2013 (Fig. 3c). In other seasons, the correlations were not obvious, especially in winter when O_3 concentrations were the lowest and neither of aminiums/ NH_4^+ was correlated with O_3 (Figure S3). In general, atmospheric oxidizing capacity is the strongest in summer (Logan, 1985; Liu et al., 2010), and the results verified that high oxidizing capacity in summer may reduce the formation of particulate aminiums by oxidizing gaseous amines. It was consistent with the diurnal pattern of gaseous amines with the lowest values at noon and the negative correlations between the concentrations of amines and O_3 observed in Shanghai during the summer of 2015 (Yao et al., 2016). It should be noted that there was no significant variation in temperature and little rainfall during the sampling periods in the summer of 2013. In other seasons, due to the relatively weak photochemistry and more complex sources and meteorology, other factors except oxidizing capacity played more important roles in affecting aerosol aminiums.

Section 3.2.4: The last sentence – fog and high RH are also favorable conditions for gas-to-particle conversion.

Response: We have rewritten this sentence as advised.

Lines 263-264: Therefore, fog and high relative humidity (RH) are also favorable conditions for gas-to-particle conversion of amines.

Section 3.3: The first paragraph – the mass fraction of aminiums is very high. Is this expected or not?

Response: This is expected. The size distributions of mass concentrations of aminiums are closely related to their formation mechanism. Previous studies have indicated that aerosol aminiums are mainly distributed in fine particles. For example, Tao et al. (2016)

found that aminiums had a mass distribution of ~74% in fine particles (PM_{1.8}) in the summer of 2013 over Shanghai. Aminiums over the western North Pacific and its marginal seas also demonstrated accumulation in fine particles, and the dominant modes varied with the phase state of aerosols and formation pathways (Xie et al., 2018). We have added the references to the manuscript.

Lines 269-271: This is consistent with the previous reports that >70% of aminiums were distributed in fine particles over Shanghai during the summer of 2013 (Tao et al., 2016) and over the western North Pacific and its marginal seas (Xie et al., 2018).

Line 216: How did you define the droplet mode and condensation mode sizes?

Response: We define the Stage 7 (0.56 – 1.0 μm) and Stage 9 (0.18 – 0.32 μm) of MOUDI as droplet mode and condensation mode, respectively. Such a definition is consistent with the traditional classification of aerosol modes based on observational results and thermodynamic calculation (John et al., 1990; Meng and Seinfeld, 1994; Seinfeld and Pandis, 2016).

Lines 238-239: Either here or in the conclusion, it would be useful to add some discussions, like “Our results consistently show that DMA was originated primarily from anthropogenic sources, as opposed to natural marine emission sources. Considering the unique role of DMA in new particle formation (Almeida et al., 2013), our results thus re-enforce that the frequent new particle formation events observed in extremely polluted Chinese cities are indeed, at least in part, due to amines (Yao et al., 2018).”

Response: Thank you for your suggestion and we have added the discussion in Section 3.4.1 and conclusion.

Lines 302-306: This suggests that anthropogenic sources may have a great contribution to the atmospheric DMA in Shanghai, which is consistent with previous findings in

Nanjing (Zheng et al., 2015). Considering the unique role of DMA in new particle formation (Almeida et al., 2013), our results re-enforce that the frequent new particle formation events observed in extremely polluted Chinese cities are indeed, at least in part, due to amines (Yao et al., 2018).

Lines 432-436: Our results indicated that marine biogenic emission of amines could not be ignored in the eastern coast of China, especially in summer. Therefore, it is necessary to add this source into the emission inventory of amines and recent modelling of amines over eastern China without marine source (Mao et al., 2018) may result in significant deviations. Besides, the role of amines in new particle formation over the open ocean is likely to be more important due to much less pollutants \compared to the coastal area, which should be further studied.

Minor suggestions:

Line 39: “other gases” should be “oxidation products” to be more specific?

Response: We have revised it.

Lines 42-44: Gaseous amines in the atmosphere can react with oxidants such as $\cdot\text{OH}$ and O_3 to form secondary organic aerosols (SOA) (Murphy et al., 2007) or gaseous oxidation products such as imines, formamides, nitrosamines and nitramines (Nielsen et al., 2012).

