Response to anonymous referee #1’s interactive comment on the manuscript “Atmospheric aerosol compositions over the South China Sea: Temporal variability and source apportionment” point by point below.

The manuscript by Xiao et al. presents a very detailed and comprehensive study of total suspended particulates (TSP) in the South China Sea. TSP was collected for the period of one year, covering all seasons, and analyzed for major ions. A variety of source apportionment methods, such as correlation analysis, principal component analysis, back trajectory analysis and positive matrix factorization, were applied to reveal the regional and source-specific origins of TSP. In addition, results are compared to previous studies from the literature and put into wider context.

Generally, this study is of scientific interest as it provides lots of detailed information on TSP in a region where various types of anthropogenic pollution as well as natural emissions from the sea contribute to the local aerosol load. However, this study shows a lack of methodological detail, the discussion is partly redundant and confusing, and a coherent storyline is missing. While this work is certainly worthwhile to be published, I recommend major revisions as detailed below.

General comments

1. The applied analysis methods must be explained in more detail. In particular, there is no information on the methodologies behind concentration weighted trajectories (CWT), the principal component analysis (PCA) and positive matrix factorization (PMF). It is not sufficient to provide references without explaining the methodology in the text. The reader must be able to understand what the authors did, on a general level, without consulting further literature. In addition, there is no information on how many blanks were produced and in which intervals. In the following I will elaborate a bit on how the PMF related part can be improved. I have less expertise for PCA and CWT but would recommend that the authors check very carefully what the standard for reporting is in the literature and include the respective information this in the manuscript. For instance, with which program were the back trajectories run, Hysplit, Flexpart, Lagranto or other.? What are the uncertainties in relation to the covered distance from the receptor?

Response: Thank you for your suggestion. We have added more information about the applied analysis methods in Section 2.4 and 2.5 (see detail information in supplementary text S2 and S3).

According to your general comments 3 and 4, we delete the analysis methods of PCA.

2. With regards to PMF, it is well established in the literature which aspects need to be explained at least (e.g., Zhang et al., 2011). In the presented manuscript, the authors do not describe how they prepared the error matrix and especially how they dealt with combining errors from different measurement techniques (i.e. TSP vs major ions). This can be very difficult and has a large effect on the results, please see for example (Crippa et al., 2013) for details. Did the authors downweight any component of the input matrix? In fact, the input matrix is not even described. Furthermore, the authors do not discuss how many solutions they explored (e.g. 1-10 solutions), the number of fpeaks and seeds and their range etc.

With regards to reporting of PMF results, here again a large discrepancy exists between what one would expect to see and what is actually reported (please see again Zhang et al., 2011). For example, as an absolute minimum the time series and profiles of the chosen factors need to be shown and discussed. Based on the presented information, I am unable to review the credibility of the presented results, because in addition to lacking methodological information, I do not know how similar or different the resulting factors are. What are the correlation coefficients between the factor time series and profiles? How do these factors relate to external variables, e.g. meteorological parameters? On the basis of what are the selected factors justified? Etc. All this information needs to be included, before the manuscript can be considered for publication.

Response: Thank you for providing literatures and suggestions. We recalculate the PMF results using PMF5.0 (United States Environmental Protection Agency, EPA) according to the methods of Zhang et al. (2011) and EPA PMF5.0 user guide (Norris et al., 2014), more information was described in Section 2.5 and its supplementary text S3.

In the revised manuscript, all ions were re-calculated without TSP concentrations. The uncertainties by ionic species were provided by the analytical library and we used the uncertainties as error matrix (Norris et al., 2014), and used ionic species and sampling time as input matrix. We downweighted Fe and F^- since they had low signal-to-noise ratios (S/N), and there were no excluded species and samples.

In addition, we added two figures of profiles and time series.

Figure 9 Profiles of five sources identified from the PMF 5.0 model, including sea salt (two species), crust, secondary inorganic aerosol and oceanic emission.

Figure 10 Time series contributions from each identified sources, including sea salt (two species), crust, secondary inorganic aerosol, and oceanic emission.

3. The manuscript is lengthy. This is in part due to redundancy in the discussion of results from different source apportionment methods, see specific comments. I suggest shortening the discussion section and focusing on a few findings instead of discussing all details. The manuscript is partly confusing for the reader and in the end it is not clear what the main points are. A consistent story line needs to be crafted.

Response: Yes, the manuscript is lengthy. We have streamlined the manuscript from 19 pages to 15 pages, excluding references.

We have deleted Lines 50-65, section 3.3.1 and 3.3.2, and other sentences in pre-revised manuscript. At the same time, we reorganized the manuscript in some sections and moved some information about the methods of Sample collection and chemical analyses (S1), Back trajectories and CWTs analysis (S2), and PMF model (S3) into supplementary text.

4. The authors use a suite of source apportionment techniques, however it is not clear what the added value is. This is due to the fact that the results are discussed one after another separately per method and no connection between them is established. Often this results in repetitive discussion. Each technique has its strengths and weaknesses that are hardly exploited in this work. When applying so many methods, I would expect that e.g. the CWT are used to supplement PMF results where the PMF results show ambiguities, or that PCA is used in addition to CWT because CWT cannot determine specific source types which PCA can help with. Conversely, CWT are helpful to determine regional provenance of TSP which PCA or PMF cannot provide. Also, in some instances, results are contradictory (see specific comments), this is however not discussed. Such discrepancies need to be addressed rather than focusing only on confirmative results.

Response: Thank you for your suggestion. In the revised manuscript, we combined CWT with PMF to explore source identification, apportionment, and region. It was shown in the new section 3.3.

5. As indicated in the specific comments sections, references are sometimes missing, while in other instances it is not clear what exactly the authors refer to in a study when providing a reference.

Response: Thank you. We have added some references in the manuscript.

Specific comments:

l. 30f: It is not clear what you mean by "Na^+ and Cl^-….made up 74 % and 82%..." These numbers clearly don't add up and information on the reference is missing.

Response: We revised the sentence in Lines 31-32.

l. 31f: What is marine aerosol in this context? How was it determined?

Response: Marine aerosols in the paper refer to those sampled at Yongxing Island over the South China Sea.

l. 34: Already in the abstract NH_4^+ is claimed to originate from marine biogenic sources. However, throughout the manuscript there is no explanation what these marine biogenic sources are, which seasonality they follow and how the measured ammonium is related to marine biological activity. Without this information, I am not convinced that the ocean is the primary source of ammonium.

Response: We change "marine biogenic sources" to "oceanic emission" in the manuscript. In addition, according the results of CWTs, air masses with high concentrations of ammonium were from the open ocean, so we suggest that ocean may be the primary source of ammonium.

l. 38f: what about the role of climate? This first sentence could use some more references since many factors are mentioned.

Response: Thank you. We have revised the sentence in Lines 39-42.

l. 40: What are "complex sources"? I could imagine that the authors wanted to express that aerosols have many sources which create a complex mixture of aerosol components? What about mineral dust emissions from wind opposed to rock weathering? Also, references are missing.

Response: Yes. We have revised the sentence in Lines 42-47.

l. 44: I find the list of aerosol components random. E.g. organics are not mentioned while it has been shown that they constitute an important fraction of aerosol chemical components. Also BC is not mentioned.

Response: We have added these information to the revised manuscript (Lines 47-49). Thank you.

l. 45: This statement is not differentiated enough. Some parts of the world have undergone significant socio-economic growth in the past decades, such as East Asia, which has led to much higher emissions. In other parts of the world, emissions have decreased due to stricter air quality legislation. This should be reflected in this sentence or the focus should clearly be on East Asia, the region relevant for the South China Sea (SCS).

Response: Thank you for your suggestion. We have revised in Lines 49-51.

l. 50 – 65: The purpose of this paragraph is not clear. What is the point of discussing aerosol deposition and ocean productivity in the context of this particular manuscript? If the idea was to provide a brief review of particulate pollutants to the ocean atmosphere it is not clear why only nitrogen containing compounds are mentioned? Also I do not see the value of reporting observation from many different locations. I would suggest focusing on what is known about the SCS and report on aspects that are of relevance to TSP observations as presented in this manuscript.

Response: Thank you. We have deleted in this paragraph.

l. 75: What is the difference between “aerosols and pollutants” in this context? Do the authors want to distinguish between natural and anthropogenic sources or particulate and gas phase pollutants?

Response: Yes. Thank you.

l. 79: Is there not a more recent reference for biomass burning emissions and resulting deposition?

Response: We have added more two recent references.

l. 95 f: a reference is missing.

Response: Thank you. We have added them.

l. 97: "In the present study, it was…" What is meant by "it"?

Response: The sampling period. We have revised it.

l. 101: What is the "local southeast"?

Response: Local and short air masses. We have revised it.

l. 101: Since the variations of temperature and the difference between what is called the "cold" and "warm" seasons are very small some more information is needed on how seasons were separated and why. Especially what qualifies as transition season?

Response: In the manuscript, we separated the seasons based on the primarily air masses directions. In generally, the temperature was lower when air masses were primarily from northeast; while the temperature was higher when air masses were primarily from southwest. The air masses of transition season were changed from northeast to southwest when cool season changed to cool season. In some year, the air masses of transition season were changed from southwest to northeast when warm season is changing to cool season. But it was not found in our sampling period.

l. 122f: what do the relative standard deviations refer to? Repeated measurements of a standard, a blank or something else? What about the number of blanks that were generated in the course of the year? Please include more detailed information.

Response: Repeated measurements of a standard. Three blank filters were taken from each package (25 filters).

We have added the detailed information in the revised manuscript (supplementary text S1).

l. 139: In how far do these references reflect what the authors did? These references point towards different tools for running PMF.

Response: We recalculate the PMF results using PMF5.0 (United States Environmental Protection Agency, EPA) according to the methods of Zhang et al. (2011) and EPA PMF5.0 user guide (Norris et al., 2014), more information was described in Section 2.5 and supplementary text S3.

l. 149: TSP mass concentrations are compared to those in other cities. The authors write “around the world”, however the references point only towards Asian cities. It is fine to compare to Asian cities only, but this should be made explicit, i.e. state the locations and reference TSP concentrations there.

Response: Thank you. We have deleted this comparison.

l. 151f: Again provide numbers for reference. Where are those places, why are they comparable?

Response: Thank you. We have deleted those places.

l. 155f: This paragraph is not readable. A table is preferable.

Response: Thank you. We have added a table.

Table 1 Annual average, minimum and maximum mass concentrations (μg/m^3) of TSP and aerosol chemical species at Yongxing Island.

	TSP	Na^+	Cl^-	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	NO_3^-	NH_4^+
Annual	89.6 ± 68.0	4.00 ± 1.88	7.73 ± 5.99	0.33 ± 0.22	2.15 ± 1.54	0.44 ± 0.33	5.54 ± 3.65	1.95 ± 1.34	0.07 ± 0.07
Minimum	16.4	0.90	0.39	0.06	0.17	0.02	0.52	0.10	0.01
Maximum	440.1	8.86	36.47	1.13	9.65	1.55	23.34	10.05	0.32

l. 162: What does the value in parenthesis represent? An annual average? What is the standard deviation?

Response: An annual average. However, we did not found the standard deviation in their papers.

l. 164: Again providing numbers for references is needed.

Response: OK. The revised sentence was shown in Lines 138-142.

l. 166: Here Fig. 5 is mentioned, while Fig. 4 has not yet been referred to. Please check the order of the figures.

Response: Thank you. We have re-checked the order.

l. 172: What is the “global ocean”? This expression is used various times. Please replace it by a more accurate description of what is meant, e.g. “among all locations”

Response: Thank you. We revised “global ocean” as “among all locations” in the manuscript.

l. 174: Are the dead corals under water or exposed to the atmosphere? If they are not exposed, I don’t understand how they can contribute to the measured calcium.

Response: Thank you. We have deleted this.

l. 175: Starting from here, the authors refer to some major ions as non-sea salt ions. However, it is not explained in the manuscript how sea salt and non-sea salt contributions to ions were determined. Please include this information in the methods section.

Response: Thank you for your suggestion. We have added this information in section 2.3.

l. 179: How can the authors show that the Sahara Desert is a source of dust for the measurement location? The way the information is provided is not convincing.

Response: Sorry to make a misunderstanding about this. We revised this sentence in Lines 158-159.

l. 179 f; l. 202: What do the authors want to say with “average Mg2+ concentrations” being “nearly consistent with…Na+”? Or NO3- concentrations “were often consistent with those of nss-SO42-“. Do the authors refer to the ion balance? Please explain and change the formulation in the manuscript.

Response: We have revised them in Lines 159-161 and Lines 187-189.

l. 201: references are missing.

Response: We have added them.

l. 216f: “most other studies”. Are there only the four that are cited or more? What are their locations? What are those studies about?

Response: Thank you. We have revised them in Lines 202-204.

l. 222: Why “many other studies” when only two are cited. Again, which locations do these studies refer to?

Response: Thank you. We have revised it in Lines 208-209.

l. 223: How can TSP and rainfall not be related if some major ions are influenced by TSP?

Response: Precipitation is a complex process that can lead to both increases in TSP (e.g. via gust fronts etc.) and decreases through wet deposition. In addition, relevant processes can occur on time scales below the four-day sample period of the filter samples (anonymous referee #2's interactive comment).

So, we have deleted this sentence.

l. 228: What is meant by "particle wetting and interaction"? From the previous paragraphs I understand that there is more rain during the warm season. So my guess would be that particle activation and scavenging is happening. Do the authors refer to aerosol cloud interactions?

Response: Thank you. We have revised them in Lines 212-214.

l. 241: This suggests, it doesn't show.

Response: OK.

l. 255 before and after: It is not clear to me, why the authors do not discuss the concentrations and ratios of major ions that may originate from sea salt in the context of their ratios in sea salt. The authors even provide a table with typical major ion ratios in sea salt but do not refer to it. The discussion could highly benefit from this addition at this point.

Response: Thank you for your suggestion. We have added the discussions of the concentrations and ratios in the manuscript. For examples:

As shown in Fig. 5, Tables 1 and 2, similar trends and strong correlation were observed among Na^+, Cl^- and Mg^{2+}, and the ratios of Mg^{2+} to Na^+ in aerosols were close to that in seawater, suggesting that Mg^{2+} may mainly derive from sea salt rather than continental sources.

l. 257: What do the authors mean with "complex"?

Response: We revised "complex" to "different".

l. 258: Please specify what is meant with “phenomenon”.

Response: It mean the same with rainwater at Yongxing Island. We revised it in Lines 234-235.

l. 259: How does the study of Moody et al. compare with this work? Why is it comparable?

Response: We have deleted it.

l. 269: Biomass burning is not a major source of sulfur containing species compared to other sources. Why do the authors refer several times to biomass burning as source of SO2 in the manuscript?

Response: Thank you for your suggestion. We have revised them.

l. 276: I suggest reformulating this sentence: “Lawrence and Leliveld (2010) attributed x % of NOx emissions to…” In the current form it sounds like these values were recently measured.

Response: Thank you for suggestion. We have revised and moved to section 3.3, in Lines 375-376.

l. 291: which time period is reflected?

Response: 2011. We have added it.

l. 296: What about the influence of anthropogenic activities?

Response: Thank you. We have added the information in the manuscript in Lines 265-266..

l. 330: What are “dynamic” smoke surface concentrations?

Response: We deleted “dynamic”.

l. 352: “Figure S2 confirms these findings” by showing and proving what?

Response: Thank you. We have revised them in Lines 319-319..

l. 363: Do the authors mean “accumulation mode” aerosol?

Response: Yes.

l. 369: After reading this long description I lost track of what the main message is. This needs to be written much more concisely by focusing on the most important findings.

Response: Thank you for your suggestion. We have deleted section 3.3.1 and reorganized them to other paragraph.

l. 381: “depletion probably occurred”. There is no evidence for it.

Response: Thank you. We have deleted it.

l. 384f: This conclusion is not evident. How can Cl- from KCl be more dominant than Cl- from sea salt? Furthermore, I do not understand what the difference is to what has been discussed before with regards to K in l. 330-338 (K as marker for biomass burning). This is confusing.

Response: Thank you. We have deleted it and reorganized them.

l. 387: I am not convinced that SO42- is a biomass burning marker. The relation between potassium and sulfate might result from the transport of air masses from the same source region with different source types.

Response: Yes. Thank you. We have revised it.

Section 3.3.1: I suggest integrating the findings from the correlation analysis into the other sections. This section is very redundant and makes the manuscript unnecessarily long.

Response: Thank you for your suggestion. We have reorganized them to other sections.

l. 404: This statement is disconnected from the previous analysis. What has been mentioned that relates to this section?

Response: We have deleted section 3.3.2 in pre-revised manuscript.

l. 408: An explanation for what CMDS is, is needed.

Response: We have deleted section 3.3.2 in pre-revised manuscript.

Section 3.3.3: Please see comments above. The lack of information and figures is not acceptable.

Response: Thank you for your suggestion. We have added two figures in this section (Figure 9 and

Figure 10).

l. 439: Why 50 % now, in l. 422 it was 58 %.

Response: We have revised them.

l. 441: I do not understand this sentence “CaSO4 and sulfate containing both K and Ca…”

Response: Thank you. We have deleted it.

l. 449f: Do the authors say that 41 % of potassium comes from biomass burning?

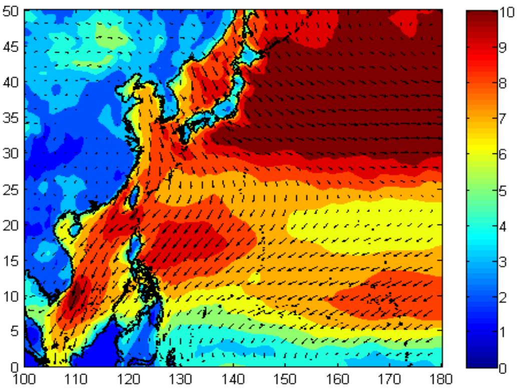
Response: Because we re-calculate PMF model, biomass burning is not a primary source and K^+ is existed the form of secondary inorganic aerosol.

l. 455: “In addition, biomass burning produces SO2 and NOx…” has been mentioned at least for the third time. Again, there are too man repetitions in this manuscript.

Response: Yes, we have reorganized them.

l. 460: What is the reason for it, a meteorological situation that favor southward transport of air masses? Again, in many cases more precise information is needed what the authors refer to exactly in the given literature.

Response: In cool season, the wind direct is from northeast. We have revised them (see below figure: wind direct and wind intensity over the northwest Pacific in Jan. 2015)



l. 485: I do not see the point of “a major discovery”. An explanation is needed why the authors think this is new knowledge.

Response: We agree. We have deleted “a major discovery”.

l. 515-520: The origin of ammonium and ammonia is discussed again here. This is repetitive and it is not clear to me, why the authors reveal the information on the nutrient situation in the marine water only at this very late point in the manuscript?

Response: We reorganize this section with PMF model and delete the discussion about nutrient situation.

Technical comments:

l. 19: “major inorganic ion concentrations” instead of “inorganic chemical ionic concentrations”

Response: Accepted.

l. 25: insert “which were” before “higher in the cool season…” and remove the “,”

Response: Accepted.

l. 26: finish the sentence after “seasons” and start a new one with “Factors of influence were…”

Response: Accepted.

l. 33: write “was the dominant source of…”

Response: Accepted.

l. 40 f: write “Aerosols have many sources. Primary aerosols, emitted directly from…”

Response: Accepted.

l. 73: remove “SCS” behind “northeast”.

Response: Accepted.

l. 94: replace “such” with “the high”

Response: Accepted.

l. 95: replace “be” with “arrive”

Response: Accepted.

l. 103: “Accumulated annual rainfall…”

Response: Accepted.

l. 113: remove “an” before “another”

Response: Accepted.

l. 120, 123, 124: “relative” instead of “relatively”

Response: Accepted.

l. 145, 160: “over the SCS”

Response: Accepted.

l. 147: remove “aerosols” behind “TSP”.

Response: Accepted.

l. 165: “annual average TSP and ionic concentration are comparable to…”

Response: Accepted.

l. 172: replace “composed” by “contributes”

Response: Accepted.

l. 205: remove “that”

Response: Accepted.

l. 215: “distinct”

Response: Accepted.

l. 221: I suggest to write: "… because 70 % of rainfall at…happens during the warm seasons..

Response: Accepted.

l. 224: replace "that" by "mass".

Response: Accepted.

l. 225: replace "strong" by "high"

Response: Accepted.

l. 247: "in contrast to"

Response: Accepted.

l. 254: "correlation" instead of "correction"

Response: Accepted.

l. 264: "suggest" instead of "show".

Response: Accepted.

l. 267: insert "were observed" after (Wang et al. 2006).

Response: Accepted.

l. 276: "emissions" instead of "emission", twice

Response: Accepted.

l. 285: replace "difficult" by "limited"

Response: Accepted.

l. 291: insert "the" before" Acid Deposition…"

Response: Accepted.

l. 313: “Excess Cl- in January has been observed by…”

Response: Accepted.

l. 316: insert “for almost all stations” at the end of the sentence.

Response: Accepted.

l. 318: no “s” in “oceans”

Response: Accepted.

l. 340: remove “the reported by”

Response: Accepted.

l. 383: insert “fuel” after “fossil”

Response: Accepted.

l. 395: Table 2, I believe. Delete “that”.

Response: Accepted.

l. 438: Remove “absolutely”

Response: Accepted.

l. 491: replace “as that” by “compared to”

Response: Accepted.

l. 532: “to help better understand their chemical…”

Response: Accepted.

l. 535: “with higher concentrations in the…”

Response: Accepted.

Response to anonymous referee #2's interactive comment on the manuscript "Atmospheric aerosol compositions over the South China Sea: Temporal variability and source apportionment" point by point below.

The manuscript presents results from observations of Total Suspended Particulate matter (TSP) from an approximately year long study in a marine region of the northern South China Sea (SCS). Four-day filters were collected and analyzed for major inorganic chemical ionic concentration observed in the marine boundary layer. Several source apportionment methods were then used to both differentiate between aerosol types that contributed to measured values and link them with potential sources. These included correlation between various factors, principal component analysis, positive matrix factorization, and backtrajectory analysis by means of concentration weighted trajectories for various identified sources. The results are interesting and provide new findings that contribute to knowledge of aerosol impacts on the northern SCS. However, the manuscript lacks a clear justification of the basis for the study or description of the implications of its findings. In addition, further information on the methods used is needed in order to fully ascertain how the study was conducted and if the findings are justified from the measurements and information described. I therefore recommend that the authors conduct major revisions to the manuscript to focus on providing more reasoning behind why the study was conducted and what conclusions regarding marine aerosol impacts are justified from TSP observations. In addition, the manuscript should be reorganized to more clearly link each part of the methods, results, and conclusions to the overall purpose of the study.