Line 80: remove “a” in “be a representative”. Line 96: remove the first “sample”. Line 105: change “might” to “may”. Line 130: “Differently” should be “By contrast”.

Response: Revised as suggested.

Line 143: “firstly” should be “for the first time” or “initially” or “previously”?

Response: We have revised it.

Lines 182-184: The aerosol TEAH⁺ concentrations in China were reported in our study for the first time and could not be compared to previous work.

Line 157: “improvement of diffusion condition” should be “enhanced diffusion”?

Response: We have changed it to “enhanced ventilation” (Line 204) by incorporating the suggestion of Referee#2.

Line 235: “on land” to “on the land”. Line 267: “judgement” to “analysis”? Line 267: “pointing directions of back trajectories” should be “forward directions of air mass trajectories”. Line 294: “The DMS” to “DMS”. Line 321: “Speculation” should better be “hypothesis” or “analysis”? Line 333: “Significantly” to “Significant”. Line 339: “Differently” should be “By contrast”. Line 348: “firstly” should be “for the first time”.

Response: Revised as suggested.

2. Response to Referee #2

The description of the chemical analysis for amines is missing some important information: 1) What is the full suite of aminium ions that could be detected (and was calibrated for) using the analytical method?

Response: We have added the description in the revised manuscript.

Lines 129-133: Six aminiums including DMAH⁺, TMAH⁺+DEAH⁺, propylaminium (MPAH⁺), triethylaminium (TEAH⁺), ethanolaminium (MEOAH⁺) and triethanolaminium (TEOAH⁺) could be effectively separated and measured using the IC method. The MMAH⁺ and MEAH⁺ in the aerosols could not be quantified because their peaks were obscured by the wide and distorted peak of NH₄⁺.

2) What were the limits of detection for the measurements of each aminium ion that was measured?

Response: We have added the detection limits for aminiums in aerosol samples.

Lines 136-140: With the sampling volumes of 144 and 86 m³ for PM_{2.5} and MOUDI samples respectively, the detection limits of DMAH⁺, TMDEAH⁺, TEAH⁺, MPAH⁺, MEOAH⁺ and TEOAH⁺ were 0.55, 0.78, 1.93, 2.59, 1.94 and 4.96 ng m⁻³ for PM_{2.5} samples and 0.20, 0.29, 0.71, 0.95, 0.56 and 1.82 ng m⁻³ for samples collected in each MOUDI stage. MPAH⁺, MEOAH⁺ and TEOAH⁺ were rarely detected in the aerosol samples (<10%) and thereby not reported in this study. The detailed information about analyses of aminiums were given in Zhou et al. (2018).

3) How were measurements that were below the detection limit incorporated into the subsequent data analysis, including the calculations of the mean and standard deviations at each site in each season.

Response: We have added the information in the revised manuscript.

Lines 159-161: It should be noted that TEAH⁺ concentrations over Huaniao Island and the YECS were mostly below the detection limits (<DL). For other aminiums and TEAH⁺ over Shanghai, the number of samples below detection limits were generally less than 30%. These undetectable concentrations were considered to be zero for the calculation of means and standard deviations.

This information is especially important because the authors go on to compare their observations with those reported from other studies. If their analysis technique was capable of measuring monomethyl- and monoethyl-amine (Lines 168-170), but did not find them above the detection limit, this is important information to include. The detection limits for the species should be included explicitly in the manuscript.

Response: We have added this information, and MMAH⁺ and MEAH⁺ cannot be quantitatively measured in our method as responded to question 1.

In Section 3.2, the authors correlate the speciated aminium loadings in the particle phase with various environmental variables. Given the time-integrated nature of the particle collection, some discussion should be made to the impact of averaging the variables over a full 24- or 48-hour collection interval.

Response: Thanks for the valuable suggestion. We have added a short discussion on it.

Lines 219-223: It should be pointed out that environmental variables like BLH and temperature are constantly changing with time and their impacts on aminium concentrations may vary within the sampling duration (24 or 48 hours). However, these variables must be averaged over the same time interval as aminium concentrations. This analysis may eliminate the instant discordance and improve the correlations between environmental variables and aminiums or aminiums/PM_{2.5}, and the results could well explain the seasonal variation of aminiums.

I do not find the analysis on the impact of oxidation on the aminium ions presented in Section 3.2.3 and Figure 3c and Figure 4 to be convincing. The relationship between the ratio of aminium/NH₄ versus ozone is only significant for TEAH⁺. For the other two aminiums, the need to separately derive a slope for a subset of the high ozone data suggests that the analysis is not robust. The accompanying text is too speculative. Similarly, the anti-correlation between particle phase aminiums and formate measured over the Yellow and East China Seas (Figure 4) could result from many different factors and there is no compelling evidence provided that it results from photo-oxidation.

Response: Thanks for the valuable comments. We have re-analyzed the correlations between ozone and aminiums and revised the text. We examined the relationships between oxidizing capacity and aminiums in each season in Shanghai and found that

all three aminium/ NH_4^+ were negatively correlated with O_3 in the summer of 2013. In the summer sampling period, there was no significant variation in temperature and only two samples encountered rainfall events, and thereby the anti-correlation between aminium/ NH_4^+ and oxidizing capacity was credible.

We agree that the concentrations of aminiums over the YECS could be affected by many other factors, such as marine productivity, boundary layer height, ambient temperature and cloud processing and the number of samples was also small (only 9 sets of amples). Therefore, previous discussion about the relationship between aminium concentrations and photo-oxidation is not robust and we have deleted this part.

Lines 232-242: Negative correlations were found between aminiums/ NH_4^+ and O_3 concentrations in Shanghai during the summer of 2013 (Fig. 3c). In other seasons, the correlations were not obvious, especially in winter when O_3 concentrations were the lowest and neither of aminiums/ NH_4^+ was correlated with O_3 (Figure S3). In general, atmospheric oxidizing capacity is the strongest in summer (Logan, 1985; Liu et al., 2010), and the results verified that high oxidizing capacity in summer may reduce the formation of particulate aminiums by oxidizing gaseous amines. It was consistent with the diurnal pattern of gaseous amines with the lowest values at noon and the negative correlations between the concentrations of amines and O_3 observed in Shanghai during the summer of 2015 (Yao et al., 2016). It should be noted that there was no significant variation in temperature and little rainfall during the sampling periods in the summer of 2013. In other seasons, due to the relatively weak photochemistry and more complex sources and meteorology, other factors except oxidizing capacity played more important roles in affecting aerosol aminiums.

In Section 3.4.3 the authors present an interesting approach to deriving the relative marine versus terrestrial contributions to the particle phase aminium ions by examining the relationship between the ratio of aminium/ NH_4^+ to $\text{MSA}/\text{SO}_4^{2-}$. The strong relationship between these two ratios indicates the possible value of this approach. However I wonder if the authors have considered the following factors in extracting quantitative values from this method: 1) while MSA and sulfate both have very low

volatility, ammonia and amines are very volatile, therefore the particle phase measurements of the S-containing species are likely very consistent with the emission ratios (of DMS and SO₂), whereas the measured ratio of particle phase aminium/NH₄⁺ may not correspond very closely to the emission ratios of amines and ammonia; this is in part because 2) the thermodynamic favourability of gas-particle partitioning the amines and ammonia are slightly different (depending on the phase and pH of particles), so the observed aminium/NH₄⁺ ratio could vary with the chemistry of the particles and not just the emission ratios of amines and ammonia. Can the authors comment on how much this might influence the robustness of their terrestrial vs marine source apportionment?

Response: Thanks for the insightful questions. 1) The approach used for estimating the marine source of aminiums was based on the close relationships between both aerosol aminiums and MSA and marine biological activities especially during warm seasons. Differently, NH₄⁺ and SO₄²⁻ in aerosols over the coastal ECS were mainly derived from anthropogenic sources. Aminiums and MSA had different transformation processes and thermodynamic properties as indicated by reviewer#2, and a poor relationship was found between their concentrations in summer (Figure C3). Nonetheless, the use of aminium/NH₄⁺ ratios was able to eliminate the effects of gas-to-particle partitioning to some extent. Accordingly, MSA concentrations were divided by nss-SO₄²⁻, and the ratios could represent the influencing extent of marine biogenic source. Based on the strong relationship between aminium/NH₄⁺ and MSA/nss-SO₄²⁻, the proportion of marine source to aminiums could be obtained.