General Comments:

1. The authors utilized only measurements of ionic concentrations of TSP and meteorological information to investigate aerosol sources and impacts on a remote marine region. This provides interesting information, but as filter collections of TSP can be dominated by larger aerosol particles, the authors should briefly discuss the limitations of such measurements in comparison to size resolved measurements.

Response: Thank you. The term "total suspended particulate" (TSP) has referred in principle to the mass concentration of all particles considered to be airborne. Samplers for "total aerosol" first emerges during the time when it is widely thought that it is sufficient to simply draw an aerosol sample through an inlet and to collect the particles on a filter. When sampling is required for health-related purposes, we now know that such sampling needs to be carried out with respect to specific particle size fractions.

2. The methods section 2 did not contain enough information to fully describe how the study was conducted. While the cited studies are helpful and needed, at least a basic description of each method, along with the specific parameters of the method used in this study are needed. Specific examples are included in the specific comments.

Response: Thank you for your suggestion. We have added more information in section 2, and supplementary text S2 and S3.

3. Several sections of the results are repetitive, and some of the sections contain information that would be more helpful to the reader by including it in the methodology section before the results are presented. Streamlining the results section to more clearly describe the results first, followed by a discussion of their implications might allow the reader to follow the logic of the study better. The results section in particular could be better organized in a way such that the results directly lead to descriptions of the findings. Specific examples are included in the specific comments.

Response: Thank you for your suggestion.

We have streamlined the manuscript from 19 pages to 15 pages, excluding references. We have deleted Lines 50-65, section 3.3.1 and 3.3.2, and other sentences in pre-revised manuscript. At the same time, we reorganized the manuscript in some sections and described the results first, followed by a discussion, and moved some information into supplementary text.

4. The authors might consider a more thorough description of the justification for the study, and specifically why TSP measurements are appropriate for identification of source types impacting remote marine regions of the SCS. The reason for inclusion of some parts of the manuscript was not immediately evident, and did not always lead to a coherent storyline or scientific narrative. A more concise description of what was conducted and why would alleviate

many of these concerns.

Response: Thank you for your suggestion. We have revised them in manuscript. Such as Lines 19-21 and Lines 65-69:

In order to evaluate impacts of different source emission on marine atmospheric particles over the South China Sea (SCS), major inorganic ionic concentrations (Na^+, Cl^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, K^+, NH_4^+, NO_3^-) were determined in total suspended particulates (TSP) at Yongxing Island from March 2014 to February 2015.

However, the observational data on aerosol chemistry over the SCS are very sparse (Xiao et al., 2015).To get better understanding of potential sources, source contributions, and spatio-temporal variations of marine aerosols over the SCS, total suspended particulate (TSP) were continuously collected at Yongxing Island from March 2014 to February 2015.

Specific Comments:

Line 30. It is not clear what “74% and 82%” are referring to in the abstract. Similarly, percentages in the rest of the abstract should be clearly described.

Response: Because we re-calculate the PMF model, some values have been changed. We revised the sentence in Lines 31-32.

L 43-45. Organics also constitute an important source, and should be mentioned even if measurements were not conducted.

Response: Yes. Thank you. We have added these information to the revised manuscript in Lines 47-49.

L 70. The description of “warm” and “cool” periods of the monsoon are not clearly linked to the description of the Boreal seasons.

Response: Yes.

In the manuscript, we separate the seasons based on the primarily air masses directions. In generally, the temperature was lower when air masses were primarily from northeast; while the temperature was higher when air masses were primarily from southwest. The air masses of transition season were changed from northeast to southwest when cool season changed to cool season. In some year, the air masses of transition season were changed from southwest to northeast when warm season is changing to cool season. But it was not found in our sampling period.

L 100. Consider changing “major” to another term such as “primarily”.

Response: Thank you. We have revised them.

L 106; Section 2.2. Additional description on how samples were collected is needed. What height was the inlet? What were the inlet dimensions and type? How was representative sampling of the aerosol assured? Importantly: Were there any local sources at the island that could contribute to TSP and skew results in comparison to background SCS marine boundary layer conditions? How were they identified and/or removed from the results? If other studies have considered this for the location, please note this and cite the study.

Response: Thank you for your suggestion. We have added the description in the manuscript (supplementary text S1). We think the samples were representative, because the sampling station is far away from continent at the island with few population and no industry.

L 123 and 124. Should be relative standard deviation?

Response: Yes and thank you.

L 127; Section 2.3. Additional information is needed on the backtrajectory model used, the version, the meteorological dataset source used, the receptor height, and how often backtrajectories were run. A brief description of why 10 day backtrajectories were selected would be helpful as well. Detailed information is not required and can be referred to the cited works, but a brief description would be helpful. Similarly, a brief description of how CWTs were used would be helpful.

Response: Thank you for your suggestion. We have revised this section 2.4 and supplementary text S2.

L 136; Section 2.4. Similarly, more detail on the PMF model setup is needed. For instance, a brief description of how and why five sources were selected by the methodology would be helpful for the reader.

Response: Thank you. We also have revised this section 2.5 and supplementary text S3.

L 153. Consider more clearly specifying that percentages are on a mass basis throughout the manuscript. This would assist the reader in more clearly describing what percentages are referring to and how they should be interpreted.

Response: Thank you for your suggestion. We have added the information into the manuscript in Lines 128-129.

L 160; Section 3.1.2. Results from this section, section 3.1.1., and section 3.2 all contain somewhat repetitive, thought slightly different descriptions, of similar results. Consider reorganizing the results in a way that presents this information, then discusses different relevant findings in a more ordered manner that leads to the study conclusions.

Response: Thank you. We have revised the sections 3.1.1.

L 223. The lack of correlation between rainfall observed at the receptor and TSP may not be sufficient to warrant the finding that "rainfall is not a major factor controlling seasonal variation of that concentration". Precipitation is a complex process that can lead to both increases in TSP (e.g. via gust fronts etc.) and decreases through wet deposition, among other processes. In addition, relevant processes can occur on time scales below the four-day sample period of the filter samples. A more nuanced discussion of the relationship between precipitation and TSP should be included.

Response: We agree and have deleted this sentence.

L 226. State the hypothesized mechanism that links decreased TSP to higher temperatures and RHs via particle hygroscopic growth and interactions. Is this finding justified by the available data or are there better source to support this finding? A significant correlation is not sufficient to justify this statement.

Response: Thank you for your suggestion. We have added a reference in the manuscript.

We discovered negative correlations between TSP concentration and temperature ($p < 0.01$) and relatively humidity (*p* < 0.01) (Table 2), indicating that warm temperatures and high relatively humidity enhance particle activation and scavenging is happening (Liu et al., 2011).

L 371; Section 3.3.1. Methods for this section could be included earlier in the methods section 2. It may help to better understand these results when they are first discussed in earlier results sections.

Response: We agree and have deleted this section. But we have reorganized them into other sections.

L 414. It can be very difficult to form valid conclusions on the composition of various particle sizes or modes from TSP observations on their own. These statements are somewhat speculative in nature, even with other studies to cite. Additional evidence or discussion should be included to support any contentions based on distinct sources associated with size distribution differences or size segregation.

Response: Thank you for your suggestion. We have deleted section 3.3.2 "Principal component analysis and classical multidimensional scaling".

L 418; Section 3.3.3. More discussion on how PMF results were linked to the identified source types would be helpful. Was this solely based on relative ion concentration? This could be added to the methods section as well.

Response: Thank you for your suggestion. We have added more information to the methods section.

L 450. Smoke can be an important source of aerosol into the southern SCS during the "warm" monsoonal season as extensive burning can occur in Borneo and Sumatra. That less evidence of this impact is found (due to the noted potassium ratios) in the study's more northern SCS marine region is interesting. Similar impacts from anthropogenic pollution are likewise noteworthy. The authors may wish to spend some time in the discussion emphasizing that there are important sources of aerosol throughout SE Asia and the maritime continent, while the CWT and ionic ratios indicate that sources important to the southern parts of the SCS may be removed or less important to northern SCS regions than those of regions around SE Asia and China.

Response: Thank you. We have re-calculated the PMF model and combined the PMF results with

CWTs results to discuss. In the revised manuscript, we found that K from biomass burning would loss its information when it transport to open ocean, because it can react with H_2SO_4 or HNO_3 in the atmosphere to form secondary aerosols.

Atmospheric aerosol compositions over the South China Sea: Temporal variability and source apportionment

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Abstract. In order to evaluate impacts of different source emission on marine atmospheric particles over the South China Sea (SCS), ~~M~~major inorganic ~~chemical~~ ionic concentrations (Na^+, Cl^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, K^+, NH_4^+, NO_3^-) were determined in total suspended particulates (TSP) at Yongxing Island~~ in the South China Sea (SCS)~~, from March 2014 to February 2015. The annual average concentration of TSP was 89.6 ± 68.0 μg/m^3, with 114.7 ± 82.1, 60.4 ± 27.0, and 59.5 ± 25.6 μg/m^3 in cool, warm, and transition seasons, respectively. Cl^- had the highest concentration, with an annual average of 7.73 ± 5.99 μg/m^3, followed by SO_4^{2-} (5.54 ± 3.65 μg/m^3), Na^+ (4.00 ± 1.88 μg/m^3), Ca^{2+} (2.15 ± 1.54 μg/m^3), NO_3^- (1.95 ± 1.34 μg/m^3), Mg^{2+} (0.44 ± 0.33 μg/m^3), K^+ (0.33 ± 0.22 μg/m^3), and NH_4^+ (0.07 ± 0.07 μg/m^3). Concentrations of TSP and the major ions showed seasonal variations~~,~~ which were higher in the cool season and lower in the warm and transition seasons~~,~~. ~~which were~~Factors of influence~~d~~ were~~by~~ wind speed, temperature, relatively humidity, rain, and air masses. Back trajectories, concentration weighted trajectories (CWT), and positive matrix factorization (PMF) of chemical compositions were analyzed for source apportionment, source contribution, and spatio-temporal variation of major ions. Back trajectories and CWTs showed that air masses at Yongxing Island were mainly from the northeast, southwest, and southeast in the cool, warm, and transition seasons, respectively. The PMF results showed that Na^+ of 77.4% and Cl^- of 99.3% were from sea salt. 60.5% of NH_4^+ was of oceanic emission.~~Na^+ and Cl^- were mainly from sea salt, which made up 74% and 82%, respectively. Asian dust contributed 50% of Ca^{2+} to the marine aerosols.~~ Anthropogenic sources were very important for atmospheric aerosols over the island. Secondary inorganic aerosol of SO_2 and NO_x from fossil fuel combustion (especially coal in Chinese coastal regions) was the dominant source of NO_3^- (69.5%) and SO_4^{2-} (57.5%).~~Fossil fuel combustion (especially coal in Chinese coastal regions) was the important sources of NO_3^- (56%) and SO_4^{2-} (22%). Biomass burning in Asia accounted for 41% of K^+. 69% of NH_4^+ and 38% of SO_4^{2-} were of marine biogenic sources.~~

Keywords: Source apportionment; ~~dust~~crust; secondary inorganic aerosol; oceanic emission~~biomass burning; fossil fuel combustion; marine biogenic source~~

1 Introduction

Aerosols or particulate matters potentially affect global atmospheric processes, chemistry, cloud formation, acid and nutrient deposition in sensitive ecosystems, ~~and~~ affect human health as air pollution, and have effects on climate (Chin, 2009; Davidson, et al., 2005; Deng et al., 2010; Liu et al., 2014; Steyn and Chaumerliac, 2016; Zhang et al., 2011; Zhang et al., 2015). Aerosols have ~~complex~~ many sources~~,~~. ~~including p~~Primary aerosols, emitted directly from natural and anthropogenic sources, such as terrestrial dust from weathering, wind-blown sand and minerals, sea spray, ~~biomass~~ combustion processes~~burning~~, and biological emissions (Chin, 2009; Davidson, et al., 2005; Rinaldi et al., 2010; Pavuluri et al., 2015). There are also secondary aerosols, which form from condensable atmospheric gases such as SO_2, NO_x, ~~and~~ NH_3~~.~~, and volatile organic compounds (Chin, 2009; Kolb and Worsnop, 2013; Xiao et al., 2012a, 2014; Zhang et al., 2011). Therefore, aerosols are composed of various ~~complex~~ chemical components (Xiao and Liu, 2004) and contain sulfate, nitrate, ammonium, ~~and~~ mineral elements, black carbon and particulate organic matter (Zhang et al., 2007; Zhang et al., 2011; Chin, 2009; Pavuluri et al., 2015; Steyn and Chaumerliac, 2016). Because of rapid economic and industrial development in the last few decades in South and East Asia, many aerosols and their precursors released by human activities have become a major environmental problem ~~worldwide~~ (Steyn and Chaumerliac, 2016~~Kolb and Worsnop, 2013~~). Aerosols from anthropogenic emissions can be transported long distances from polluted regions to remote open oceans, which is well recognized as a major pathway for the supply of anthropogenic material to ocean surface waters (Duce et al., 2008; Lawrence and Lelieveld, 2010; Jung et al., 2012).

~~Atmospheric aerosol deposition over remote open oceans can increase ocean productivity and carbon sequestration (Duce et al., 2008; Kim et al., 2014; Landing and Paytan, 2010), but aerosol input to such oceans varies considerably in both time and space. Such variations are modulated by sources, chemical processes, and environmental parameters, e.g., wind and temperature (Landing and Paytan, 2010; Xiao et al., 2015). Time-series measurements of aerosol particles over the subarctic Northeast Pacific Ocean have indicated that major contributions to the aerosol mass were from the oxidation of dimethyl sulfide (DMS), sea salt, and ship emissions (Phinney et al., 2006). High NH_4^+ and NO_3^- concentrations have been found in North and South Pacific Ocean when air masses were derived from the Asian continent and the Kamchatka Peninsula, whereas low concentrations were observed when air masses were from the central Pacific Ocean (Jung et al., 2012); therefore, NH_3 and NO_x are influenced by both natural and anthropogenic sources. In the North Sea, the anthropogenic fraction is lower for air masses from the North Atlantic than for those from the European continent (Ebert et al., 2000). There are four discrete transport regimes over the western North Atlantic Ocean at Bermuda that affect the sources (Keene et al., 2005). The East China Sea was more influenced by Asian dust storms whereas the Yellow Sea was more influenced by human activities, during March and April, 2011 (Zhao et al., 2015). Dust from the Gobi Desert with pollutants from eastern China transports numerous dust elements and secondary pollutants to the South China Sea (SCS) (Liu et al., 2014).~~

The South China Sea (SCS) is in the tropical–subtropical rim of the Northwest Pacific Ocean and is one of the largest marginal seas in the world (Fig. 1). The SCS is adjacent to several rapidly growing Asian economies, including China, the Philippines, Malaysia, Vietnam, and Indonesia (Kim et al., 2014). Consequently, the sea receives substantial amounts of aerosols from surrounding regions through long-range atmospheric transport (Fig. 1; Atwood et al., 2013; Jung et al., 2012). The SCS has a monsoon climate, with a northeast monsoon in winter and spring and a southwest monsoon in summer and autumn (Cui et al., 2016). Thus, aerosol optical thickness (AOT) shows spatial and seasonal variations, with higher AOT in the northern SCS during the cool season and higher AOT in the southern SCS in the warm season (Fig. 1). The SCS receives dust and pollutions from the northeast ~~SCS~~ in winter and spring, e.g., from China and Japan (Liu et al., 2014; Wang et al., 2013; Xiao et al., 2015); during summer and autumn, the SCS receives particulate and gas phase pollutants ~~aerosols and pollutants~~ from biomass burning in the southwest of SCS, e.g., from Malaysia and Indonesia (Atwood et al., 2013). However, the observational data on aerosol chemistry over the SCS are very sparse (Xiao et al., 2015). ~~According to Lawrence~~

~~and Lelieveld (2010), emissions of SO_2 and NO_x in Northeast Asia are mainly from fossil fuel combustion and industrial processes, and from fossil fuel combustion and biofuel burning in South Asia. Biomass burning in Asian countries is an important contributor to aerosol deposition in the SCS (Streets et al., 2003).~~

To get better understanding of potential sources, source contributions, and spatio-temporal variations of marine aerosols over the SCS, total suspended particulate (TSP) were continuously collected at Yongxing Island from March 2014 to February 2015. The concentrations of major inorganic water-soluble ions were determined. Furthermore, back trajectories, concentration-weighted trajectory (CWT) and positive matrix factorization (PMF) analyses were also used to identify and apportion the main sources of aerosols and their chemical composition over the SCS.

2 Materials and Methods

2.1 Study site

Aerosol samples were collected from March 2014 through February 2015 on the rooftop of Xisha Deep Sea Marine Environment Observation and Research Station, South China Sea Institute of Oceanology, Chinese Academy of Sciences (SCSIO, CAS). This station is at the Yongxing Island (YXI, Fig. 1; 16.83°N, 112.33°E). This island has a tropical monsoon climate, with northeast monsoon in winter and spring, and southwest monsoon in summer and autumn (Xiao et al., 2015). The island is located in the high aerosol concentrations area of the northern SCS during winter and spring, and also at the periphery of ~~such~~ the high concentrations area of the southern SCS during summer and autumn (Fig. 1). Therefore pollutants can ~~be~~ arrive from Northeast Asia in winter and spring, and Southeast Asia in summer and autumn (Liu et al., 2014; Wang et al., 2013; Xiao et al., 2015; Atwood et al., 2013). It is also influenced by local SCS marine sources. More information about Yongxing Island is given elsewhere (Xiao et al., 2015 and 2016). In the present study, the sampling period~~it~~ was divided into three seasons ~~according to~~based on wind direction and back trajectories. The cool season was March, April, October, November, December 2014 and January, February 2015, with principal air masses from the northeast and 25.9 °C of temperature, and the warm season was June–September 2014, with air masses ~~major~~ primarily from the southwest and 29.7 °C of temperature. The transition season was May 2014, with ~~major~~ local and short air masses primarily from the ~~local~~ southeast. Yongxing Island has an annual average temperature of 27.7 ± 2.7 °C, relative humidity (RH) of 80 ± 7%, and wind speeds of 3.6 ± 1.8 m/s. There were strong seasonal variations between March 2014 and February 2015 (Fig. 2). Accumulated ~~Annual~~ annual rainfall was 1526 mm during this period, with about 30% occurring in the cool season (Fig. 2).

2.2 Sample collection and chemical analyses

Aerosol was collected on quartz filters~~ (8 × 10 inch, Tissuquartz™ Filters, 2500 QAT-UP, Pallflex, Washington, USA)~~ using a special high-flow rate (1.05 ± 0.03 m^3/min) KC-1000 sampler~~ (Laoshan Institute for Electronic Equipment, Qingdao, China).~~, ~~The sampling time was nominally 96 hours (4 days one sample). All samples were stored in a refrigerator at −20°C until analysis in the laboratory.~~

~~In the laboratory, one eighth filters were cut and placed in a clean 50-ml Nalgene tube with additional 35-ml ultrapure water. These tubes were washed for 30 minutes using ultrasonic vibration. They were then shaken for 30 minutes on a horizontal shaker at a rate of ~300 rpm and left to rest for an another 30 minutes at room temperature. The extract was filtered using pinhole filters, which were then rinsed twice with 5-ml ultrapure water. The extract and rinse were put into 50-ml tubes together and stored in a refrigerator at −20 °C until chemical analyses.~~

and aerosol water-soluble ~~M~~major anion concentrations (F^-, Cl^-, NO_3^-, SO_4^{2-}, Br^-) were determined by ICS-90 ion chromatography (Dionex, California, USA~~).~~) and ~~Water~~water-soluble metal and nonmetal elemental concentrations (Al, Ca, Fe, K, Mg, Mn, Na, SiO_2, Sr) were analyzed by an MPX inductively coupled plasma optical emission spectrometer (ICP-OES, Vista, CA, USA~~).~~), NH_4^+ concentration was determined by spectrophotometry after treatment with Nessler's reagent, as described in detail information in supplementary text S1.