2) We agree that aminium/NH₄⁺ ratios could vary with the chemistry of aerosols due to slightly different gas-to-particle partitioning of the amines and NH₃. For example, amines have stronger affinities than NH₃ for the mostly organic phases and aminium/NH₄⁺ ratios in these phases are larger than those in the mostly water phase (Pankow, 2015; Xie et al., 2018). The NH₃/amines exchange reaction is also related to solid phase state of aminium salts (Chan and Chan, 2013). Moreover, marine aminiums may also partially originated from primary source, which makes this issue cannot be

completely considered from the perspective of gas-to-particle partitioning. Our discussion was constrained on the source analysis of aerosol aminiums, which assumed that the aminium/ NH_4^+ derived from terrestrial and marine sources both had relatively conservative values and the ratios measured in aerosols were mixture of the two end-members. We recently analyzed the aerosols collected in Huaniao Island during the winter of 2017, and the data (aminium/ NH_4^+ vs. $\text{MSA}/\text{nss-SO}_4^{2-}$) also distributed near the linear fitting lines obtained according to the data of the autumn of 2016 and the summer of 2017 (Figure C4). This indicates that relationship between aminium/ NH_4^+ and the proportion of marine source is universal (Figure 13), at least, over Huaniao Island. In other words, the values of aminium/ NH_4^+ from terrestrial source were in a relatively narrow range compared to those from marine source. Therefore, applying this approach to extract quantitative contributions of two sources is reasonable.

Although there are a certain degree of uncertainties, our method is the first attempt to calculate the contributions of marine biogenic and terrestrial sources to aerosol aminiums over the coastal sea, which will provide an insight of sources and roles of amines in the atmosphere.

We have added a short discussion in the revised manuscript.

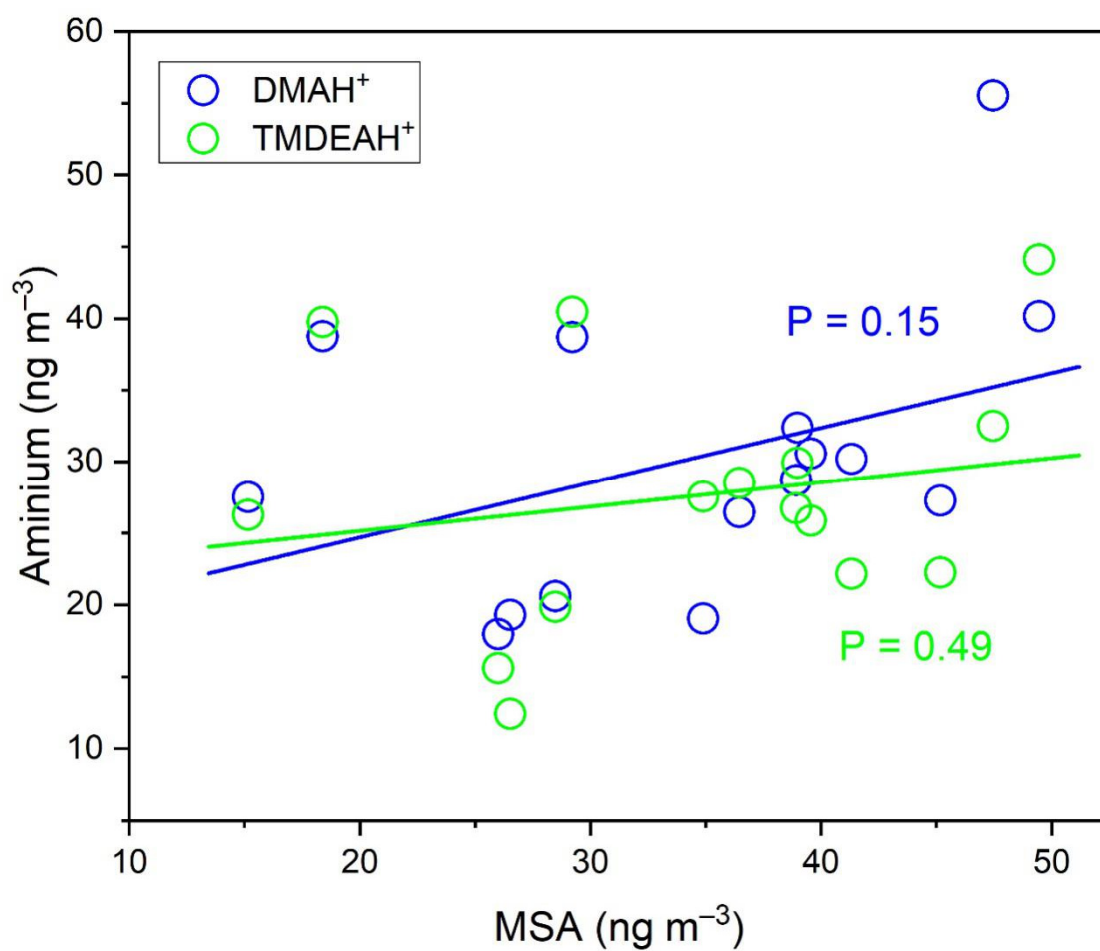


Figure C3. Correlations between aminiums and MSA in the summer of 2017 over Huaniao Island.

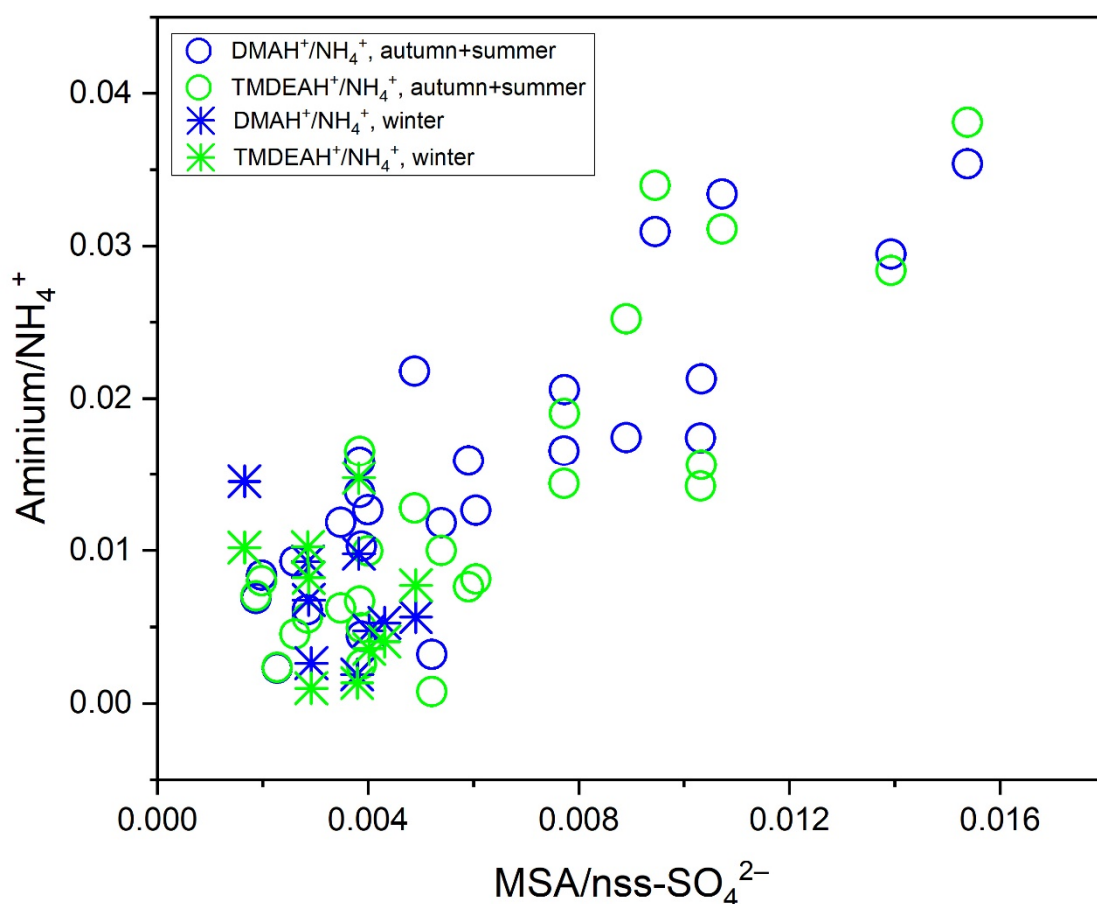


Figure C4. Relationships between aminoium/ NH_4^+ and $\text{MSA}/\text{nss-SO}_4^{2-}$ over Huaniao Island during the autumn of 2016, the summer and winter of 2017.