2.3 Sea salt and non-sea salt contributions

In order to determine the source contributions to the ionic compositions in TSP, the sea salt ion (SS) and the non-sea salt ion (NSS), are calculated using Na as a reference element for marine origin by the following equations (Eq. 1 and 2; Xiao et al., 2013):

$$SS(\%) = 100(X/Na^+)_{sea}/(X/Na^+)_{TSP} \qquad (1)$$

$$NSS(\%) = 100 - SS \qquad (2)$$

where X represents the ionic composition and the data of $(X/Na^+)_{sea}$ comes from Keene et al., (1986).~~ The detection limits of F^-, Cl^-, NO_3^-, SO_4^{2-}, Br^- were 0.03, 0.03, 0.08, 0.075 and 0.1 mg/L, respectively, and the relatively standard deviation of these ions were 0.57%, 2.55%, 1.16%, 1.36% and 11.36%, respectively (Xiao et al., 2013 and 2016). The detection limits of Al, Ca, Fe, K, Mg, Mn, Na, SiO_2, Sr were 0.025, 0.003, 0.002, 0.06, 0.0005, 0.0005, 0.02, 0.015 and 0.00008 mg/L, respectively, and the relatively standard deviation of these ions were less than 1.5% (Xiao et al., 2013 and 2016). The detection limit of NH_4^+ was 0.1 mg/L and its relatively standard~~

~~deviation was less than 5.0% (Xiao et al., 2013 and 2016). In this study, Al in most of samples was less than the detection limit.~~

2.~~3~~ 4 Back trajectories and concentration weighted trajectories~~CWT~~ analysis

Back trajectories and concentration weighted trajectories (CWT) are used to determine the long-distance transport of atmospheric pollutants and regional source areas by the program of TrajStat (Cheng et al., 2013; Wang et al., 2009; Xiao et al., 2014 and 2015). The detail methods were described in supplementary text S2.~~. Detailed principles of back trajectories and CWT were given in our previous studies (Xiao et al., 2014; Xiao et al., 2015). For each day, 10-day (240 hours) back trajectories of air masses arriving at Yongxing Island were computed. CWT modeled TSP, and Ca^{2+}, Mg^{2+}, K^{+}, SO$_4^{2-}$, NO$_3^{-}$ and NH$_4^{+}$ concentrations at the island. The region from 70°E to 160°E and from 20°S to 60°N was defined as the source domain based on back trajectories during the sampling period, containing 14,400 grid cells of 0.5° × 0.5°.~~

2.~~4~~ 5 Positive matrix factorization model~~PMF model~~

Receptor models are used to quantify the contributions of sources based on the composition or fingerprints of the sources (Norris et al., 2014). The positive matrix factorization (PMF) is an effective source apportionment receptor model that does not require source profiles prior to analysis and has no limitation on source numbers (Crippa et al., 2013; Tiwari et al., 2013; Zhang et al., 2011; Zhang et al., 2015). ~~The principles of PMF are detailed elsewhere (Han et al., 2006; Hien et al., 2004; Schmale et al., 2013; Yu et al., 2013).~~ In our study, EPA PMF 5.0 ~~(United States Environmental Protection Agency)~~ was used to determine source apportionment of ~~TSP and~~ each major ion. The detail methods were described in supplementary text S3.~~based on TSP, F^{-}, Cl^{-}, NO$_3^{-}$, SO$_4^{2-}$, Ca, K, Mg, Mn, Na, and Sr. Five physically realistic sources for TSP and major ions were identified, i.e., sea salt, crust, biomass burning, fossil fuel combustion, and marine biogenic.~~

3 Results and Discussion

3.1 Aerosol chemical composition over the SCS and comparison with global marine aerosols

3.1.1 Aerosol characteristics over the SCS

Fig~~ures~~s. 3~~ and~~, 4 and Table 1, provide information on atmospheric concentrations of TSP ~~aerosols~~ and major inorganic ions during the sampling period at Yongxing Island. The annual average TSP concentration at the island was 89.6 ± 68.0 μg/m^3, with a range of 16.4 to 440.1 μg/m^3. ~~This TSP level is much lower than cities around the~~

~~world (Wang et al., 2006; Xiao and Liu, 2004; Deng et al., 2011; Naga et al., 2014). It is also lower than some remote sites, such as Mountain Tai (Deng et al., 2011). Of course, it is higher than lots of remote sites, such as Tianchi, Qinghai Lake (Deng et al., 2011; Zhang et al., 2014).~~

The major inorganic ionic concentrations (Na^+, Cl^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, K^+, NH_4^+, and NO_3^-) accounted for 24.8% of TSP. Total major inorganic ionic concentrations was 22.21 μg/m^3. Cl^- had the highest concentration among these ions, from 0.39 to 36.47 μg/m^3, with an annual average of 7.73 ± 5.99 μg/m^3. It was followed by SO_4^{2-} (range 0.52–23.34 μg/m^3, average 5.54 ± 3.65 μg/m^3), Na^+ (0.9 –8.86 μg/m^3, average 4.00 ± 1.88 μg/m^3), Ca^{2+} (0.17–9.65 μg/m^3, average 2.15 ± 1.54 μg/m^3), NO_3^- (0.10–10.05 μg/m^3, average 1.95 ± 1.34 μg/m^3), Mg^{2+} (0.02–1.55 μg/m^3, average 0.44 ± 0.33 μg/m^3), K^+ (0.06–1.13 μg/m^3, average 0.33 ± 0.22 μg/m^3), NH_4^+ (0.01–0.32 μg/m^3, average 0.07 ± 0.07 μg/m^3) ~~(Fig. 3)~~.

3.1.2 Aerosols over SCS compared with global marine aerosols

The annual average TSP concentration at Yongxing Island is also lower than ~~those~~ the annual average value ~~in~~ over the northern Yellow Sea (123.2 μg/m^3), another Chinese marginal sea (Wang et al., 2013). However, the mean TSP concentration at Yongxing Island is not lower than those at other remote islands or other seas, such as the Indian Ocean (21.1 μg/m^3), ~~and~~ Pacific O~~o~~cean~~s~~ (36.7 μg/m^3), Mediterranean Sea (46.9 μg/m^3), Southern Atlantic (39.1 μg/m^3), and three islands of Okinawa (22.6 μg/m^3 in summer and 44.5 μg/m^3 in spring) (Arakaki et al., 2014; Balasubramanian et al., 2013; Zhang et al., 2010~~; Zhang et al., 2014~~).

The aforementioned annual average TSP and ionic concentration~~s and orders of ionic concentration~~ are comparable ~~with~~to those reported in many remote oceans (Fig. 5), e.g., Hedo, which is at the junction of the East China Sea and Northwest Pacific. The marine ions (Na^+ and Cl^-) accounted for 53% of total major ions (Fig. 4). Na^+ and Cl^- concentrations at Yongxing Island were higher than most reported values ~~in global ocean~~among all locations and remote sites (Fig. 5), such as the Indian Ocean (3.0 and 4.4 μg/m^3, respectively), Arabian Sea (1.9 and 2.2 μg/m^3, respectively), Oki (3.3 and 4.3 μg/m^3, respectively) and Rishiri islands (1.2 and 2.7 μg/m^3, respectively) in the Sea of Japan, Amsterdam Island (1.4 and 2.3 μg/m^3, respectively) in the Southern Ocean, Bermuda (3.3 and 4.8 μg/m^3, respectively) in the Atlantic Ocean, and Hawaii (0.5 and 0.4 μg/m^3, respectively) in the Pacific (Kumar et al., 2008; Okuda et al., 2006; Claeys et al., 2010; Moody et al., 2014; Carrillo et al., 2002). However, Na^+ and Cl^- concentrations were lower than samples from cruises, such as over the nor~~sou~~thern Atlantic-2 (7.0 and 9.6 μg/m^3, respectively) and Pacific (5.8 and 9.0 μg/m^3, respectively) (Zhang et al., 2010). The Ca^{2+} concentration was the highest among all locations~~in all global oceans~~ and contributes~~mposed~~ 10% of major ions

(Fig. 4), followed by the Mediterranean Sea, southern Atlantic and northern Atlantic-2 (Fig. 5). The relatively high Ca^{2+} concentration may be because of Asian terrestrial dust transported to Yongxing Island. ~~and dust from local weathered dead coral from Yongxing Island development (Xiao et al., 2016). As a tracer for dust, non-sea salt~~ Nss-Ca^{2+} ~~(nss-Ca^{2+})~~ accounted for 93% of total Ca^{2+}, ranging from 0.14 to 9.31 μg/m^3 with an annual average of 1.99 μg/m^3. Large contributions of nss-Ca^{2+} were also found in the Mediterranean Sea, southern Atlantic and northern Atlantic-2, being at 88.4%, 90.3% and 90.0%, respectively (Zhang et al., 2010). The relatively high nss-Ca^{2+} concentrations in those oceans were potentially from the crust or dust from ~~the Sahara~~some ~~Desert~~ deserts (Zhang et al., 2010). Comparing Yongxing Island with among all locations~~global oceans~~, average Mg^{2+}concentrations were higher at Yongxing Island than most reported values among all locations ~~nearly consistent with those of Na^+~~ (Fig. 5). K^+ was also the highest among ~~the global oceans~~all locations (Fig. 5). ~~As a tracer for biomass/biofuel burning, n~~Nss-K^+ ranged from 0 to 0.87 μg/m^3, with an annual average of 0.18 μg/m^3 and a contribution of 55% to total water soluble K^+ at Yongxing. In general, SO_4^{2-}, NO_3^- and NH_4^+ were major in the form of secondary inorganic aerosols. They accounted for only 34.0% of total inorganic ionic concentrations, giving them an intermediate position among ~~the global ocean~~all locations (Fig. 5). The average SO_4^{2-} concentration at Yongxing was the highest among ~~those in the global ocean~~all locations. As shown in Fig. 4, the mean contribution of SO_4^{2-} to major inorganic ionic components was ~ 25% at Yongxing. The nss-SO_4^{2-} concentration was 3.66 μg/m^3, with a contribution of 66.1% to total SO_4^{2-}. Similar to SO_4^{2-}, the average concentration of NO_3^- in this study was the highest among ~~those in the global ocean~~all locations. It accounted for 9% of major ions at Yongxing Island. This indicates that a large number of anthropogenic sources affected the concentrations of SO_4^{2-} and NO_3^-. It was surprising that NH_4^+ had relatively low concentrations over most oceans, except for the southern Atlantic and Mediterranean Sea (Fig. 5). The average NH_4^+ concentration was 0.07 ± 0.07 μg/m^3 in aerosol at Yongxing Island (Fig. 3), representing < 1% of total major ions (Fig. 4). Further, low concentrations of NH_4^+ were also observed in rainwater on the island (Xiao et al., 2016).

3.1.3 Global marine aerosol chemical patterns

Globally, sea salt ions (Na^+ and Cl^-) were the most important components in marine atmospheric aerosol, with higher concentration of Cl^- than Na^+, except over the Mediterranean and North seas (Fig. 5; Zhang et al., 2010; Ebert et al., 2000). In the marine atmosphere, sea salt aerosol (NaCl) can react with sulfuric acid and nitric acid to release HCl, which results in a deficit of Cl^- relative to Na^+ (Zhang et al., 2010). It is also found that a deficit of Cl^- in transition season at Yongxing Island (Fig. 4 and Table 2), was most likely because air masses were primarily from local oceanic areas far from the continent (Fig. 1), where wind is weak (Fig. 2). The mole equivalent ratios of Cl^-/Na^+ (neq/L) in aerosols were slightly larger than seawater in annual, cool and warm seasons at Yongxing Island (Table 2). This suggests that Cl^- enrichment had an anthropogenic or other natural origin (Duan et al., 2006; Jung et al., 2012; Xiao et al., 2013). For SO_4^{2-} with ss-SO_4^{2-} and nss-SO_4^{2-}, nss-SO_4^{2-} was greatly influenced by anthropogenic sources from developed industrial areas, leading to higher concentrations of SO_4^{2-} than Na^+ and Cl^-. Examples were Bermuda, Ogasawara, and the Arabian Sea (Fig. 5; Moody et al., 2014; Kumar et al., 2008), where nss-SO_4^{2-} was the preferred species for acid displacement (Zhang et al., 2010). As another import ion of anthropogenic sources, NO_3^- concentrations were often ~~consistent~~ good relationships with those of nss-SO_4^{2-} (Zhang et al., 2010), with relatively high concentrations among major ions (Fig. 5). Relatively high concentrations of SO_4^{2-} and NO_3^- were also found over the SCS (Figs. 3 and 4). NH_4^+ had the lowest concentrations among the major ions in most marine atmospheric aerosols, suggesting ~~that~~ little ammonia transport to the open ocean, such as Yongxing Island. However, there were some exceptions. For example, the southern Atlantic and Mediterranean Sea had the highest NH_4^+ concentrations among major ions (Fig. 5). Over most seas, the order was $Ca^{2+} > Mg^{2+} > K^+$. However, we found that Mg^{2+} had higher concentrations than Ca^{2+} in some remote ocean areas, such as in the Pacific, Atlantic and Southern oceans (Zhang et al., 2010). This indicates that Ca^{2+} of crustal origin was difficult to transport to the remote oceans, and Mg^{2+} may mainly be from sea salt over the open ocean (Moody et al., 2014).

3.2 Seasonal patterns of aerosol chemical species over SCS and adjacent areas

3.2.1 Seasonal characteristics at Yongxing Island

As illustrated in Figs. 4 and 6, seasonal and monthly TSP concentrations and major inorganic water-soluble ion concentrations had distinct~~ive~~ features at Yongxing Island. Generally, concentrations of TSP and major inorganic ions were higher in the cool season than in the warm season (Fig. 6). Seasonal variations were the same as those in ~~most~~ other studies, such as Okinawa, and 18 urban, rural and remote sites in various regions of China (Arakaki et al., 2014; Wang et al., 2006; Xiao and Liu, 2004; Zhang et al., 2012).

Average TSP concentrations were 114.7 ± 82.1, 60.4 ± 27.0 and 59.5 ± 25.6 $\mu g/m^3$ in the cool, warm and transition seasons, respectively, with the highest monthly average in November 2014 and the lowest in April (39.4 $\mu g/m^3$) and September (39.9 $\mu g/m^3$) of that year (Fig. 6). There were lower concentrations in the warm season than in the cool season, because 70% of rainfall at Yongxing Island ~~concentrates in the former season~~happens during the warm season (Fig. 2), being the same as ~~many~~ other studies, such as Shanghai and over the China Sea (Wang et al., 2006; Zhao et al., 2015). ~~However, there was no relationship between TSP concentration and rainfall ($p >$~~

~~0.05; Table 1), indicating that rainfall is not a major factor controlling seasonal variation of that concentration.~~ The positive correlation between TSP concentration and wind speed ($p < 0.01$) shown in Table ~~1~~ 3 suggests that relatively ~~strong~~ high speeds can produce many particles from both sea spray and terrigenous matter. We discovered negative correlations between TSP concentration and temperature ($p < 0.01$) and relatively humidity ($p < 0.01$) (Table ~~1~~2), indicating that warm temperatures and high relatively humidity enhance particle activation and scavenging is happening (Liu et al., 2011)~~wetting and interaction~~. ~~Figure S1 also shows that meteorological parameters affected the major ions, with wind speed having a positive influence and relatively humidity, temperature and rainfall a negative one. Based on the arrow lengths in the figure, rainfall had less effects on major ions than others.~~

As shown in Figs. 4 and 6, sea salt ions Na^+ and Cl^- were characterized by a gradual increase from the transition to cool season. Their concentrations (in $\mu g/m^3$) in the cool, warm and transition seasons were 4.91 ± 1.82 and 3.04 ± 1.08, 2.28 ± 1.35 and 9.93 ± 6.78, and 5.25 ± 2.63 and 3.73 ± 3.63, respectively, with corresponding contributions of 52%, 57% and 57% to total major ions in those seasons. The highest Na^+ and Cl^- concentrations in a single sample were found in November, with the lowest concentrations in May and April, respectively. The highest average monthly concentrations were in November. Positive relationships between Na^+ or Cl^- and wind speed in Table ~~1~~ 3 ($p < 0.01$, correlation coefficient $R = 0.44$ and $p < 0.01$, $R = 0.43$, respectively) ~~and small angles (<< 90°) between Na^+ or Cl^- and wind speed (long arrows) in Fig. S1~~ at Yongxing Island suggest that sea salt concentrations were dependent on wind speed. This is consistent with results at Chichijima Island (Boreddy and Kawamura, 2015). There was a low negative relationship between Na^+ and rainfall ($p < 0.05$, $R=0.27$) but no relationship between Cl^- and rainfall ($p > 0.05$) in Table 3, suggesting~~showing~~ that Na^+ mainly existed in coarse particles and was readily removed by rainfall ~~(Fig. S1)~~. As shown in Table ~~1~~ 3~~and Fig. S1~~, concentrations of Na^+ and Cl^- were also negatively influenced by temperature and relatively humidity. Although Mg^{2+} is often treated as crustal-derived ions and elements in continental studies (Zhang et al., 2015), its highest monthly average concentrations were in November at Yongxing Island, the same as Na^+ and Cl^- (Fig. 5). As shown in Fig. 5, Tables 1 and ~~Table 1~~2, similar trends and strong corre~~ction~~lation were observed among Na^+, Cl^- and Mg^{2+}, and the ratios of Mg^{2+} to Na^+ in aerosols were close to that in seawater, suggesting that Mg^{2+} may mainly derive from sea salt rather than continental sources. However, there were no relationships between Mg^{2+} and wind speed, temperature, relatively humidity, or rainfall (Table ~~1~~2), in contrast to other ions, such as Na^+ and Cl^-. ~~These results reveal that Mg^{2+} has complex sources or behaviors in the marine atmosphere at Yongxing Island.~~ These results reveal that Mg^{2+} has different behaviors in the marine atmosphere at Yongxing Island. The different behaviors of Mg^{2+} was also found in rainwater at

Yongxing Island (Xiao et al., 2016).~~The same phenomenon was found in rainwater (Xiao et al., 2016). Moody et al. (2014) suggested that Na$^+$ may exist in super-micron size aerosols, whereas Mg^{2+} in sub-micron size aerosols are slightly influenced by meteorological parameters.~~

As shown in Fig. 6, the highest monthly average concentrations of Ca^{2+} were in February. Its monthly trends were different from those of TSP, Na$^+$ and Cl$^-$, and the ratios of Ca^{2+} to Na$^+$ in aerosols were much higher than those in seawater (Table 2), suggesting that Ca^{2+} from terrestrial dust sources may be influenced by different factors. Ca^{2+} accounted for 10%, 13% and 8% of total major ions in the cool, transition and warm seasons, respectively (Fig. 4). There was no correlation between Ca^{2+} and wind speed, in contrast ~~with~~ to TSP, Na$^+$ and Cl$^-$ (Table ~~1~~3). However, there was a negative relationship between Ca^{2+} and rainfall ($p < 0.05$; Table ~~1 and Fig. S1~~3). These results suggest that Ca^{2+} existed in coarse particles that can be readily removed by rainfall~~, the same as Na$^+$~~. Thus, a low mass concentration was observed for Ca^{2+} in the rainy (warm) season (Fig. 6), with a low percentage being in the warm season in Fig. 4.

~~Although Mg^{2+} is often treated as crustal-derived ions and elements in continental studies (Zhang et al., 2015), its highest monthly average concentrations were in November at Yongxing Island, the same as Na$^+$ and Cl$^-$ (Fig. 5). As shown in Fig. 5 and Table 1, similar trends and strong correction were observed among Na$^+$, Cl$^-$ and Mg^{2+}, suggesting that Mg^{2+} may mainly derive from sea salt rather than continental sources. However, there were no relationships between Mg^{2+} and wind speed, temperature, relatively humidity, or rainfall (Table 1), in contrast to other ions, such as Na$^+$ and Cl$^-$. These results reveal that Mg^{2+} has complex sources or behaviors in the marine atmosphere at Yongxing Island. The same phenomenon was found in rainwater (Xiao et al., 2016). Moody et al. (2014) suggested that Na$^+$ may exist in super-micron size aerosols, whereas Mg^{2+} in sub-micron size aerosols are slightly influenced by meteorological parameters.~~

~~As a tracer for biomass burning,~~ K$^+$ concentrations were 0.42 ± 0.23 μg/m^3 in the cool season, 0.22 ± 0.18 μg/m^3 in warm season, and 0.15 ± 0.07 μg/m^3 in the transition season at Yongxing, with the maximum monthly average concentrations in February and the minimum in July (Fig. 6). However, the lowest nss-K$^+$ monthly average concentration was in August. The results ~~show~~ suggest that nss-K$^+$ is derived from Chinese biomass/biofuel burning in the cool season (Lawrence and Lelieveld, 2010). Streets et al. (2003) computed that China contributes 25% of total biomass burning in Asia. ~~Many s~~Sites in Chinese coastal regions had higher K$^+$ and nss-K$^+$ concentrations than those at Yongxing Island (Wang et al. 2006) were observed, further indicating that Chinese and other Northeast Asian regions' biomass/biofuel burning have a strong influence on atmospheric composition over the SCS.

~~Biomass/biofuel burning releases not only K^+ but also SO_2 and NO_x (Lawrence and Lelieveld, 2010). Furthermore, considerable fossil fuel burning and industrial processes generate large amounts of SO_2 and NO_x in northern Asia (Lawrence and Lelieveld, 2010), resulting in the transport of substantial secondary inorganic aerosols containing SO_4^{2-} and NO_3^- to the SCS. Therefore, s~~Similar to K^+, the highest monthly concentrations of SO_4^{2-} and NO_3^- were observed in February, being at 13.08 ± 9.04 and 4.99 ± 4.33 μg/m^3, respectively (Fig. 6). As shown in the figure, SO_4^{2-} concentrations in the cool and warm seasons were 7.22 ± 3.92 and 3.26 ± 1.26 μg/m^3, respectively, accounting for 26% and 22% of total major ions, and NO_3^- concentrations were 2.43 ± 1.54 and 1.30 ± 0.64 μg/m^3, accounting for 9% and 9%. ~~NO_x emission from fossil fuel combustion made up 61% and 76% of total NO_x emission in southern and northern Asia, respectively, and SO_2 from the same source made up 77% and 75% (Lawrence and Lelieveld, 2010). According to the aerosol δ^{15}N-NO_3^- at Yongxing Island, NO_3^- mainly came from coal combustion in China during the cool season, and from natural emissions during the warm season (Xiao et al., 2015). In recent years, NO_x emission has also increased greatly because of increasing energy demand, although coal-fired power plants have been restricted (Zhao et al., 2015).~~

The NH_4^+ showed maxima in the cool season and minima in the warm season, being 0.08 ± 0.08 and 0.04 ± 0.03 μg/m^3, respectively. ~~Atmospheric NH_x is usually rapidly deposited near source regions and has a short residence time, about several hours in the marine boundary layer (Boreddy and Kawamura, 2015; Xiao et al., 2012a; Xiao and Liu, 2002). Thus, NH_x transportation from continental to remote sea sites is difficult. Therefore, NH_4^+ in aerosol at Yongxing Island was possibly from marine biogenic emissions, as being reported at other marine sites (Altieri et al., 2014; Jickells et al., 2003).~~

3.2.2 Seasonal patterns over SCS and adjacent areas

The spatial variability in seasonal patterns of the major inorganic ionic components at Yongxing Island and adjacent sites of the Acid Deposition Monitoring Network in East Asia (EANET) in 2011 is portrayed in Fig. 7. In general, total major inorganic ionic concentrations tended to be higher in cool seasons and lower in warm seasons to the north of Phnom Penh, including Phnom Penh, Hoa Binh, Hanoi, Hongwen, Hedo, Ogasawara, and Yongxing Island, consistent with previous studies (Boreddy and Kawamura, 2015; Wang et al., 2006; Xiao and Liu, 2004). There was no substantial seasonal variation at other sites of EANET, and there was no strong seasonal variation of rainfall there either. These results suggest that rainfall and wind patterns, anthropogenic activities influence the ionic seasonal variations (Lawrence and Lelieveld, 2010; Wang et al., 2006; Xiao et al., 2013; Xiao and Liu, 2004).

Additionally, total major ionic concentrations were higher in the north than in the south, indicating more anthropogenic pollutants in the north, such as SO_4^{2-} and NO_3^- (Lawrence and Lelieveld, 2010). As it is well known, the most densely populated regions in the north, including Hanoi, northeastern China, Pearl River Delta of China, Korea, and Japan release large amounts of pollutants (Lawrence and Lelieveld, 2010), which then transport to the SCS in the cool seasons (Fig. 1).

The total ionic concentrations were higher at the three islands than sites to the south of Phnom Penh. As shown in Fig. 7, relatively high concentrations of Na^+ and Cl^- were found at those islands, suggesting that ions from sea salt had large contributions to total major ions, i.e., 52.8%, 62.5% and 55.6% at Yongxing, Ogasawara and Hedo, respectively. This represents high mass concentrations of sea salt in the marine atmospheric aerosol. The highest concentrations of both Na^+ and Cl^- appeared in November at Yongxing and Hedo islands, which were influenced by a strong northeast monsoon. The highest concentrations of both Na^+ and Cl^- were in September at Ogasawara Island, which were influenced by a strong southeast monsoon from the Pacific. The relationship between Na^+, Cl^- and wind speed at Yongxing ($p < 0.01$) is shown in Table ~~1 ~~3~~and Fig. S1~~. Other sites in Fig. 7 were also influenced by wind speed and winds directly from the ocean. However, the highest Na^+ and Cl^- concentrations at some sites did not appear in the same month, e.g., at Hongwen, the highest concentrations of Na^+ were in April and the highest of Cl^- were in January. Excess Cl^- in January ~~there may ~~ha~~ve~~s been observed by anthropogenic sources~~come from biomass burning and coal combustion~~ in China (Duan et al., 2006).

The highest concentrations of Mg^{2+} were in the same months as Na^+ at most sites, indicating that Mg^{2+} may be from sea salt with Na^+ for almost all stations. The exceptions were at Hoa Binh and Tanah Rata with the maximum Mg^{2+} concentrations being in December and July, respectively. This suggests that Mg^{2+} originates from the crust rather than oceans (Xiao and Liu, 2004), or from both crust and ocean~~s~~ at these sites. Hoa Binh was influenced by the northeast monsoon, which carries strongly weathering crustal matters from China Yunnan-Guizhou Plateau karst (Hien et al., 2004; Xiao et al., 2013), and there was a strong relationship between Mg^{2+} and Ca^{2+} ($R = 0.7$, $p < 0.05$). Ca^{2+}~~, a tracer for dust,~~ had its highest concentrations in July at Phnom Penh, Tanah Rata, Petaling Jaya, Serpong, and Danum Valley, all of which are located in the south of the SCS. In these regions, relatively little rainfall (rainfall data from EANET) and strong sunlight were observed in that month, leading to strong weathering that generated Ca^{2+}. However, the highest Ca^{2+} concentrations were found at other sites in the cool season, during which there was much dust from Northeast Asia (Fig. ~~S2~~S1; Boreddy and Kawamura, 2015; Liu et al., 2014; Wang et al., 2011). This result is consistent with earlier studies (Boreddy and Kawamura, 2015;

Cheng et al., 2000; Liu et al., 2014; Zhao et al., 2015). The Ca^{2+} data also proved that Asian dust can affect the northern SCS, but it is difficult for Asian dust to be transported to the southern SCS (Fig~~s~~. S1~~ and S2~~).

Figure 8 shows fire spot data from MODIS global fire mapping around the SCS during March 2014 through February 2015. Additionally, ~~dynamic~~ smoke surface concentrations every day in that period and region is shown in Fig. ~~S2~~S1. The fire spot and smoke data give information on seasonal variations of biomass burning around the SCS. This activity was strong from January to April in the west of the SCS, including Vietnam, Thailand and Laos, and between July and October in the south of the SCS, including Malaysia and Indonesia (Figs. 8 and ~~S2~~S1). These data are consistent with other studies showing substantial monthly CO emissions from biomass burning during February–April and August–October in Southeast Asia, and February–May in southern China and Taiwan (Streets et al., 2003). K^+ is commonly used as a tracer of biomass and biofuel burning (Deng et al., 2010). As shown in Fig. 7, we found that the maximum K^+ was in the aforementioned months at most sites, suggesting that Asian biomass burning ~~heavily~~ influenced the SCS region.

~~f~~Fossil fuel combustion, industrial processes, biofuel burning, agricultural and waste handling ~~also~~often generate large quantities of SO_2, NO_x, NH_3 in Asia (Lawrence and Lelieveld, 2010; Liu et al., 2013; Xiao et al., 2012a; Xiao et al., 2014; Xiao et al., 2015)~~.~~, although natural emissions of SO_2 and NH_3 include from ~~B~~biomass burning, marine and soil biological processes ~~is an important source of atmospheric pollutants, such SO_2, NO_x, and NH_3~~ (Streets et al., 2003; Altieri et al., 2014; Boreddy and Kawamura, 2015; Xiao et al., 2012a), and NO_x from those processes and lightning (Price et al., 1997; Xiao et al., 2015)~~.~~. ~~According to the reported by Streets et al. (2003), emissions of biomass burning in Asia contribute 0.37 Tg of SO_2, 2.8 Tg of NO_x, and 0.92 Tg of NH_3, or 1.1%, 11% and 3.3% of total Asian emissions, respectively. Natural emissions include SO_2 and NH_3 from marine and soil biological processes (Altieri et al., 2014; Boreddy and Kawamura, 2015; Xiao et al., 2012a), and NO_x from those processes and lightning (Price et al., 1997; Xiao et al., 2015). Certainly, fossil fuel combustion, industrial processes, biofuel burning, agricultural and waste handling also generate large quantities of SO_2, NO_x, NH_3 in Asia (Lawrence and Lelieveld, 2010; Liu et al., 2013; Xiao et al., 2012a; Xiao et al., 2014; Xiao et al., 2015).~~ In general, the three marine sites (Yongxing, Hedo, and Ogasawara islands) had smaller proportions of SO_4^{2-}, NO_3^- and NH_4^+ than inland sites, with the three ions accounting for ~35% at the three marine sites and up to 65% at the other sites. This indicates that anthropogenic contributions are smaller over remote open oceans than at continental sites. Figure 6 shows that the highest SO_4^{2-}, NO_3^- and NH_4^+ concentrations were found during the cool season in the north of Phnom Penh, including Phnom Penh, Hoa Binh, Hanoi, Hongwen, Hedo, Ogasawara, and Yongxing, consistent with total inorganic major ions. This indicates that the pollutants from Northeast Asia have a great impact on the

Northwest Pacific. Figure ~~S2~~ S1 confirms these findings that pollutants from nature and anthropogenic activities effect the Northwest Pacific. We also found that most sites in the south of Phnom Penh had maximum SO_4^{2-} and NO_3^- concentrations in the same months as the highest K^+ concentrations occurred, suggesting that biomass and biofuel burning are important sources for SO_4^{2-} and NO_3^- in those regions. Lawrence and Lelieveld (2010) found that such burning was important in the emissions of SO_4^{2-} and NO_3^- in southern Asia, whereas fossil fuel combustion and industrial processes tended to be dominant in northern Asia (Xiao et al., 2015). However, maximum NH_4^+ concentrations at some sites (e.g., Petaling Jaya, Serpong, Danum Valley) were inconsistent with SO_4^{2-} and NO_3^-. Moreover, there was no relationship between SO_4^{2-} or NO_3^- and NH_4^+ at these sites in the south of Phnom Penh, including Phnom Penh and Yongxing Island (both $p > 0.05$). The results are inconsistent with previous studies (Boreddy and Kawamura, 2015; Hsu et al., 2007; Wang et al., 2006; Xiao et al., 2013; Xiao and Liu, 2004). In the marine atmosphere, SO_4^{2-} and NO_3^- are predominant in coarse particles~~H_2SO_4 and HNO_3 can react with NaCl to generate Na_2SO_4, $NaNO_3$ in coarse particles, and HCl~~ (Boreddy and Kawamura, 2015; Xiao et al., 2015~~).~~); while NH_4^+ is often predominant in fine particles and may exist in the form of $(NH_4)_2SO_4$ in their accumulation mode (Ooki et al., 2007; Ottley and Harrison, 1992). ~~However, ratios of NH_4^+ to nss-SO_4^{2-} in the size range D > 0.22 μm (D = diameter) decreased with particle size (Ooki et al., 2007). Ooki et al. (2007) found that in the range 0.06 < D < 0.22 μm, $(NH_4)_2SO_4$ was mainly derived from marine biogenic sources. In addition, ammonium salts such as NH_4Cl and NH_4NO_3 are readily dissociable by evaporation in the marine atmosphere (Ottley and Harrison, 1992), which caused a weak relationship between NH_4^+ and other ions at Yongxing Island.~~

3.3 Source identification, apportionment, and region~~Aerosol chemical principal component analysis~~

~~3.3.1 Correlation analysis~~

~~Correlation analysis was used to characterize relationships among the ions and distinguish potential sources of ionic constituents (Xiao et al., 2013; Xiao and Liu, 2004). As shown in Table 1, *p*-values among all ions except NH_4^+ were < 0.01 at Yongxing Island, indicating that the correlation between each two ions was statistically significant. *R* between Na^+ and Cl^- was > 0.8, suggesting that they have a major common source and may exist in NaCl within aerosols in the marine atmosphere. The mole equivalent ratios of Cl^-/Na^+ (neq/L) in aerosols were slightly larger than seawater in annual, cool and warm seasons at Yongxing Island (Table 2). This suggests that Cl^- enrichment had an anthropogenic or natural biomass burning origin (Duan et al., 2006; Jung et al., 2012; Xiao et al., 2013). However, as shown in Table 2, the ratio of Cl^-/Na^+ was slightly smaller than seawater in the transition season, most likely because air masses were primarily from local areas far from the continent (Fig. 1), where wind~~

~~is weak (Fig. 2). Thus, Cl^- depletion occurred through the volatilization of HCl during the reaction of NaCl with N_xO_y, HNO_3, or H_2SO_4 (Hsu et al., 2007; Jung et al., 2012; Xiao et al., 2015). Nevertheless, most Na^+ originates from sea salt, but part is from dust, fossil combustion, and biomass burning (Tiwari et al., 2013; Xiao et al., 2016; Zhang et al., 2015). There was a strong relationship between K^+ and Cl^- (Table 1), indicating that KCl is partly from sylvite weathering and biomass burning (Xiao et al., 2013). In addition, K^+ had strong correlation with Ca^{2+}, implying that they may come from crustal components. According to the ratio of K^+/Na^+ at Yongxing Island and in seawater (Table 3), a part of K^+ is from seawater. Further, a strong relationship between K^+ and SO_4^{2-} was found (Table 1), indicating that they have a common source, i.e., biomass burning (Li et al., 2003; Streets et al., 2003). There was also a strong relationship between Ca^{2+} and SO_4^{2-}, meaning that they may exist in the form of $CaSO_4$ in the marine atmosphere. The secondary aerosols SO_4^{2-} and NO_3^- were also strongly correlated, which may be attributed to similarity of their chemical behavior and a common source of their precursors SO_2 and NO_x (Xiao et al., 2013). Ratios of Mg^{2+}/Na^+ were equal to those of seawater throughout the year at Yongxing (Table 2), indicating that most Mg^{2+} was likely from sea salt. However, R between Mg^{2+} and Na^+ was much smaller than that between Cl^- and Na^+, suggestive of a different behavior of Mg^{2+} to that of Na^+. The ratios of NO_3^-/nss-SO_4^{2-} and NH_4^+/nss-Ca^{2+} were about 0.7 and 0.07 at Yongxing (Table 3), respectively. This may be because that nss-SO_4^{2-} and nss-Ca^{2+} were the major components from the continent, and demonstrated the presence of $CaSO_4$. There were large R among most ions (Table 2), suggesting that they existed in the following forms: NaCl, $CaCl_2$, $MgCl_2$, KCl, Na_2SO_4, $CaSO_4$, $MgSO_4$, K_2SO_4, $(NH_4)_2SO_4$, $NaNO_3$, $Ca(NO_3)_2$, $Mg(NO_3)_2$, KNO_3, and NH_4NO_3.~~

~~3.3.2 Principal component analysis and classical multidimensional scaling~~

~~Principal component analysis (PCA) was also used to explore the relationship among the aerosol ions at Yongxing Island (Fig. 9a). As seen in the figure, the first two components (PC1 and PC2) explained 96.0% of the variance in total and 84.5% and 11.5% individually. The first component captured the variance of Cl^-, Na^+, Ca^{2+}, K^+, Mg^{2+}, SO_4^{2-} and NO_3^-, indicating that they had common sources or chemical behaviors, as mentioned above. The angle between two ions and arrow lengths reflect their relationship and the contribution of different ions to the principal component. As shown in Fig. 9a, the samples from the cool season had a greater contribution to PC1 than in other seasons.~~

~~To better classify the ions, classical multidimensional scaling (CMDS) of the correlation coefficients based on Table 2 is plotted in Fig. 9b. As shown in that figure, in the same quadrant, they may have common sources or behaviors. For example, Na^+ and Cl^- in the same quadrant indicates that they possibly derived from sea salt. SO_4^{2-}~~

~~and Ca^{2+} in the same quadrant implies that they likely existed in the form of $CaSO_4$ in the marine atmosphere. Although Mg^{2+} was alone in a quadrant, it was in the lower right quadrant with Na^+ and Cl^-, suggesting that they had a common source from sea salt, but different behaviors. Previous study reported that Na^+ may exist in super-micron size aerosol, and Mg^{2+} in sub-micron size aerosol (Moody et al., 2014). SO_4^{2-}, Ca^{2+}, K^+, Cl^- and Na^+ in the positive Dimension 1 indicates that they may exist in coarse particles. It was clear that NH_4^+ is widely separated from other ions, indicating that it was from a unique source.~~

~~3.3.3 Source identification and apportionment~~

Based on the PMF 5.0 model, five potential sources of atmospheric chemical components at Yongxing Island were identified: sea salt (two species), crust, SIA, and oceanic emission~~biomass burning, fossil fuel combustion, and marine biogenic~~. Table ~~3~~ 4 summarizes source apportionment of the relative contributions of each identified source to ~~the TSP and~~ major ions. Figs. 9 and 10 show the modeled source profiles and the time series of modeled concentrations for each identified main source.

Further, CWTs were plotted for TSP and major ions (Fig. 1~~0~~1) to explore likely regional sources and transport pathways for the island. Air masses at Yongxing Island had obvious unique and seasonal variations, from northeast of the island in the cool season, southwest in the warm season, and southeast in the transition season (Fig. 1~~0~~1). This reveals that aerosol or chemical compositions at the island originated from different regions in different seasons (Figs. 1, 8, 1~~0~~1 and S~~2~~1). ~~A major discovery was that~~ The air masses with high TSP concentrations were from China coastal regions bordering the Yellow and East China Seas and northern South China (Fig. 1~~0~~1). This is consistent with the seasonal variations of TSP concentrations in Fig. 6. The average aerosol optical thickness (AOT) over the Northwest Pacific (Fig. 1) confirmed this result. A relatively large average AOT was found over the northern SCS and East China Sea in the cool season, and Karimata Strait in the warm season (Fig. 1). But there was a relatively low average AOT over the entire SCS in the transition season (Fig. 1). ~~These sources have average contributions of 26% for sea salt and 53% for crust to TSP, and < 10% for others.~~

The first source, sea salt, generally has strong marine elements, such as Na^+ (~~and~~ Cl^-) and Mg^{2+}, which Na^+ exists in super-micron size aerosols, whereas Mg^{2+} in sub-micron size aerosols (Moody et al., 2014). They contributed ~~74~~77.4% (Na^+), ~~and 82~~93.9% (Cl^-) and 70.4% (Mg^{2+}) from sea salt at Yongxing Island (Table ~~3~~4). Although the CWT for Mg^{2+} was ~~also~~ larger in the cool season and lower in the warm season, air masses with relatively high concentrations of Mg^{2+} originated offshore of China (Fig. 1~~0~~0). This further indicates that Mg^{2+} was mainly from sea salt~~, consistent with the PMF results (Table 3).~~ Other significant sources were crust, SIA and oceanic emission~~biomass burning, fossil fuel combustion and marine biogenic~~, with contributions < 10% for Na^+ and Cl^-, and <16% for Mg^{2+}. According to data of rainwater at Yongxing Island, a part of Na^+ and Cl^- could be from crust and produced by burning (Xiao et al., 2016). Coal combustion and biomass burning also produce Na^+ and Cl^- (Liu et al., 2000; Tiwari et al., 2013; Zhang et al., 2015). Zhang et al. (2015) found that coal combustion was the most likely dominant source of Cl^- in Beijing. The mole equivalent Cl^-/Na^+ ratios were larger in the cool season than in the transition and warm seasons at Yongxing, indicating that the crust, fossil combustion, and biofuel and biomass burning affected Na^+ and Cl^- concentrations over the Northwest Pacific (Figs. 8 and ~~S2~~S1). As shown in Table ~~2~~3, there were strong relationships between Na^+ (Cl^-) and SO_4^{2-} (Ca^{2+}, K^+), further proving that crust, fossil combustion and biomass burning can generate Na^+ and Cl^-. Moreover, NaCl can react with acids such as H_2SO_4, HNO_3 and $H_2C_2O_4$, altering Na^+ and Cl^- concentrations in the marine atmosphere and producing secondary chlorine-containing salt (Boreddy and Kawamura, 2015). Sea salt provided K^+, ~~Mg^2~~Ca^{2+} and SO_4^{2-}, constituting ~~42~~53.2%, ~~63~~33.9% and ~~31~~24.0%, respectively. The rations of K^+/Na^+, Ca^{2+}/Na^+ and SO_4^{2-}/Na^+ in Table 2 also indicate that part of them are from sea salt. The results are consistent with other studies (Boreddy and Kawamura, 2015).

The second source, crust, has a substantial crustal elements Ca^{2+} and Mn (Fig. 9), which ~~is~~ are~~a~~ tracers of crust (Suzuki and Tsunogai, 1988; Xiao et al., 2013; Xiao and Liu, 2004; Norris et al., 2014). However, Ca^{2+} from the crust, only had a contribution of 9.8% (Table 4). The result indicates that it is difficult for Ca^{2+} directly derived from crust to transport to open ocean. But CWTs for Ca^{2+} were larger in the cool season and lower in the warm season, indicating that dust from Northeast Asia influenced aerosol chemistry in the remote marine areas (Figs. 1, 11 and S1). The result suggests that when it reacts with H_2SO_4 and HNO_3 to generate secondary inorganic aerosol, e.g. $CaSO_4$ and $Ca(NO_3)_2$, it may transport to a longer distance.~~Absolutely, Ca^{2+} mainly came from the crust, which had a contribution of 50% (Table 3). A strong relationship between TSP and Ca^{2+} observed at Yongxing Island (*R*=0.92, *p*<0.01, Table 1) indicated that crust had a large contribution to TSP (53%; Table 3). Biomass burning and fossil combustion also had contributions (9% and 18%, respectively) to Ca^{2+}. CaSO$_4$ and sulfate containing both K and Ca have been observed in smoke and have been reported to originate from biomass burning (Allen and Miguel, 1995; Li et al., 2003). This implies that Asian biomass and biofuel burning increased Ca^{2+} concentrations of aerosols in the marine atmosphere. Studies have found that atmospheric Ca^{2+} also derives from fossil fuel combustion (Hutton and Symon, 1986). Some Ca^{2+} may be affected by local coral (Suzuki and Tsunogai, 1988; Xiao et al., 2016). There is a large percentage of live coral cover (Huang et al., 2006). Large corals have been dying~~

~~with rapid development of the Xisha islands (including Yongxing), which have generated large amounts of $CaCO_3$ and become a source of Ca^{2+} in marine atmospheric aerosols (Xiao et al., 2014; Xiao et al., 2016).~~

The third source is relevant to secondary inorganic aerosol, which are typically characterized by remarkable SO_4^{2-} and NO_3^-. They contributed 57.5% and 69.5% from SIA at Yongxing Island (Table 4) and good relationship between them was observed (Table 2). Fossil fuel (especially coal) combustion releases large amounts of SO_2 and NO_x (Xiao et al., 2012b, 2014 and 2015). Lawrence and Lelieveld (2010) attributed 61% of total NO_x and 77% of total SO_2 emissions from fossil fuel combustion in southern Asia, 76% of total NO_x and 75% of total SO_2 in northern Asia, resulting in the transport of substantial secondary inorganic aerosols containing SO_4^{2-} and NO_3^- to the SCS (Figs. 1, 11 and S1). As with TSP and Ca^{2+}, air masses from China coastal regions had high SO_4^{2-} and NO_3^- concentrations in the cool season (Fig. 11), owing to rapid economic development and great coal demand in the country, especially in its coastal regions (Lawrence and Lelieveld, 2010). Figure S1 also shows that SO_4^{2-} from central and eastern China reached coastal regions in the cool season. In Chinese coastal provinces, emission intensities of SO_2 and NO_x were about 10 and 15 tons/km^2, respectively, much higher than other Chinese provinces (China Environment Statistical Yearbook, 2014). Rapidly growing economies and high population densities in these regions (Kim et al., 2014) release pollutants that are transported to the Northwest Pacific. In the atmosphere, the products (H_2SO_4 and HNO_3) of SO_2 and NO_x can easily combine alkaline ions, such as Ca^{2+} and K^+ (Xiao et al., 2013), which K^+ is characterized as an effective tracer of biomass and biofuel burning aerosols (Zhang et al., 2015). As shown in Table 4, SIA had much bigger contributions of 56.3% to Ca^{2+} and 27.7% to K^+. We found that there were strong relationships between SO_4^{2-} (NO_3^-) and Ca^{2+} (K^+) (Table 3). These suggest that SO_4^{2-} and NO_3^- changed source attribution of some alkaline ions to transport to open ocean. In this case, it is difficult to distinguish the Ca^{2+} and K^+ sources using PMF model.