Lines 397-400: It should be pointed out that aminoium/ NH_4^+ ratios could vary with the chemistry of aerosols due to slightly different gas-to-particle partitioning of the amines and NH_3 (Chan and Chan, 2013; Pankow, 2015; Xie et al., 2018) and marine aminoiums may also partially originated from primary source as discussed above. Therefore, our discussion is constrained on the source analysis of aerosol aminoiums, but not gaseous or total amines (gaseous amines + aerosol aminoiums).

Lines 404-407: Nonetheless, our method is the first attempt to calculate the contributions of marine biogenic and terrestrial sources to aerosol aminoiums over the coastal sea, which will provide an insight of sources and roles of amines in the atmosphere.

Section 3.2.1 – ‘Diffusion’ is not the right term to distinguish the differences in dilution or ventilation under different wind speed and boundary layer height conditions.

Response: Thanks. We have changed them as below.

Lines 204: “due to the enhanced ventilation.”

Lines 208-210: Thus, the generally stagnant meteorology in winter (Liu et al., 2013) could cause a substantial accumulation of aerosol aminiums and lead to the seasonal variation of aminiums in Shanghai.

Figure 3 caption should specify that this analysis is only for the Shanghai data.

Response: We have corrected it.

Lines 698-700: **Figure 3. (a)** Relationships between concentrations of aminiums and boundary layer height (BLH) over Shanghai in 2013. **(b)** Relationships between mass ratios of aminiums and NH_4^+ to $\text{PM}_{2.5}$ and temperature over Shanghai in 2013. **(c)** Relationships between mass ratios of aminiums to NH_4^+ and O_3 concentrations over Shanghai during the summer of 2013.

Figure 7 – would be easier to read if there was a line (or a different symbol) indicating the average value for a rather than a bar that arbitrarily extends to a value of 1.

Response: This is a good suggestion and we have made a revision.

Line 292 – ‘fold’ should be ‘factor’

Response: Revised.

Line 296 – ‘folds’ should be ‘times’

Response: Revised.

3. The revision of estimating terrestrial MSA/nss-SO₄²⁻

In previous version of the manuscript, we used the average of 5 smallest values of MSA/nss-SO₄²⁻ in the winters of 2014 and 2015 to represent the terrestrial MSA/nss-SO₄²⁻. However, according to recent analysis of multiyear observation data of MSA and nss-SO₄²⁻ over Huaniao Island, we found that MSA/nss-SO₄²⁻ increased with the increasing retention percentage of air mass over the land (R_L) in the winter, and the terrestrial MSA/nss-SO₄²⁻ could be larger than marine MSA/nss-SO₄²⁻. In addition, terrestrial MSA/nss-SO₄²⁻ in different seasons were slightly different. Therefore, it is more reasonable to extract the value of terrestrial MSA/nss-SO₄²⁻ by identifying the samples dominantly controlled by terrestrial air masses for the autumn of 2016 and the summer of 2017 and to calculate the average MSA/nss-SO₄²⁻ in these samples. Fortunately, we have simultaneously measured MSA and nss-SO₄²⁻ in a total of 64 TSP samples collected in these two seasons. The R_L was calculated for each sample based on three-day backward trajectories (Figure S9 and see supplementary text for more information). Samples with the largest 10% R_L values (n=7, R_L>74%) were considered to be terrestrial-dominant with the average MSA/nss-SO₄²⁻ (± 1 standard deviation) of 0.0021±0.0013. Therefore, this value was regarded as the terrestrial MSA/nss-SO₄²⁻ in these seasons and used in the calculation of source contributions to aminiums. As a result, the specific values in Table 3 were also changed. But the main conclusion was not influenced by this revision.