~~The third source, biomass burning, is characterized by substantial K^+, which is an effective tracer of biomass and biofuel burning aerosols (Zhang et al., 2015), with a contribution of 41% from such burning at Yongxing Island. K^+ salts and organic particles are the dominant species in smoke, with more KCl in young smoke, and K_2SO_4 and KNO_3 in aged smoke from biomass burning (Li et al., 2003). As shown in Figs. 8 and S2, biomass burning was more frequent in the cool season than in the warm and transition seasons over the Northwest Pacific, yielding ratios of K^+/Na^+ (neq/L) that were larger in the cool season (Table 2). Another main source for K^+ was sea salt, with a contribution of 42% (Table 3). In addition, biomass burning produces SO_2 and NO_x (Streets et al., 2003; Xiao et al., 2015; Zhang et al., 2015); they accounted for 7% of SO_4^{2-} and 1% of NO_3^-.~~

~~The fourth source is fossil fuel (especially coal) combustion, which releases large amounts of SO_2, NO_x and NH_3 (Xiao et al., 2012b; Xiao et al., 2014; Pan et al., 2016). Accordingly, fossil combustion contributed 22%, 56% and 26% to SO_4^{2-}, NO_3^- and NH_4^+ at Yongxing Island, respectively. SO_4^{2-} and NO_3^- emissions from fossil combustion may originate from Northern Asia in the cool season (Lawrence and Lelieveld, 2010; Xiao et al., 2015). In Chinese coastal provinces, emission intensities of SO_2 and NO_x were about 10 and 15 tons/km^2, respectively, much higher than other Chinese provinces (China Environment Statistical Yearbook, 2014). These results indicate that human activities clearly affected marine atmospheric chemical compositions.~~

The ~~fifth~~ fourth source is oceanic emission~~marine biogenic~~, which released NO_x, NH_3 and DMS (Altieri et al., 2014; Jickells et al., 2003; Boreddy and Kawamura, 2015; Phinney et al., 2006), with respective contributions of ~~19~~1.6% to NO_3^-, ~~69~~60.5% to NH_4^+, and ~~38~~6.9% to SO_4^{2-} at Yongxing Island (Table ~~3~~4). As shown in Fig. 11, air masses with high NH_4^+ concentrations were from remote open oceans such as the southeastern and northeastern SCS. There were relatively higher NH_4^+ concentrations in the cool season and lower values in the warm season at Yongxing Island (Fig. 6). These suggest that it is feasible for the ocean to be a NH_4^+ source. Substantial NH_x may be released from degraded organic nitrogen-containing compounds and excretion from zooplankton in the ocean (Norman and Leck, 2005). Altieri et al. (2014) suggested that the efficient kinetics of ammonia evasion from surface seawater causes NH_3 to accumulate in the marine atmosphere. The contribution of oceanic emission~~marine biogenic sources~~ to NH_4^+ was much larger at Yongxing than at global marine atmospheric NH_x sources in the review of Duce et al. (2008), which showed 87.5% from anthropogenic sources. However, Altieri et al. (2014) found that the anthropogenic contribution was < 87.5% at Bermuda, an island in the North Atlantic Ocean (Fig. 5). Atmospheric NH_x is usually rapidly deposited near source regions and has a short residence time, about several hours in the marine boundary layer (Boreddy and Kawamura, 2015; Xiao et al., 2012a; Xiao and Liu, 2002). Thus, NH_x transportation from continental to remote sea sites is limited. Therefore, NH_4^+ in aerosol at Yongxing Island was possibly from oceanic emission, as being reported at other marine sites (Altieri et al., 2014; Jickells et al., 2003). DMS is the most abundant marine biogenic volatile sulfur emitted from the ocean surface to atmosphere, and can be oxidized to SO_4^{2-} in the marine atmosphere (Phinney et al., 2006). Yang et al. (2015) reported that biogenic SO_4^{2-} from the Bohai and northern Yellow seas near China was 0.114–0.551 μg/m^3, with an average of 0.247 μg/m^3, accounting for 1.4% of nss-SO_4^{2-}. Biogenic SO_4^{2-} in the northern SCS was ~1.2 and 0.6 μg/m^3 in summer and winter, respectively (Zhang et al., 2007), constituting ~8% and 12% of nss-SO_4^{2-}. CWTs for SO_4^{2-} in Fig. 11, also show some SO_4^{2-} were from marine biogenic source.~~However, large ratios of biogenic SO_4^{2-} to nss-SO_4^{2-} were observed at the remote Pacific islands of Oahu and Midway, at 55% and 70% (Arimoto et al., 1996), being~~

~~consistent with our results.~~ Thus, natural sources had large contributions to marine atmospheric aerosols over the Northwest Pacific.

~~3.4 Regional sources deduced from trajectory and CWT analyses~~

~~Air masses at Yongxing Island had obvious unique and seasonal variations, from northeast of the island in the cool season, southwest in the warm season, and southeast in the transition season (Fig. 10). This reveals that aerosol or chemical compositions at the island originated from different regions in different seasons (Figs. 1, 8, 10 and S2). CWTs were plotted for TSP and major ions (Fig. 10) to explore likely regional sources and transport pathways for the island. A major discovery was that air masses with high TSP concentrations were from China coastal regions bordering the Yellow and East China Seas and northern South China (Fig. 10). This is consistent with the seasonal variations of TSP concentrations in Fig. 6. The average aerosol optical thickness (AOT) over the Northwest Pacific (Fig. 1) confirmed this result. A relatively large average AOT was found over the northern SCS and East China Sea in the cool season, and Karimata Strait in the warm season (Fig. 1). But there was a relatively low average AOT over the entire SCS in the transition season (Fig. 1).~~

~~CWTs for Ca^{2+} had a similar trend as that of TSP, larger in the cool season and lower in the warm season, indicating that dust from Northeast Asia influenced aerosol chemistry in the remote marine atmosphere (Figs. 1, 10 and S2). Although the CWT for Mg^{2+} was also larger in the cool season and lower in the warm season, air masses with relatively high concentrations of Mg^{2+} originated offshore of China (Fig. 10). This indicates that Mg^{2+} was mainly from sea salt, consistent with the PMF results (Table 3).~~

~~CWTs for K^+, SO_4^{2-}, and NO_3^- concentrations showed considerable seasonal variations, higher in the cool season and lower in the warm and transition seasons (Fig. 10). As with TSP and Ca^{2+}, air masses from China coastal regions had high SO_4^{2-} and NO_3^- concentrations in the cool season (Fig. 10), owing to rapid economic development and great coal demand in the country, especially in its coastal regions (Lawrence and Lelieveld, 2010). However, the three ions may have different sources; K^+ was mainly derived from biomass and biofuel burning in Northeast Asia (Fig. 8; Atwood et al., 2013; Streets et al., 2003), whereas NO_3^- and SO_4^{2-} were mainly from fossil fuel combustion in that region (Table 3; Xiao et al., 2014 and 2015a; Lawrence and Lelieveld, 2010). Figure S2 also shows that SO_4^{2-} from central and eastern China reached coastal regions in the cool season. According to data from the China Environment Statistical Yearbook (2014), average SO_2, NO_x, and soot and dust emissions from Chinese coastal regions (Liaoning, Hebei, Shandong, Jiangsu, Zhejiang, Fujian and Guangdong provinces, and the cities of Shanghai, Beijing and Tianjin) exceeded 10, 15 and 5 tons/km^2, respectively, much greater than other provinces or~~

~~cities in the country. In addition, higher concentrations of SO_2 and NO_x in Northeast Asia than South Asia (Lawrence and Lelieveld, 2010) indicate that the marine atmospheric aerosol chemical compositions were influenced by Northeast Asia, especially China coastal regions in the cool season. Rapidly growing economies and high population densities in these regions (Kim et al., 2014) release pollutants that are transported to the Northwest Pacific. Biogenic SO_4^{2-} from the Chinese seas may affect the atmospheric aerosol chemical compositions.~~

~~As mentioned above, in Table 3, NH_4^+ may largely come from marine biogenic sources, and air masses with high NH_4^+ concentrations were from remote open oceans such as the southeastern and northeastern SCS (Fig. 10). This suggests that it is feasible for the ocean to be a NH_4^+ source. Globally, 87.5% of marine atmospheric NH_x is from human activities (Duce et al., 2008). However, there was little NH_x from such activities at Yongxing Island, consistent with Altieri et al. (2014). There were relatively higher NH_4^+ concentrations in the cool season and lower values in the warm season at Yongxing Island (Fig. 6). The Northwest Pacific Ocean including the SCS has oligotrophic surface water and is a nitrogen-limited region (Chen et al., 2004; Kim et al., 2014; Wu et al., 2001), with only a hundred nanomoles per liter of NH_4^+ in surface water (Lin, 2013). Thus, it is in some ways counterintuitive that marine atmospheric aerosol NH_4^+ at Yongxing Island is from marine sources. Altieri et al. (2014) suggested that the efficient kinetics of ammonia evasion from surface seawater causes NH_3 to accumulate in the marine atmosphere. NH_3 may be released from degraded organic nitrogen-containing compounds and excretion from zooplankton (Norman and Leck, 2005). Lin (2013) found average N_2 fixation rates in the SCS of 4.9 and 0.7 μmol N/m³/d in the cool season and warm seasons, respectively. He suggested that this seasonal variation may be caused by the intensity of the Kuroshio intrusion in the SCS and Fe supply from the atmosphere in the cool season, which enhances primary productivity. The unique temporal variations of N_2 fixation rates in the SCS are consistent with our CWT results. Moreover, as shown in Figs. 1 and S2, dust was transported to remote open oceans in the cool season, likely containing substantial Fe (Wu et al., 2001). Increased Fe would greatly increase productivity in these marine regions (Wu et al., 2001).~~ Figure 10 illustrates the time series of daily concentrations contributed by each identified source. In order to examine if the results are reasonable, we compared the modeled results of each source with the observed seasonal variations of the specific chemical species (Figs. 6 and 11). As shown in Fig. 9, the highest and lowest contributions of sea salt were in November-December and April-May, respectively, which are consistent with the seasonal variations of aerosol Na^+, Cl^- and Mg^{2+}. For crust, the resulting time series show that it has a higher concentration in March, 2014 and February, 2015, relatively close to the obersved values of Ca^{2+} and K^+ (Figs. 6 and 11). SIA has higher contributions from November, 2014 to February, 2015 and lower other months, which also consistent with the observed and CWTs data of SO_4^{2-} and NO_3^-

shown in Figs. 6 and 11. This result is definitely related to the photochemistry that accounts for SIA formation (Zhang et al., 2013). The formed SIA species may not appear in their original emission sources (Zhang et al., 2013), such as coal combustion, biomass burning and crust. It is obvious that oceanic emission has highest contribution in March, and secondary highest in October, consistent with the seasonal change of NH_4^+. The PMF and CWTs modeled results seem to be promising because the corresponding time series of each source's contribution are very consistent with the observations.

4 Conclusions

Chemical compositions of 1-year aerosols at Yongxing Island were investigated to help better ~~understanding~~ understand~~of~~ their chemical characteristics, sources, and transport pathways over the SCS. Sea salt (Na^+ and Cl^-) had the greatest contribution to total major inorganic ions in aerosols at the island, followed by SO_4^{2-}, Ca^{2+}, NO_3^-, Mg^{2+}, K^+ and NH_4^+. The concentrations of TSP and all major inorganic ions showed seasonal variations, with higher concentrations in the cool season and lower in the warm season, which was influenced by meteorological parameters (e.g., wind speed, temperature, relative humidity and rainfall) and air masses. Using PMF and CWT models, fire spot and AOT, we found that Na^+, Cl^-, and Mg^{2+} were mainly derived from sea salt, SO_4^{2-} and NO_3^- of secondary inorganic aerosol mainly came from fossil fuel combustion (especially coal combustion in the Northern Asia). NH_4^+ was mainly from oceanic emission in the remote ocean. In summary, fossil fuel combustion seriously affected marine atmospheric aerosol chemical compositions over the Northwest Pacific.~~Ca^{2+} from soil dust, K^+ from biomass burning, and NO_3^- from fossil fuel combustion (especially coal combustion in the Northern Asia). SO_4^{2-} was from marine biogenic sources, sea salt, and fossil fuel combustion. Surprisingly, NH_4^+ was mainly from marine biogenic processes in the remote ocean. In summary, Asian dust, biomass burning and fossil fuel combustion seriously affected marine atmospheric aerosol chemical compositions over the Northwest Pacific.~~

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References

Altieri, K.E., Hastings, M.G., Peters, A.J., Oleynik, S. and Sigman, D.M.: Isotopic evidence for a marine ammonium source in rainwater at Bermuda, Global Biogeochemical Cycles, 28(10), 1066 – 1080, 2014.

Aouizerats, B., Van Der Werf, G. R., Balasubramanian, R. and Betha, R.: Importance of transboundary transport of biomass burning emissions to regional air quality in Southeast Asia during a high fire event, Atmospheric Chemistry and Physics, 15, 363-373, 2015.

Arakaki, T., Azechi, S., Somada, Y., Ijyu, M., Nakaema, F., Hitomi, Y., Handa, D., Oshiro, Y., Miyagi, Y. and Ai, T.: Spatial and temporal variations of chemicals in the TSP aerosols simultaneously collected at three islands in Okinawa, Japan, Atmospheric Environment, 97, 479-485, 2014.

Atwood, S.A., Reid, J.S., Kreidenweis, S.M., Cliff, S.S., Zhao, Y., Lin, N.H., Tsay, S.C., Chu, Y.C. and Westphal, D.L.: Size resolved measurements of springtime aerosol particles over the northern South China Sea, Atmospheric Environment, 78(676), 134-143, 2013.

Balasubramanian, R., Karthikeyan, S., Potter, J., Wurl, O. and Durville, C.: Chemical characterization of aerosols in the equatorial atmosphere over the Indian Ocean, Atmospheric Environment, 78(3), 268-276, 2013.

Boreddy, S. and Kawamura, K.: A 12-year observation of water-soluble ions in TSP aerosols collected at a remote marine location in the western North Pacific: an outflow region of Asian dust, Atmospheric chemistry and physics, 15(11), 6437-6453, 2015.

Carrillo, J.H., Hastings, M.G., Sigman, D.M. and Huebert, B.J.: Atmospheric deposition of inorganic and organic nitrogen and base cations in Hawaii, Global Biogeochemical Cycles, 16(4), doi: 10.1029/2002GB001892, 2002

Cheng, I., Zhang, L., Blanchard, P., Dalziel, J. and Tordon, R.: Concentration-weighted trajectory approach to identifying potential sources of speciated atmospheric mercury at an urban coastal site in Nova Scotia, Canada, Atmospheric Chemistry And Physics, 13(12), 6031-6048, 2013.

Cheng, Z.L., Lam, K.S., Chan, L.Y., Wang, T. and Cheng, K.K.: Chemical characteristics of aerosols at coastal station in Hong Kong. I. Seasonal variation of major ions, halogens and mineral dusts between 1995 and 1996, Atmospheric Environment, 34(17), 2771-2783, 2000.

Chin, M: Atmospheric Aerosol Properties and Climate Impacts, DIANE Publishing, 2009.

Claeys, M., Wang, W., Vermeylen, R., Kourtchev, I., Chi, X., Farhat, Y., Surratt, J.D., Gómez-González, Y., Sciare, J. and Maenhaut, W.: Chemical characterisation of marine aerosol at Amsterdam Island during the austral summer of 2006–2007, Aerosol Science, 41, 13-22, 2010.

Crippa, M., Canonaco, F., Slowik, J. G., El Haddad, I., DeCarlo, P. F., Mohr, C., Heringa, M.F., Chirico, R., Marchand, N., Temime-Roussel, B., Abidi, E., Poulain, L., Wiedensohler, A., Baltensperger, U. and Prévôt, A.S.H: Primary and secondary organic aerosol origin by combined gas-particle phase source apportionment, Atmospheric Chemistry &

Physics, 13(16), 8411-8426, 2013.

Cui, D.Y., Wang, J.T., Tan, L.J. and Dong, Z.Y.: Impact of atmospheric wet deposition on phytoplankton community structure in the South China Sea, Estuarine Coastal & Shelf Science, 173, 1 – 8, 2016.

Davidson, C.I., Phalen, R.F. and Solomon, P.A.: Airborne particulate matter and human health: a review, Aerosol Science and Technology, 39, 737–749, 2005.

Deng, C., Zhuang, G., Huang, K., Li, J., Zhang, R., Wang, Q., Liu, T., Sun, Y., Guo, Z. and Fu, J.S.: Chemical characterization of aerosols at the summit of Mountain Tai in Central East China, Atmospheric Chemistry & Physics, 11(14), 7319-7332, 2010.

Duan, F.K., He, K.B., Ma, Y.L., Yang, F.M., Yu, X.C., Cadle, S.H., Chan, T. and Mulawa, P.A.: Concentration and chemical characteristics of $PM_{2.5}$ in Beijing, China: 2001 – 2002, Science of the Total Environment, 355(1-3), 264-75, 2006.

Duce, R.A., Laroche, J., Altieri, K., Arrigo, K.R., Baker, A.R., Capone, D.G., Cornell, S., Dentener, F., Galloway, J. and Ganeshram, R.S.: Impacts of atmospheric anthropogenic nitrogen on the open ocean, Science, 320(5878), 893-7, 2008.

Ebert, M., Weinbruch, S., Hoffmann, P. and Ortner, H.M.: Chemical characterization of North Sea aerosol particles, Journal of Aerosol Science, 31(31), 613-632, 2000.

Fang, Y.T., Koba, K., Wang, X.M., Wen, D.Z., Li, J., Takebayashi, Y., Liu, X.Y. and Yoh, M.: Anthropogenic imprints on nitrogen and oxygen isotopic composition of precipitation nitrate in a nitrogen-polluted city in southern China, Atmospheric Chemistry and Physics, 11(3), 1313-1325, 2011.

Han, J.S., Moon, K.J., Lee, S.J., Kim, Y.J., Ryu, S.Y., Cliff, S.S. and Yi, S.M.: Size-resolved source apportionment of ambient particles by positive matrix factorization at Gosan background site in East Asia, Atmospheric Chemistry & Physics, 5(4), 211-223, 2006.

Hien, P.D., Bac, V.T. and Thinh, N.: PMF receptor modelling of fine and coarse PM_{10} in air masses governing monsoon conditions in Hanoi, northern Vietnam, Atmospheric Environment, 38(2), 189-201, 2004.

Hsu, S.C., Liu, S.C., Kao, S.J., Jeng, W.L., Huang, Y.T., Tseng, C.M., Tsai, F., Tu, J.Y. and Yang, Y.: Water-soluble species in the marine aerosol from the northern South China Sea: High chloride depletion related to air pollution, Journal of Geophysical Research Atmospheres, 112(D19), 216-229, 2007.

Jia, G. and Chen, F.: Monthly variations in nitrogen isotopes of ammonium and nitrate in wet deposition at Guangzhou, south China, Atmospheric Environment, 44(19), 2309-2315, 2010.

Jickells, T.D., Kelly, S.D., Baker, A.R., Biswas, K., Dennis, P.F., Spokes, L.J., Witt, M. and Yeatman, S.G.: Isotopic evidence for a marine ammonia source, Geophysical Research Letters, 30(7), 359-376, 2003.

Jung, J., Furutani, H. and Uematsu, M.: Atmospheric inorganic nitrogen in marine aerosol and precipitation and its deposition to the North and South Pacific Oceans, Journal of Atmospheric Chemistry, 68(2), 157-181, 2012.

Keene, W.C., Moody, J.L., Galloway, J.N., Prospero, J.M., Cooper, O.R., Eckhardt, S. and Maben, J.R.: Long-term trends in aerosol and precipitation composition over the western North Atlantic Ocean at Bermuda, Atmospheric Chemistry &

Physics, 29(14), 292-303, 2005.

Kim, T.W., Lee, K., Duce, R. and Liss, P.: Impact of atmospheric nitrogen deposition on phytoplankton productivity in the South China Sea, Geophysical Research Letters, 41(9), 3156-3162, 2014.

Kolb, C.E. and Worsnop, D.R.: ChemInform Abstract: Chemistry and Composition of Atmospheric Aerosol Particles, Annual Review of Physical Chemistry, 44(63), 471-491, 2013.

Kumar, A., Sudheer, A.K. and Sarin, M.M.: Chemical characteristics of aerosols in MABL of Bay of Bengal and Arabian Sea during spring inter-monsoon: A comparative study, Journal of Earth System Science, 117(S1), 325-332, 2008.

Lawrence, M.G. and Lelieveld, J.: Atmospheric pollutant outflow from southern Asia: a review, Atmospheric Chemistry & Physics, 10(22), 11017-11096, 2010.

Lin, N. H., Tsay, S. C., Maring, H. B., Yen, M. C., Sheu, G. R., Wang, S. H., Chi, K.H., Chuang, M.T., Ou-Yang, C.F., Fu, J.S., Reid, J.S., Lee, L.C., Wang, L.C., Wang, J.L., Hsu, C.N., Sayer, A.M., Holben, B.N., Chu, Y.C., Nguyen, X.A., Sopajaree, K., Chen, S.J., Cheng, M.T., Tsuang, B.J., Tsai, C.J., Peng, C.M., Schnell, R.C., Conway, T., Chang, C.T., Lin, K.S., Tsai, Y.I., Lee, W.J., Change, S.C., Liu, J.J., Chiang, W.L., Huang, S.J., Lin, T.H. and Liu, G.R.: An overview of regional experiments on biomass burning aerosols and related pollutants in Southeast Asia: From BASE-ASIA and the Dongsha Experiment to 7-SEAS, Atmospheric Environment, 78, 1-19, 2013.

Liu, P. F., Zhao, C. S., Göbel, T., Hallbauer, E., Nowak, A., Ran, L., Xu, W.Y., Deng, Z.Z., Ma, N., Mildeberger, K., Henning, S., Stratmann, F. and Henning, S.: Hygroscopic properties of aerosol particles at high relative humidity and their diurnal variations in the North China Plain. Atmospheric Chemistry and Physics, 11(7), 3479-3494, 2011.

Liu, S., Chen, M. and Zhuang, Q: Aerosol effects on global land surface energy fluxes during 2003–2010, Geophysical Research Letters, doi: 10.1002/2014GL061640, 2014.

Liu, X., Espen, P.V., Adams, F., Cafmeyer, J. and Maenhaut, W.: Biomass Burning in Southern Africa: Individual Particle Characterization of Atmospheric Aerosols and Savanna Fire Samples, Journal of Atmospheric Chemistry, 36(2), 135-155, 2000.

Liu, X., Zhang, Y., Han, W., Tang, A., Shen, J., Cui, Z., Vitousek, P., Erisman, J.W., Goulding, K. and Christie, P.: Enhanced nitrogen deposition over China, Nature, 494(7438), 459-62, 2013.

Liu, Y., Sun, L., Zhou, X., Luo, Y., Huang, W., Yang, C., Wang, Y. and Huang, T.: A 1400-year terrigenous dust record on a coral island in South China Sea, Scientific Reports, 4(20), 4994-4994, 2014.

Moody, J.L., Keene, W.C., Cooper, O.R., Voss, K.J., Aryal, R., Eckhardt, S., Holben, B., Maben, J.R., Izaguirre, A. and Galloway, J.N.: Flow climatology for physicochemical properties ofdichotomous aerosol over the western North Atlantic Ocean at Bermuda, Atmospheric Chemistry and Physics, 14, 691-717, 2014.

Norris, G. A., Duvall, R., Brown, S. G. and Bai, S.: EPA Positive Matrix Factorization (PMF) 5.0 fundamentals and User Guide Prepared for the US Environmental Protection Agency Office of Research and Development, Washington, DC. DC EPA/600/R-14/108, 2014.

Norman, M. and Leck, C.: Distribution of marine boundary layer ammonia over the Atlantic and Indian Oceans during the

Aerosols99 cruise, Journal of Geophysical Research, doi:10.1029/2005JD005866, 2005.

Okuda, T., Tenmoku, M., Kato, J., Mori, J., Sato, T., Yokochi, R. and Tanaka, S.: Long-term observation of trace metal concentration in aerosols at a remote island, Rishiri, Japan by using inductively coupled plasma mass spectrometry equipped with laser ablation, Water, Air, and Soil Pollution, 174, 3-17, 2006.

Ooki, A., Uematsu, M. and Noriki, S.: Size-resolved sulfate and ammonium measurements in marine boundary layer over the North and South Pacific, Atmospheric Environment, 41(1), 81-91, 2007.

Ottley, C.J. and Harrison, R.M.: The spatial distribution and particle size of some inorganic nitrogen, sulphur and chlorine species over the North Sea, Atmospheric Environment. Part A. General Topics, 26(9), 1689-1699, 1992.

Paatero, P., Eberly, S., Brown, S. G. and Norris, G. A.: Methods for estimating uncertainty in factor analytic solutions. Atmospheric Measurement Techniques, 7(3), 781-797, 2014.

Pan, Y., Tian, S., Liu, D., Fang, Y., Zhu, X., Zhang, Q., Zheng, B., Michalshi, G., and Wang, Y.: Fossil fuel combustion-related emissions dominate atmospheric ammonia sources during severe haze episodes: Evidence from 15N-stable isotope in size-resolved aerosol ammonium, Environmental Science & Technology, DOI: 10.1021/acs.est.6b00634.

Pavuluri, C.M., Kawamura, K., and Fu, P.Q.: Atmospheric chemistry of nitrogenous aerosols in northeastern Asia: biological sources and secondary formation, Atmospheric Chemistry and Physics, 15, 9883-9896, 2015.

Phinney, L., Leaitch, W.R., Lohmann, U., Boudries, H., Worsnop, D.R., Jayne, J.T., Toom-Sauntry, D., Wadleigh, M., Sharma, S. and Shantz, N.: Characterization of the aerosol over the sub-arctic north east Pacific Ocean, Deep Sea Research Part II Topical Studies in Oceanography, 53(20 – 22), 2410-2433, 2006.

Price, C., Penner, J. and Prather, M.: NO$_x$ from lightning: 1. Global distribution based on lightning physics, Journal of Geophysical Research Atmospheres, 102(D5), 5929-5942, 1997.

Rinaldi, M., Decesari, S., Finessi, E., Giulianelli, L., Carbone, C., Fuzzi, S., O'Dowd, C., Ceburnis, D. and Facchini, M.C.: Primary and secondary organic marine aerosol and oceanic biological activity: Recent results and new perspectives for future studies, Advances in Meteorology, doi:10.1155/2010/310682, 2010.

Schmale, J., Schneider, J., Nemitz, E., Tang, Y.S., Dragosits, U., Blackall, T.D., Trathan, P.N., Phillips, G.J., Sutton, M. and Braban, C.F.: Sub-Antarctic marine aerosol: dominant contributions from biogenic sources, Atmospheric Chemistry & Physics, 13(17), 8669-8694, 2013.

Šmilauer, P. and Lepš, J.: Multivariate analysis of ecological data using CANOCO 5, Cambridge University Press, 2014.

Steyn, D.G. and Chaumerliac, N.: Air Pollution Modeling and its Application XXIV, Utrecht: Springer, 2016.

Streets, D.G., Yarber, K.F., Woo, J.H. and Carmichael, G.R.: Biomass burning in Asia: annual and seasonal estimates and atmospheric emissions, Global Biogeochem Cycles, 17(4), 1759-1768, 2003.

Suzuki, T. and Tsunogai, S.: Origin of calcium in aerosols over the western north Pacific, Journal of Atmospheric Chemistry, 6(4), 363-374, 1988.Tiwari, S., Pervez, S., Cinzia, P., Bisht, D.S., Kumar, A. and Chate, D.: Chemical characterization of atmospheric particulate matter in Delhi, India, part II: Source apportionment studies using PMF 3.0, Sustainable

Environment Research, 23, 295-306, 2013.

Tiwari, S., Pervez, S., Cinzia, P., Bisht, D.S., Kumar, A. and Chate, D.: Chemical characterization of atmospheric particulate matter in Delhi, India, part II: Source apportionment studies using PMF 3.0, Sustainable Environment Research, 23, 295-306, 2013.

Wang, J.: Classical multidimensional scaling. In Geometric Structure of High-Dimensional Data and Dimensionality Reduction (pp. 115-129). Springer Berlin Heidelberg, 2012

Wang, L., Qi, J.H., Shi, J.H., Chen, X.J. and Gao, H.W.: Source apportionment of particulate pollutants in the atmosphere over the Northern Yellow Sea, Atmospheric Environment, 70(4), 425-434, 2013.

Wang, S.H., Hsu, N.C., Tsay, S.C., Lin, N.H., Sayer, A.M., Huang, S.J. and Lau, W.K.: Can Asian dust trigger phytoplankton blooms in the oligotrophic northern South China Sea?, Geophysical Research Letters, 39(5), 2012.

Wang, S.H., Tsay, S.C., Lin, N.H., Chang, S.C., Li, C., Welton, E.J., Holben, B.N., Hsu, N.C., Lau, W.K.M. and Lolli, S.: Origin, transport, and vertical distribution of atmospheric pollutants over the northern South China Sea during the 7-SEAS/Dongsha Experiment, Atmospheric Environment, 78(3), 124 - 133, 2013.

Wang, S.H., Tsay, S.C., Lin, N.H., Hsu, N.C., Bell, S.W., Li, C., Ji, Q., Jeong, M.J., Hansell, R.A. and Welton, E.J.: First detailed observations of long-range transported dust over the northern South China Sea, Atmospheric Environment, 45(27), 4804-4808, 2011.

Wang, Y., Zhuang, G., Zhang, X., Huang, K., Xu, C., Tang, A., Chen, J. and An, Z.: The ion chemistry, seasonal cycle, and sources of $PM_{2.5}$ and TSP aerosol in Shanghai, Atmospheric Environment, 40(16), 2935-2952, 2006.

Wang, Y.Q., Zhang, X.Y. and Draxler, R.: TrajStat: GIS-based software that uses various trajectory statistical analysis methods to identify potential sources from long-term air pollution measurement data, Environmental Modelling & Software, 24: 938-939, 2009.

Xiao, H., Long, A., Xie, L., Xiao, H. and Liu, C.: Chemical characteristics of precipitation in South China Sea, Environmental Science, 35(2), 475-480, 2014 (Chinese with English Abstract).

Xiao, H., Xiao, H., Long, A. and Wang, Y.: Who controls the monthly variations of NH_4^+ nitrogen isotope composition in precipitation?, Atmospheric Environment, 54, 201-206, 2012a.

Xiao, H., Xiao, H., Long, A. and Wang, Y.: Nitrogen isotopic composition and source of nitrate in precipitation at Guiyang, Acta Scientiae Circumstantiae, 32(4), 940-945, 2012b (Chinese with English Abstract).

Xiao, H., Xiao, H., Long, A., Wang, Y. and Liu, C.: Chemical composition and source apportionment of rainwater at Guiyang, SW China, Journal of Atmospheric Chemistry, 70(3), 269-281, 2013.

Xiao, H., Xiao, H., Long, A., Wang, Y. and Liu, C.: Sources and meteorological factors that control seasonal variation of $\delta^{34}S$ values in rainwater, Atmospheric Research, 149, 154-165, 2014.

Xiao, H., Xiao, H., Zhang, Z., Wang, Y., Long, A. and Liu, C.: Chemical characteristics and source apportionment sources of precipitation in Yongxing Island, China Environmental Science, 36(11), 3237-3244, 2016 (Chinese with English

Abstract).

Xiao, H., Xie, L., Long, A., Ye, F., Pan, Y., Li, D., Long, Z., Chen, L., Xiao, H. and Liu, C.: Use of isotopic compositions of nitrate in TSP to identify sources and chemistry in South China Sea, Atmospheric Environment, 109, 70-78, 2015.

Xiao, H.Y. and Liu, C.Q.: Sources of nitrogen and sulfur in wet deposition at Guiyang, southwest China, Atmospheric Environment, 36(33), 5121-5130, 2002.

Xiao, H.Y. and Liu, C.Q.: Chemical characteristics of water-soluble components in TSP over Guiyang, SW China, 2003, Atmospheric Environment, 38(37), 6297-6306, 2004.

Yu, L., Wang, G., Zhang, R., Zhang, L., Song, Y., Wu, B., Li, X., An, K. and Chu, J.: Characterization and Source Apportionment of $PM_{2.5}$ in an Urban Environment in Beijing, Aerosol & Air Quality Research, 13(2), 574-583, 2013.

Zhang, M., Chen, J.M., Wang, T., Cheng, T.T., Lin, L., Bhatia, R.S. and Havey, M.: Chemical characterization of aerosols over the Atlantic Ocean and the Pacific Ocean during two cruises in 2007 and 2008, Journal of Geophysical Research, 115, 1842-1851, 2010.

Zhang, N., Cao, J., Liu, S., Zhao, Z.Z., Xu, H. and Xiao, S.: Chemical composition and sources of $PM_{2.5}$ and TSP collected at Qinghai Lake during summertime, Atmospheric Research, 138(3), 213－222, 2014.

Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Ulbrich, I. M., Ng, N. L., Worsnop, D. R., and Sun, Y. L.: Understanding atmospheric organic aerosols via factor analysis of aerosol mass spectrometry: a review, Analytical and Bioanalytical Chemistry, 401, 3045-3067, 2011.

Zhang, R., Jing, J., Tao, J., Hsu, S.C., Wang, G., Cao, J., Lee, C.S.L., Zhu, L., Chen, Z. and Zhao, Y.: Chemical characterization and source apportionment of PM2.5 in Beijing: Seasonal perspective, Atmospheric Chemistry and Physics, 7053-7074, 2015.

Zhang, X., Zhuang, G., Guo, J., Yin, K. and Zhang, P.: Characterization of aerosol over the Northern South China Sea during two cruises in 2003, Atmospheric Environment, 41(36), 7821-7836, 2007.

Zhang, X.Y., Wang, Y.Q., Niu, T., Zhang, X.C., Gong, S.L., Zhang, Y.M. and Sun, J.Y.: Atmospheric aerosol compositions in China: spatial/temporal variability, chemical signature, regional haze distribution and comparisons with global aerosols, Atmospheric Chemistry and Physics, 12(2), 779-799, 2012.

Zhao, R., Han, B., Lu, B., Zhang, N., Zhu, L. and Bai, Z.: Element composition and source apportionment of atmospheric aerosols over the China Sea, Atmospheric Pollution Research, 6(2), 191-201, 2015.

Table Captions

Table 1 Annual average, minimum and maximum mass concentrations (μg/m^3) of TSP and aerosol chemical species at Yongxing Island.

Table 2 Mole equivalent ratios for major ionic species in aerosols at Yongxing Island (annual, cool, transition and warm seasons), together with seawater ratios for comparison.

Table 3 Correlation coefficients among major ions in aerosol and meteorological parameters.

Table 4 Relative contributions (%) for different major ions from potential five sources of TSP at Yongxing Island over the year, based on PMF 5.0 model.

Figure Captions

Figure 1 Distribution of seasonal average aerosol optical thickness (AOT) at 550 nm (T550) over Northwest Pacific in cool, warm and transition seasons during sampling period. Monthly AOT products (from Moderate Resolution Imaging Spectrometer, MODIS) with 4-km resolution were downloaded from Globcolour (http://hermes.acri.fr/). The GlobColour project began in 2005 as an ESA Data User Element project to provide a continuous dataset of merged Level 3 Ocean Colour products.

Figure 2 Three-hour temperature, relative humidity, wind speed and precipitation at Yongxing Island during sampling period (March 2014 through February 2015).

Figure 3 Annual average mass concentrations of aerosol chemical species at Yongxing Island. Box boundary indicates 25th and 75th percentile. Lines within the box show the mean. Whiskers above and below the box indicate 90th and 10th percentiles.

Figure 4 Mean contributions of each major ionic component to total ionic mass concentration of (a) Yongxing Island (YXI) annual, (b) YXI cool season, (c) YXI warm season, and (d) YXI transition season.

Figure 5 Comparisons of major ions in aerosol at Yongxing Island with global ocean. Data of Oki, Ogasawara and Hedo are from EANET (www.eanet.asia); those of Rishiri Island are from Okuda et al. (2006); those of Hawaii are from Carrillo et al. (2002); those of Bermuda are from Moody et al. (2014); those of Amsterdam Island are from Claeys et al. (2010); those of the Arabian Sea and Indian Ocean are from Kumar et al. (2008); those of Helgoland are from Ebert et al. (2000); those of the Mediterranean Sea, northern Atlantic-1 and 2, Pacific and southern Atlantic are from Zhang et al. (2010). Pentagrams represent sampling sites on islands; others represent cruises. N.A. indicates no data.

Figure 6 Seasonal variations of TSP mass concentration and associated species, including Na^+, Cl^-, SO_4^{2-}, Mg^{2+}, K^+, Ca^{2+}, NH_4^+, and NO_3^- at Yongxing Island (cool season: C; warm season: W; annual: A). Shown are the mean and standard deviation for each bar.

Figure 7 Comparison of aerosol chemical species between Yongxing Island and around the South China Sea (data from EANET).

Figure 8 Fire spot data from MODIS global fire mapping from March 2014 to February 2015 around South China Sea (https://firms.modaps.eosdis.nasa.gov/firemap/).

Figure 9 Profiles of five sources identified from the PMF 5.0 model, including sea salt (two species), crust, secondary inorganic aerosol and oceanic emission.

Figure 10 Time series contributions from each identified sources, including sea salt (two species), crust, secondary inorganic aerosol, and oceanic emission.

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Supporting Information

Figure S1. Modeled NAAPS total aerosol optical depth (AOD) for every month of March 2014 through February 2015, for total, sulfate, dust and smoke (data from http://www.nrlmry.navy.mil/aerosol/#aerosolobservations).

Table 1 Annual average, minimum and maximum mass concentrations (μg/m^3) of TSP and aerosol chemical species at Yongxing Island.

	TSP	Na^+	Cl^-	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	NO_3^-	NH_4^+
Annual	89.6 ± 68.0	4.00 ± 1.88	7.73 ± 5.99	0.33 ± 0.22	2.15 ± 1.54	0.44 ± 0.33	5.54 ± 3.65	1.95 ± 1.34	0.07 ± 0.07
Minimum	16.4	0.90	0.39	0.06	0.17	0.02	0.52	0.10	0.01
Maximum	440.1	8.86	36.47	1.13	9.65	1.55	23.34	10.05	0.32

Table 2 Mole equivalent ratios for major ionic species in aerosols at Yongxing Island (annual, cool, transition and warm seasons), together with seawater ratios for comparison.

	Yongxing Island				Seawater[a]
	annual	cool	transition	warm	
Cl^-/Na^+	1.25	1.31	1.06	1.12	1.17
Mg^{2+}/Na^+	0.21	0.21	0.19	0.23	0.22
K^+/Na^+	0.048	0.051	0.040	0.042	0.021
Ca^{2+}/Na^+	0.62	0.64	0.83	0.47	0.044
SO_4^{2-}/Na^+	0.66	0.71	0.73	0.51	0.12
nss-SO_4^{2-}/Na^+	0.54	0.58	0.61	0.39	-
NO_3^-/Na^+	0.18	0.18	0.22	0.16	-
NH_4^+/Na^+	0.022	0.021	0.044	0.016	-
NO_3^-/nss-SO_4^{2-}	0.34	0.32	0.36	0.41	-
NH_4^+/nss-Ca^{2+}	0.038	0.035	0.056	0.038	-

[a] Seawater ratios from Keene et al. (1986).

Table 3 Correlation coefficients among major ions in aerosol and meteorological parameters.

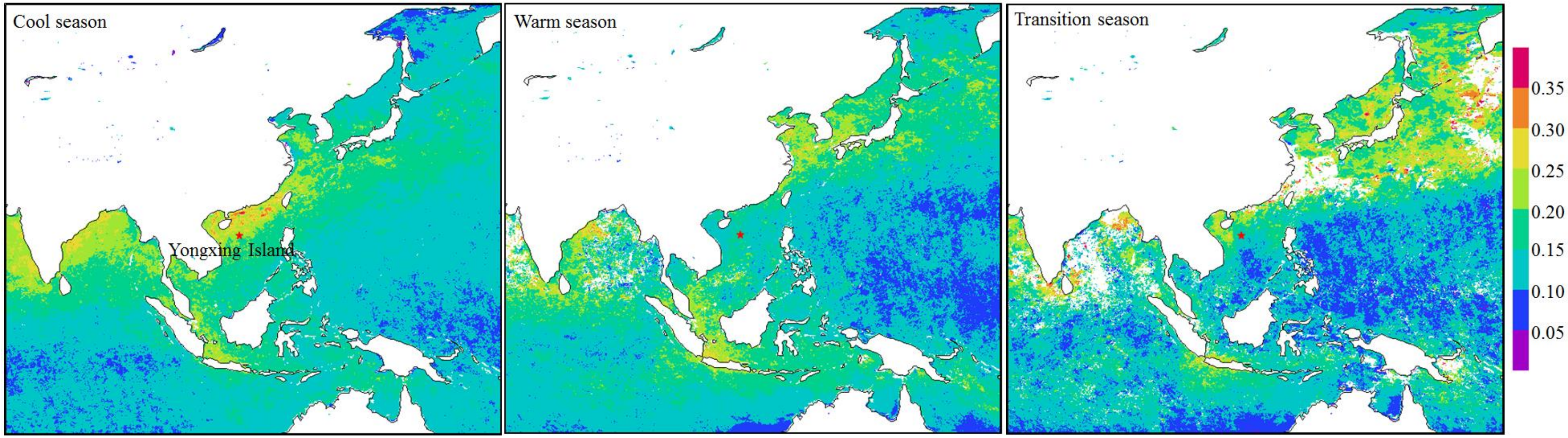
	TSP	Na^+	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	K^+	NH_4^+	NO_3^-	WS	T	RH	R
TSP	1	0.77**	0.92**	0.77**	0.92**	0.32**	0.75**	-0.05	0.52**	0.36**	-0.47**	-0.44**	-0.20
Na^+		1	0.91**	0.69**	0.72**	0.57**	0.78**	-0.03	0.48**	0.44**	-0.51**	-0.46**	-0.27*
Cl^-			1	0.71**	0.83**	0.49**	0.77**	-0.04	0.45**	0.43**	-0.37**	-0.36**	-0.19
SO_4^{2-}				1	0.86**	0.56**	0.85**	0.26*	0.87**	0.04	-0.56**	-0.58**	-0.29*
Ca^{2+}					1	0.36**	0.81**	-0.03	0.69**	0.24	-0.51**	-0.53**	-0.27*
Mg^{2+}						1	0.63**	0.45**	0.59**	0.04	-0.12	-0.08	-0.18
K^+							1	-0.18	0.72**	0.15	-0.51**	-0.45**	-0.27*
NH_4^+								1	0.36**	-0.13	-0.18	0.11	-0.18
NO_3^-									1	-0.05	-0.50**	-0.50**	-0.31**

**Correlation significant at 0.01 level (2-tailed), * significant at 0.05 level (2-tailed). WS: wind speed (m/s); T: temperature (˚C); RH: relative humidity (%); R: rainfall (mm/h)

Table 4 Relative contributions (%) for different major ions from potential five sources of TSP at Yongxing Island over the year, based on PMF 5.0 model.

Source	Na^+	Cl^-	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	NO_3^-	NH_4^+
Sea salt (two species)	77.4	93.9	53.2	33.9	70.4	24.0	13.1	6.7
Crust	6.1	5.5	10.8	9.8	11.9	11.5	15.9	23.6
SIA	8.8	0.0	27.7	56.3	15.8	57.5	69.5	9.1
Oceanic emission	7.7	0.6	8.3	0.0	2.0	6.9	1.6	60.5

Figure 1 Distribution of seasonal average aerosol optical thickness (AOT) at 550 nm (T550) over Northwest Pacific in cool, warm and transition seasons during sampling period. Monthly AOT products (from Moderate Resolution Imaging Spectrometer, MODIS) with 4-km resolution were downloaded from Globcolour (http://hermes.acri.fr/). The GlobColour project began in 2005 as an ESA Data User Element project to provide a continuous dataset of merged Level 3 Ocean Colour products.