Lines 383-388: We have simultaneously measured MSA and nss-SO₄²⁻ in a total of 64 total suspended particle (TSP) samples collected in the autumn of 2016 and the summer of 2017. The retention percentage of air mass over the land (R_L) was calculated for each sample based on three-day backward trajectories (Figure S9 and see supplementary text for more information). Samples with the largest 10% R_L values (n=7, R_L>74%) were considered to be terrestrial-dominant with the average MSA/nss-SO₄²⁻ (± 1 standard

deviation) of 0.0021 ± 0.0013 . Therefore, this value was regarded as the end member value of terrestrial $\text{MSA}/\text{nss-SO}_4^{2-}$ in these seasons.

Supplement:

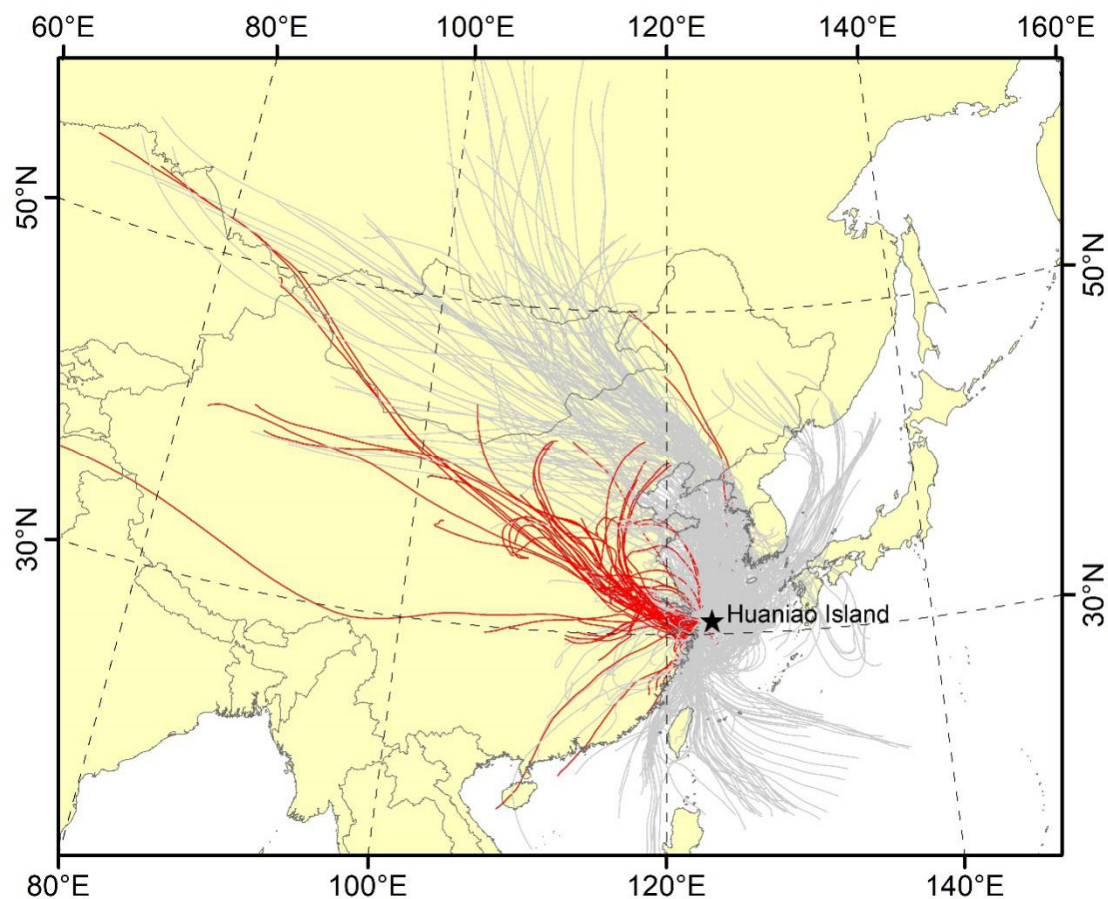


Figure S9. The three-day backward trajectories starting from Huaniao Island during the autumn of 2016 and the summer of 2017 corresponding to TSP samples. A new trajectory was calculated every 3 hours during the sampling period of each sample. The red trajectories corresponded to the samples identified as terrestrial dominated.

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