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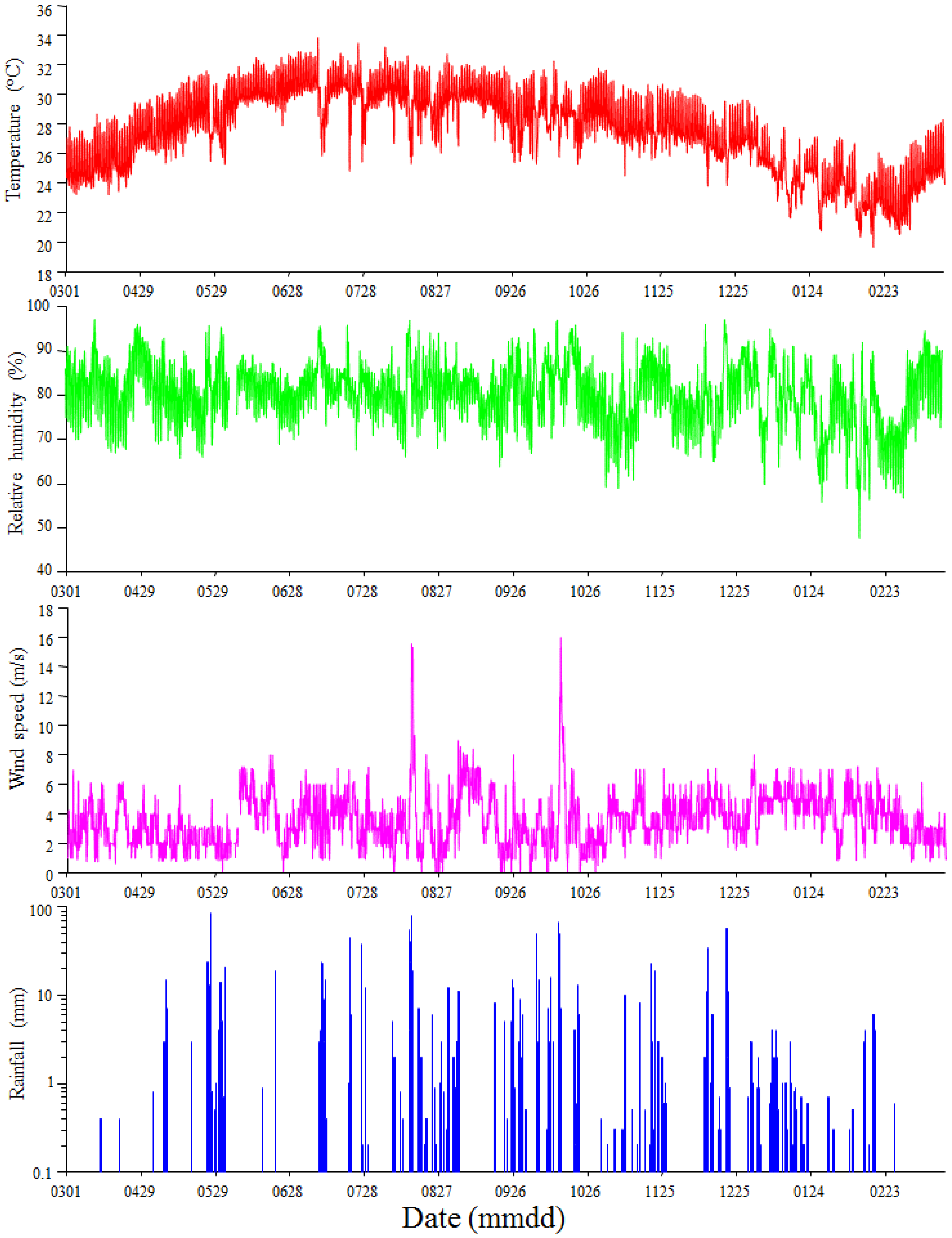

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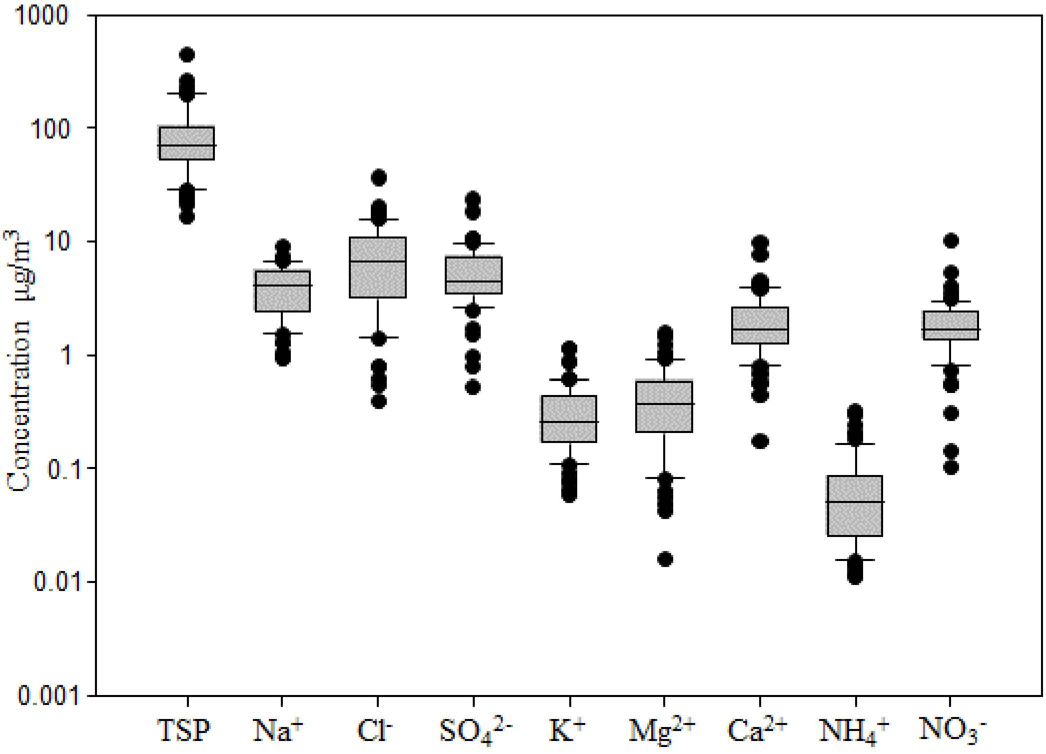

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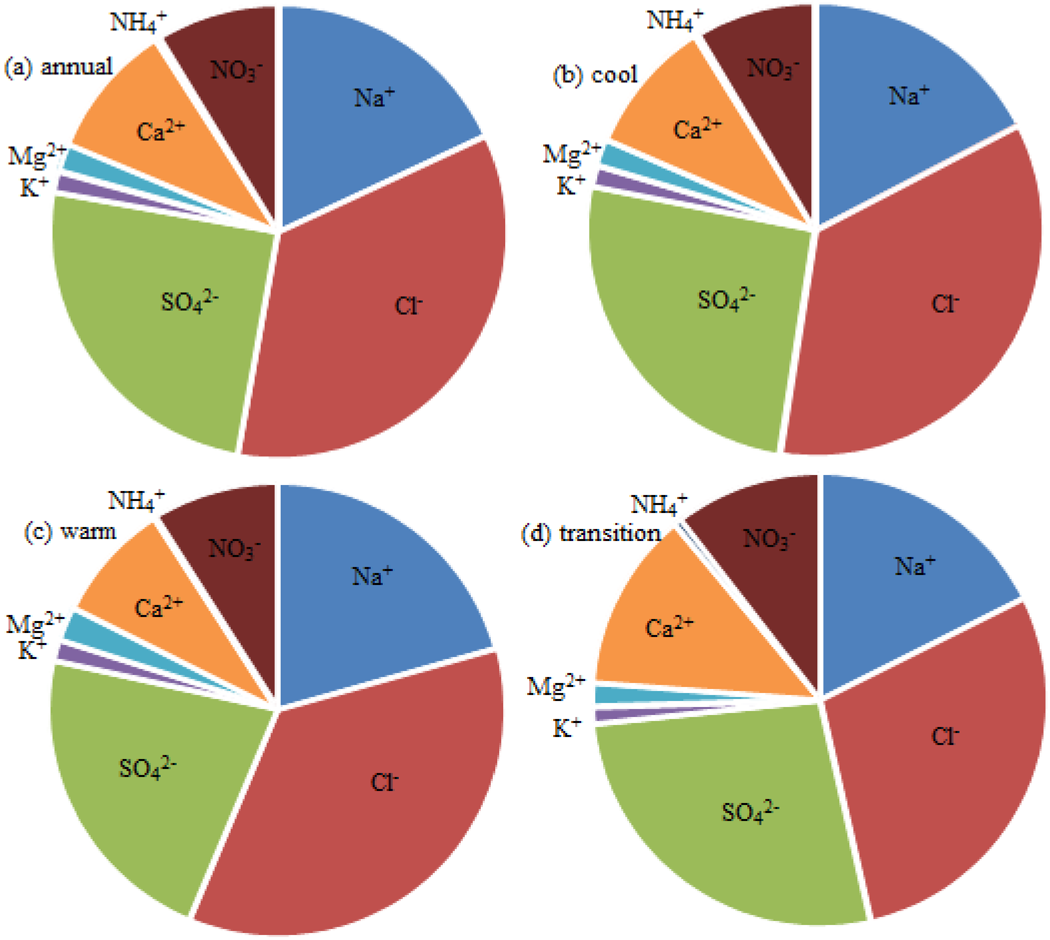

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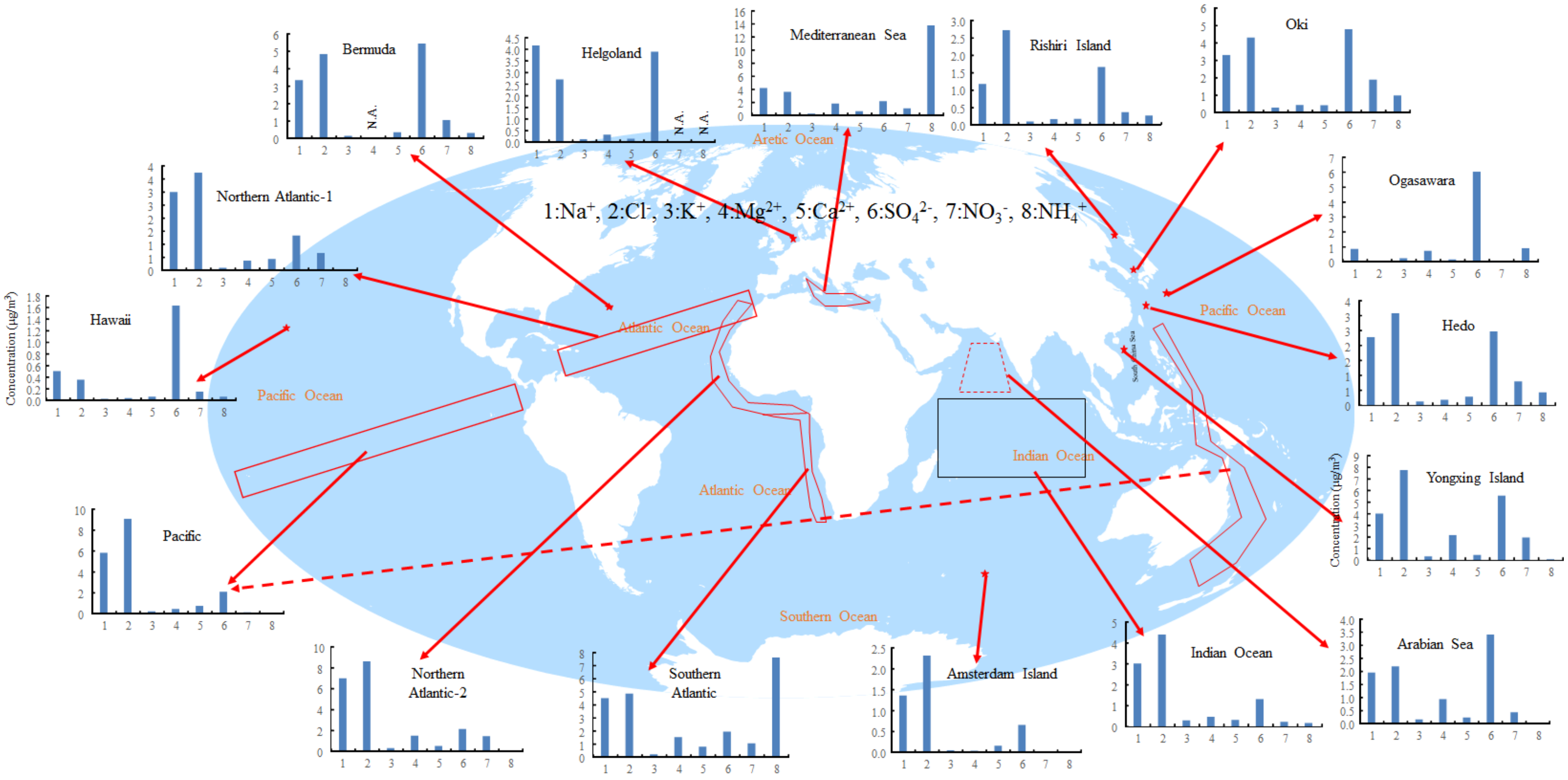

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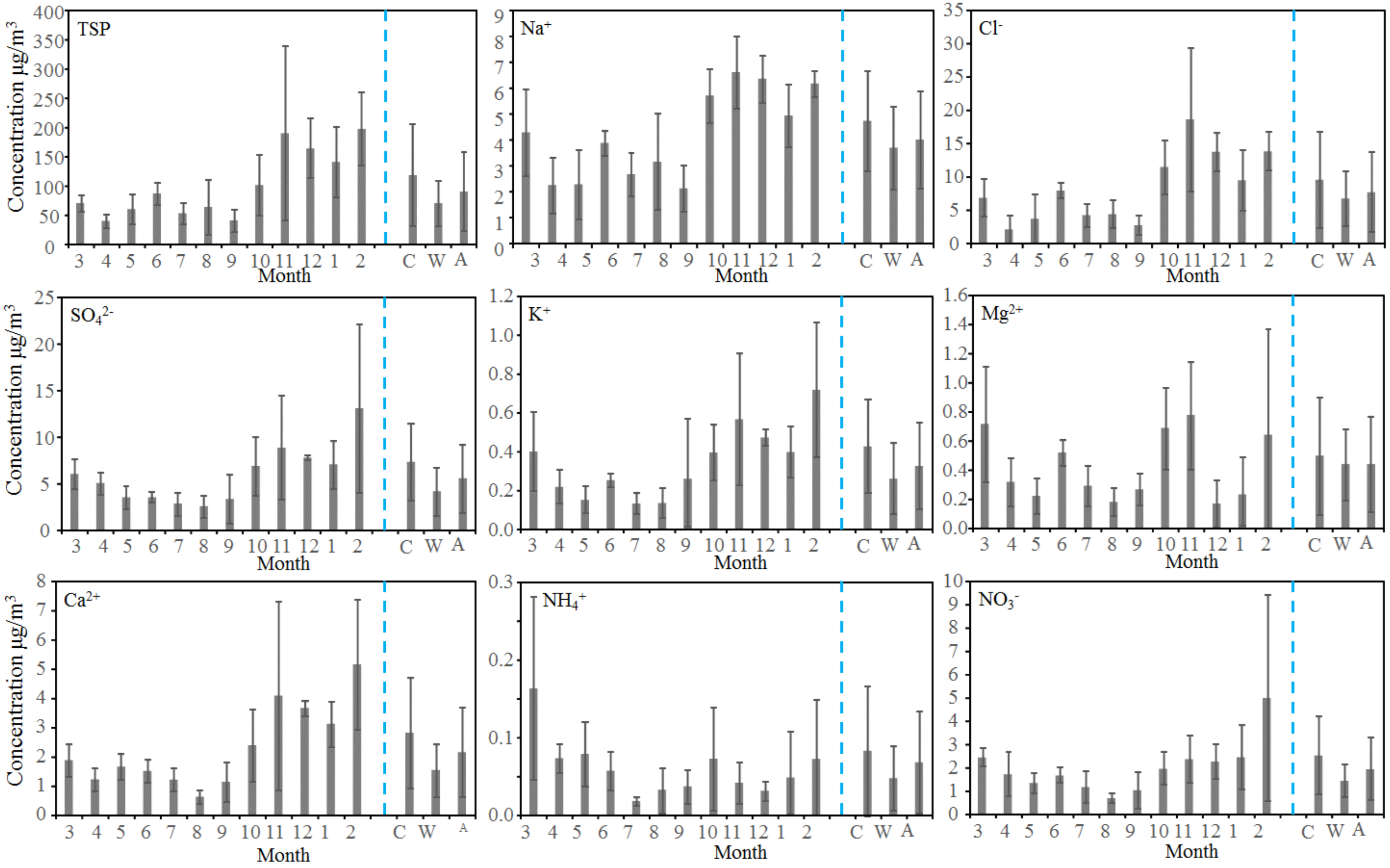

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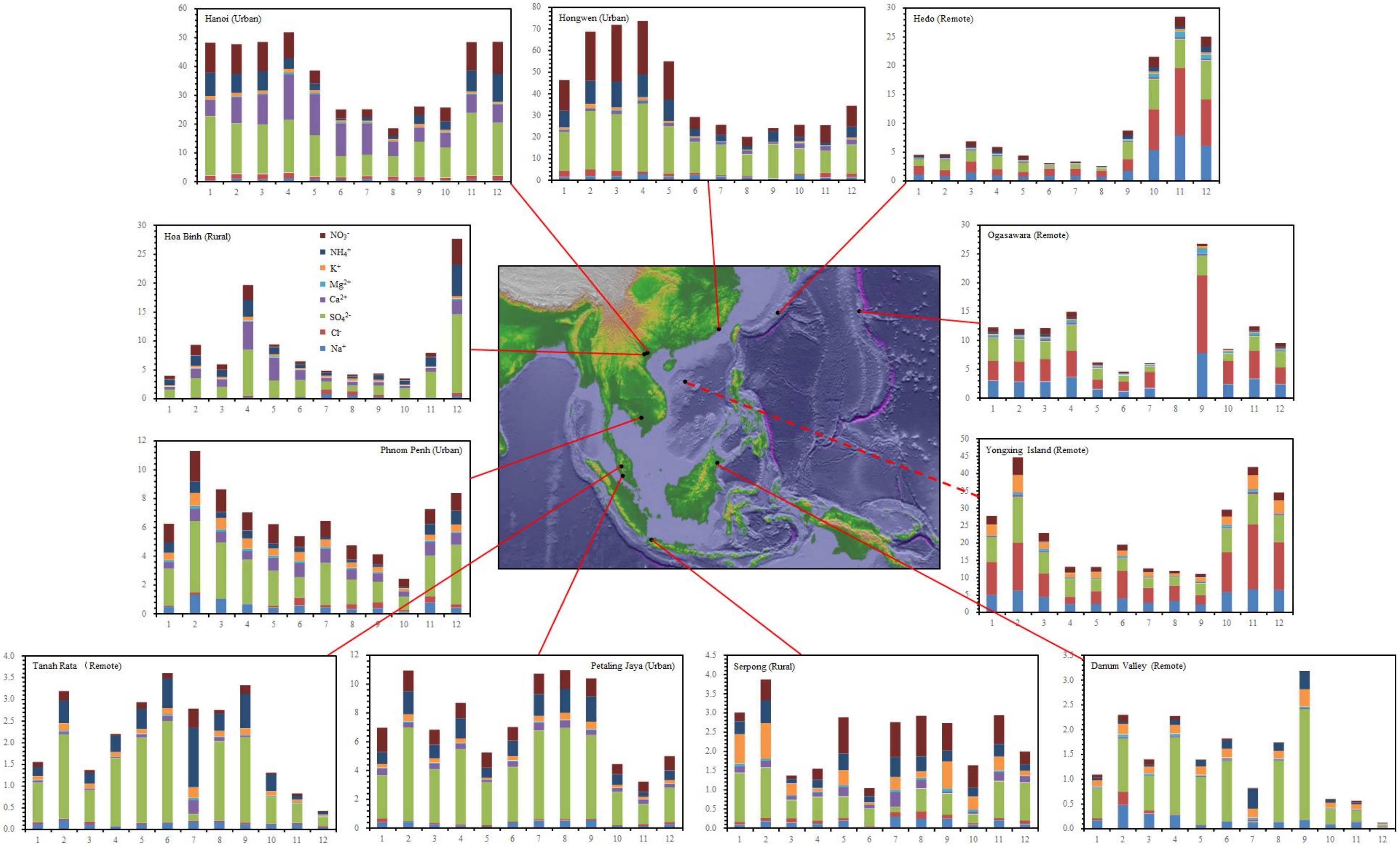

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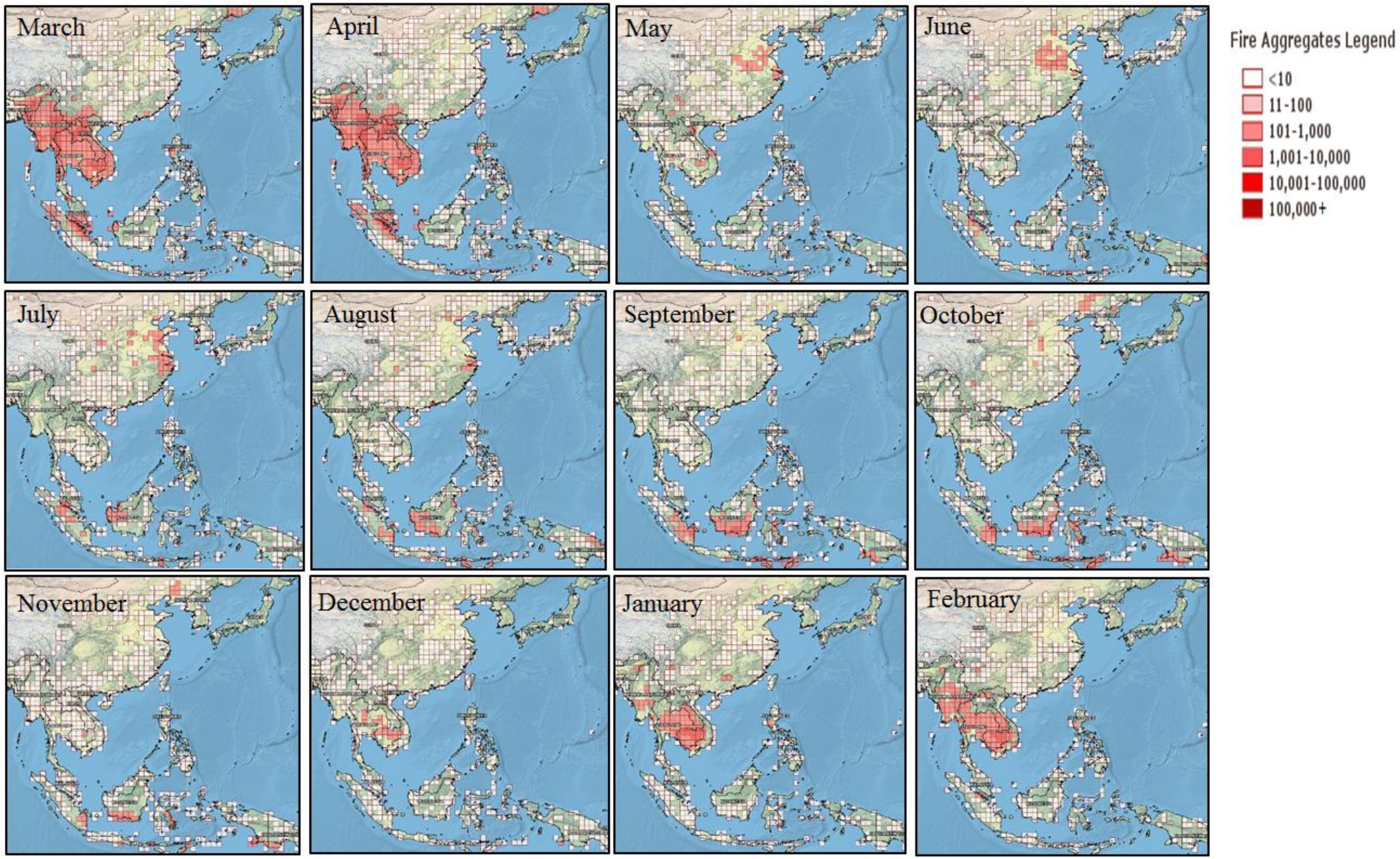

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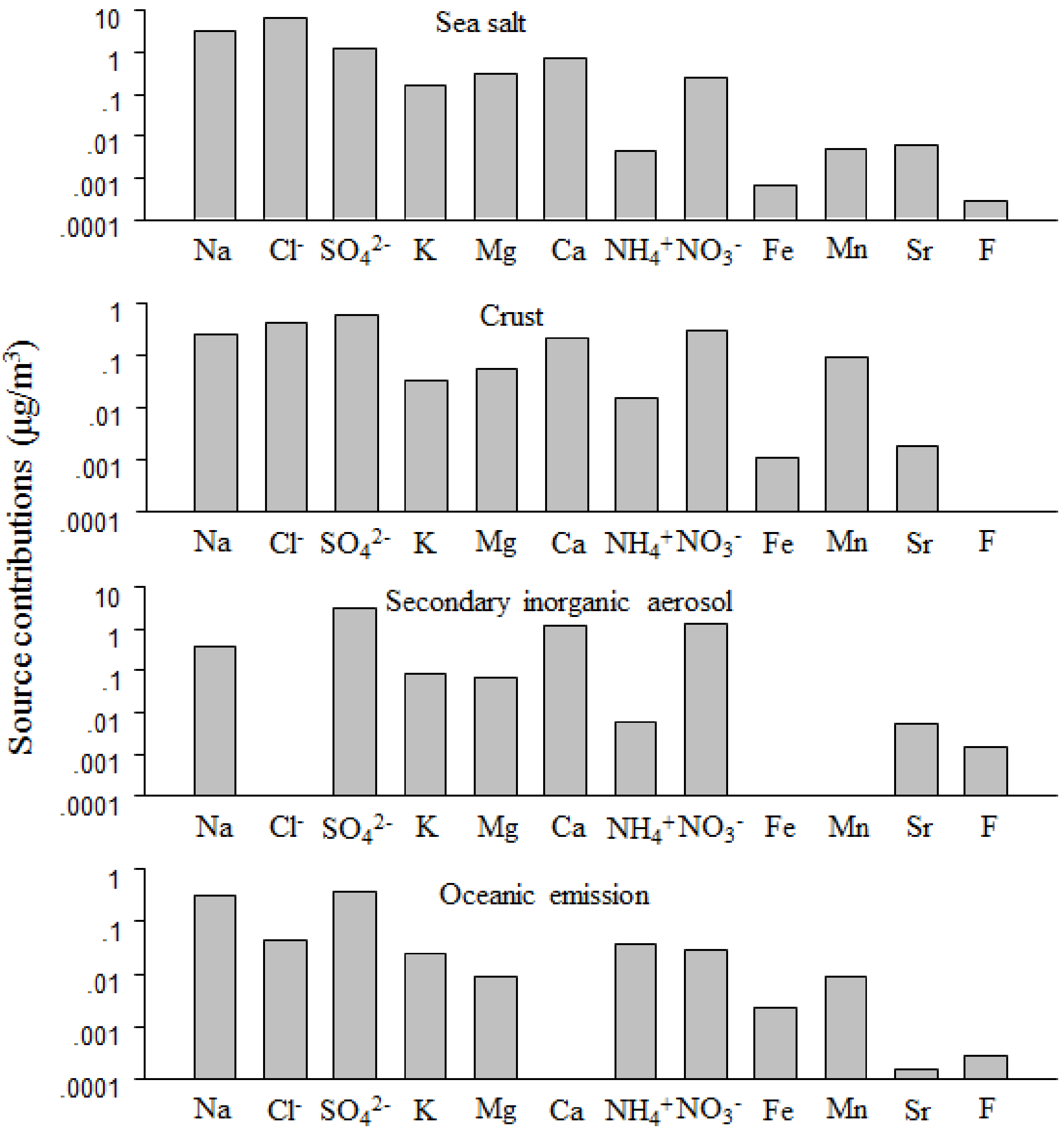
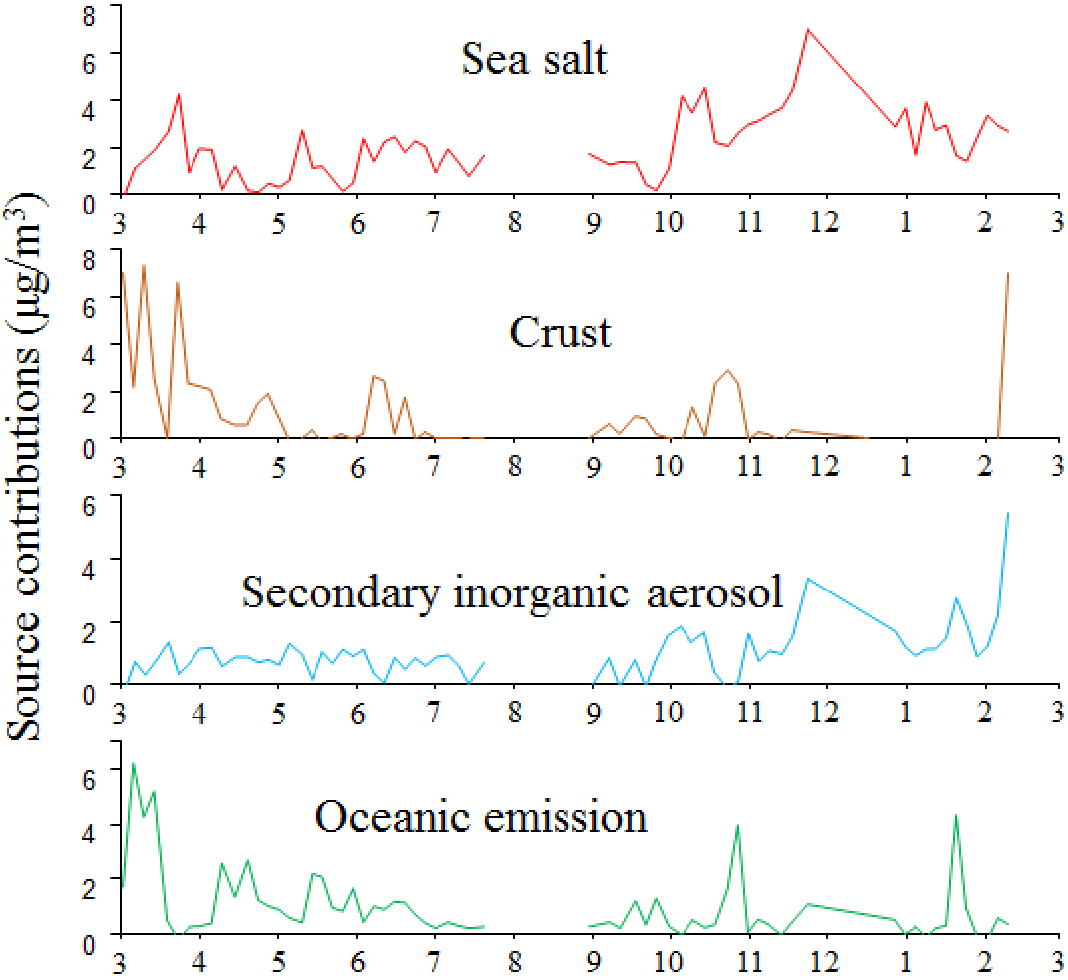


Figure 10 Time series contributions from each identified sources, including sea salt (two species), crust, secondary inorganic aerosol, and oceanic emission.f



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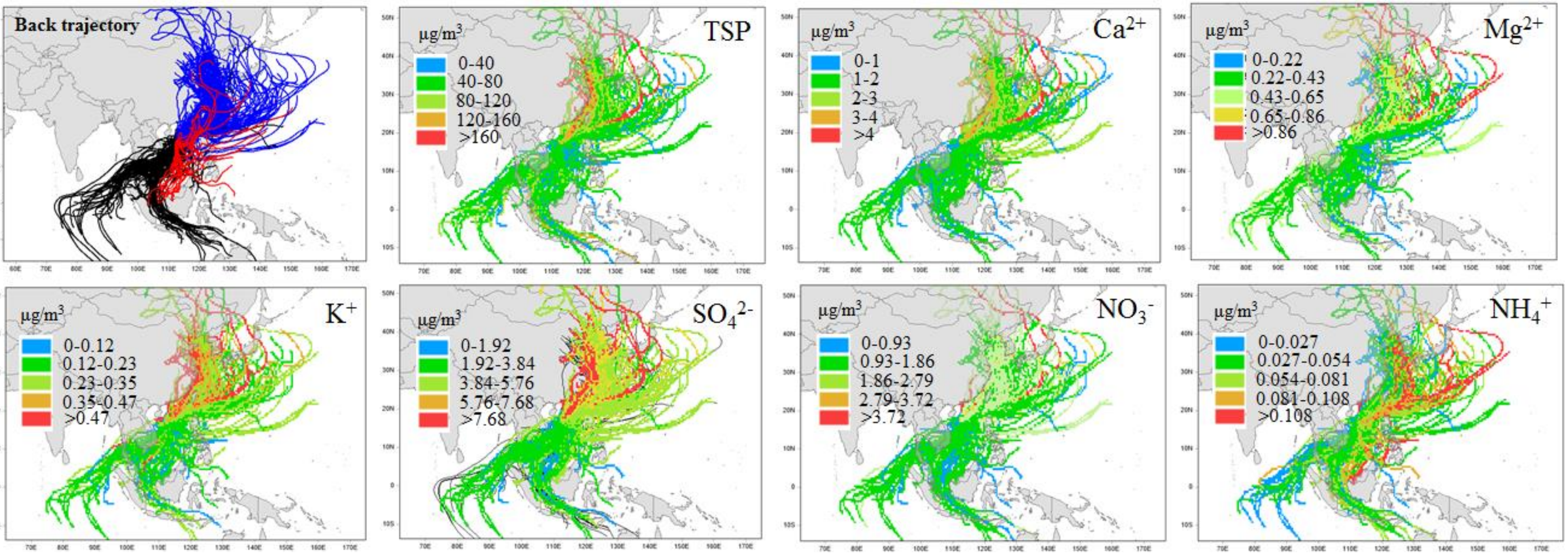

Supplementary Materials for

Atmospheric aerosol compositions over the South China Sea: Temporal variability and source apportionment

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This PDF file includes:

Supplementary Text: S1, S2 and S3

Reference List

S1 Sample collection and chemical analyses

Aerosol was collected on quartz filters (8 × 10 inch, Tissuquartz™ Filters, 2500 QAT-UP, Pallflex, Washington, USA) using a special high-flow rate (1.05 ± 0.03 m^3/min) KC-1000 sampler (Laoshan Institute for Electronic Equipment, Qingdao, China), which were installed 1m above the building (about 15m) roof's surface of the station of SCSIO, CAS, and there was not obvious pollution around this station. The sampling time was nominally 96 hours (4 days one sample). Three blank filters were taken from each package (25 filters). All samples and blank filters were stored in a refrigerator at −20°C until analysis in the laboratory.

In the laboratory, one eighth filters were cut and placed in a clean 50-ml Nalgene tube with additional 35-ml ultrapure water. These tubes were washed for 30 minutes using ultrasonic vibration. They were then shaken for 30 minutes on a horizontal shaker at a rate of ~300 rpm and left to rest for another 30 minutes at room temperature. The extract was filtered using pinhole filters, which were then rinsed twice with 5-ml ultrapure water. The extract and rinse were put into 50-ml tubes together and stored in a refrigerator at −20 °C until chemical analyses.

Major anion concentrations (F^-, Cl^-, NO_3^-, SO_4^{2-}, Br^-) were determined by ICS-90 ion chromatography (Dionex, California, USA). Water-soluble metal and nonmetal elemental concentrations (Al, Ca, Fe, K, Mg, Mn, Na, SiO_2, Sr) were analyzed by an MPX inductively coupled plasma optical emission spectrometer (ICP-OES, Vista, CA, USA). NH_4^+

concentration was determined by spectrophotometry after treatment with Nessler's reagent. The detection limits of F^-, Cl^-, NO_3^-, SO_4^{2-}, Br^- were 0.03, 0.03, 0.08, 0.075 and 0.1 mg/L, respectively, and the relative standard deviation of these ions of standard samples were 0.57%, 2.55%, 1.16%, 1.36% and 11.36%, respectively (Xiao et al., 2013 and 2016). The detection limits of Al, Ca, Fe, K, Mg, Mn, Na, SiO_2, Sr were 0.025, 0.003, 0.002, 0.06, 0.0005, 0.0005, 0.02, 0.015 and 0.00008 mg/L, respectively, and the relative standard deviation of these ions of standard samples were less than 1.5% (Xiao et al., 2013 and 2016). The detection limit of NH_4^+ was 0.1 mg/L and its relative standard deviation was less than 5.0% (Xiao et al., 2013 and 2016). In this study, Al and Br^- in most of samples was less than the detection limit.

S2 Back trajectories and concentration weighted trajectories analysis

Back trajectories and concentration weighted trajectories (CWT) are used to determine the long-distance transport of atmospheric pollutants and regional source areas (Cheng et al., 2013; Xiao et al., 2014 and 2015). The CWT is a good model to estimate potential sources areas, when grid cells are more than 2 trajectory segment endpoint (Cheng et al., 2013). For each day, 10-day (240 hours) back trajectories of air masses (Pavuluri et al., 2015) arriving at Yongxing Island were computed by the program of TrajStat (version 1.2.26) (Wang et al., 2009). 10-day back trajectories are used in this study since trajectories of a short duration are not long enough to indicate possible distant sources regions (Harris and Kahl, 1990). We also used the program of TrajStat to model CWT of TSP, and Ca^{2+}, Mg^{2+}, K^+, SO_4^{2-}, NO_3^- and NH_4^+ concentrations at the island. In CWT model, each grid cell receives a weighted concentration obtained by averaging sample concentrations that have associated trajectories crossing the grid cell as follows (Eq. S1; Wang et al., 2009; Xiao et al., 2014 and 2015).

$$C_{ij} = \frac{1}{\sum_{l=1}^{M} \tau_{ijl}} \sum_{l=1}^{M} C_l \tau_{ijl} \qquad \text{(S1)}$$

where C_{ij} is the average weighted concentration in grid cell (i, j); l is the index of the trajectory; C_l is the measured ionic concentration, corresponding with the arrival of back-trajectory l at the sampling site; τ_{ijl} is the time spent in the grid cell (i, j) by trajectory l; M is the total number of back trajectories. The region from 70°E to 160°E and from 20°S to 60°N was defined as the source domain based on back trajectories during the sampling period, containing 14,400 grid cells of 0.5° × 0.5°.

S3 Positive matrix factorization model

Receptor models are used to quantify the contributions of sources to samples based on the composition or fingerprints of the sources (Norris et al., 2014). The positive matrix factorization (PMF) is an effective source apportionment receptor model that does not require source profiles prior to analysis and has no limitation on source numbers (Crippa et al., 2013; Tiwari et al., 2013; Zhang et al., 2011; Zhang et al., 2015). The PMF model describes the observation (x_{ij}) as a linear combination of a number of factors *p* for each time step *i* and *j*, whose contribution over time is always positive (g_k) and whose mass spectra (f_k) are static (see Eq. S2; Crippa et al., 2013; Paatero et al., 2014).

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{ki} + e_{ij} \qquad \text{(S2)}$$

where e_{ij} is the residual. PMF decomposes the matrix of speciated sample data into two matrices: factor contributions (G) and factor profiles (F) (Norris et al., 2014). G and F are derived by the PMF model minimizing the objective function Q (Eq. S3):

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{e_{ij}}{u_{ij}} \right]^2 \qquad \text{(S3)}$$

where u_{ij} is the measurement uncertainty. In our study, PMF 5.0 (United States Environmental Protection Agency) was used to determine source apportionment of each major ion based on F^-, Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Ca, K, Mg, Mn, Fe, Na, and Sr by sampling time, with uncertainties by species provided by the analytical library. However, we downweighted Fe and F^- since they had low signal-to-noise ratios (S/N), and there were no excluded species and samples. We run PMF for the range of number factors from 2 to 10, and examine the Q(Robust)/Qexp to choose the best model number of factors (*P*). Five physically realistic sources major ions were identified, i.e., sea salt (two species, Na and Mg), secondary inorganic aerosol (SIA; F^-, SO_4^{2-} and NO_3^-), oceanic emission (NH_4^+), and crust (Mn). The model results show that there are good relationships between observed (input data) values and predicted (modeled) values of each major ion except Sr and F^- (correlation coefficients R^2 were 0.94, 0.93, 0.94, 0.80, 1.00, 0.93, 0.95, 0.91, 0.59, 1.00, 0.40 and 0.40 for Na, Cl^-, SO_4^{2-}, K, Mg, Ca, NH_4^+, NO_3^-, Fe, Mn, Sr, and F^-,respectively), and the modeled values of time series are fitting the observed values well. For the best solution chosen above, we run PMF for Fpeak in Rotational Tools (-1.0, -0.8, -0.6, -0.4, -0.2, -0.01, 0.01, 0.2, 0.4, 0.6, 0.8 and 1.0). The results show that the best solution is the Fpeak near to zero (-0.01 and 0.01) for *P* 5.

References

Cheng, I., Zhang, L., Blanchard, P., Dalziel, J. and Tordon, R.: Concentration-weighted trajectory approach to identifying potential sources of speciated atmospheric mercury at an urban coastal site in Nova Scotia, Canada, Atmospheric Chemistry And Physics, 13(12), 6031-6048, 2013.

Crippa, M., Canonaco, F., Slowik, J. G., El Haddad, I., DeCarlo, P. F., Mohr, C., Heringa, M.F., Chirico, R., Marchand, N., Temime-Roussel, B., Abidi, E., Poulain, L., Wiedensohler, A., Baltensperger, U. and Prévôt, A.S.H: Primary and secondary organic aerosol origin by combined gas-particle phase source apportionment, Atmospheric Chemistry & Physics, 13(16), 8411-8426, 2013.

Harris, J. M. and Kahl, J. D.: A Descriptive Atmospheric Transport Climatology for the Mauna-Loa-Observatory, Using Clustered Trajectories, Journal of Geophysical Research: Atmospheres, 95, 13651–13667, 1990.

Norris, G. A., Duvall, R., Brown, S. G. and Bai, S.: EPA Positive Matrix Factorization (PMF) 5.0 fundamentals and User Guide Prepared for the US Environmental Protection Agency Office of Research and Development, Washington, DC. DC EPA/600/R-14/108, 2014.

Pavuluri, C.M., Kawamura, K., and Fu, P.Q.: Atmospheric chemistry of nitrogenous aerosols in northeastern Asia: biological sources and secondary formation, Atmospheric Chemistry and Physics, 15, 9883-9896, 2015.

Tiwari, S., Pervez, S., Cinzia, P., Bisht, D.S., Kumar, A. and Chate, D.: Chemical characterization of atmospheric particulate matter in Delhi, India, part II: Source apportionment studies using PMF 3.0, Sustainable Environment Research, 23, 295-306, 2013.

Wang, Y.Q., Zhang, X.Y. and Draxler, R.: TrajStat: GIS-based software that uses various trajectory statistical analysis methods to identify potential sources from long-term air pollution measurement data, Environmental Modelling & Software, 24: 938-939, 2009.

Xiao, H., Xiao, H., Long, A., Wang, Y. and Liu, C.: Chemical composition and source apportionment of rainwater at Guiyang, SW China, Journal of Atmospheric Chemistry, 70(3), 269-281, 2013.

Xiao, H., Xiao, H., Long, A., Wang, Y. and Liu, C.: Sources and meteorological factors that control seasonal variation of $\delta^{34}S$ values in rainwater, Atmospheric Research, 149, 154-165, 2014.

Xiao, H., Xie, L., Long, A., Ye, F., Pan, Y., Li, D., Long, Z., Chen, L., Xiao, H. and Liu, C.: Use of isotopic compositions of nitrate in TSP to identify sources and chemistry in South China Sea, Atmospheric Environment, 109, 70-78, 2015.

Xiao, H., Xiao, H., Zhang, Z., Wang, Y., Long, A. and Liu, C.: Chemical characteristics and source apportionment sources of precipitation in Yongxing Island, China Environmental Science, 36(11), 3237-3244, 2016 (Chinese with English Abstract).

Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Ulbrich, I. M., Ng, N. L., Worsnop, D. R., and Sun, Y. L.: Understanding atmospheric organic aerosols via factor analysis of aerosol mass spectrometry: a review, Analytical and Bioanalytical Chemistry, 401, 3045-3067, 2011.

Zhang, R., Jing, J., Tao, J., Hsu, S.C., Wang, G., Cao, J., Lee, C.S.L., Zhu, L., Chen, Z. and Zhao, Y.: Chemical characterization and source apportionment of PM2.5 in Beijing: Seasonal perspective, Atmospheric Chemistry and Physics, 7053-7074, 2015.