# Interactive comment on "One-year observations of carbonaceous and nitrogenous components and major ions in the aerosols from subtropical Okinawa Island, an outflow region of Asian dusts" by B. Kunwar and K. Kawamura

**Anonymous Referee #1**

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The paper of Kunwar and Kawamura presents and discusses a one year observation period of complete characterisation of total suspended particulate matter in the outflow region of Asian dust. Scientific significance of the paper is rather weak, but given appropriately used methods and thoroughly discussed results can be considered for publication in Atmospheric Chemistry and Physics after addressing quite numerous comments.

The first major problem with the paper is the undefined size of the particulate matter (TSP). It is important to size segregate for air quality studies while the fine fraction has important climatic implications. Both implications are poorly addressed since the TSP mass is often dominated by the large particles having short residence time in the atmosphere while at the same it is impossible to tell whether obtained results apply to fine particles.

Response: Thank you for your valuable suggestions and comments. Although size segregated samples are very important, we decided to collect TSP samples because TSP contains important information of pollens and other bio-aerosols, which are another topic of our study. In near future, we plan to analyze the size-segregated samples from the same site.

The second major problem is a one-year measurement campaign claiming seasonal differences and patters. It is rather obvious to everyone that any given year cannot be claimed as typical thereby reducing the significance of the obtained seasonal pattern.

A more general problem is an excessive focus on correlations without considering their significance and more importantly lacking cross-check balance with absolute concentrations considering whether they make sense with the claimed pattern. Existence or absence of a correlation is not a proof of causality, therefore, needs better context every time discussing observed correlations.

Response: Thank you for your suggestions. Following the reviewer's comment, we decided to use the term of seasonal changes instead of seasonal trends. This time we used correlation with significance. Please see footnote of Tables 4, 5 and 6. Following the reviewer's suggestion we deleted all the correlations and related discussion, which are statistically not significant.

Comments in sequence of their appearance in the paper:

Abstract

The abstract should clearly specify 12 months period of observations and weekly concentrations as this information is at a core of the paper. The use of expression "growing season" should be substituted with more scientific "active biota season".

Response: By following reviewer's comment, we added a phrase of 12 months and also changed "growing season" to "active biota season" in the revised manuscript. Please see lines, 17 and 25.

Introduction
The second paragraph seems out context to me as it presents anything known in aerosol science, but without contextual relevance to the study.
Response: Thank you for the suggestion. We have deleted the paragraph in the revised manuscript.

P22062, line 6. Are the claimed 70% relevant on regional or global scale? Be more specific.
Response: Thank you for the suggestion. This % is on regional scale. So, we have added the following sentence "About one fourth of the global anthropogenic carbonaceous aerosols are emitted from China, 70% of which are originated solely from coal burning (Cooke et al., 1999)." Please see lines 58 to 59.

Line 20. How significant is the claim of the first time ever measurements at Cape Hedo without considering other studies in the region of similar scope: seasonal patters, chemical species etc.
Response: Thank you for your suggestion. We deleted "for the first time" in the revised manuscript.

Line 24. Seasonal trends based on one year only can be misleading – be careful not to over-interpret.
Response: We reworded to "seasonal changes" instead of seasonal trends. Please see line 74.

Methods
I am confused about TSP mass measurements which were not introduced, but the pie charts suggest they were made. OC concentrations were probably significantly overestimated without using quartz-behind-quartz double filter approach. The artefact should at least be acknowledged and discussed accordingly.
Response: We measured TSP mass gravimetrically. Following the reviewer's comment, we added following sentences in the revised manuscript. "Before the analysis, TSP mass was gravimetrically determined at room temperature of 20°C and 50% relative humidity. However, the TSP mass may be overestimated due to the water contained in the marine aerosol filters." Please see lines 101 to 103.
Yes, we also agree that quartz fibre filters may adsorb organic vapours, causing positive artefacts on OC measurements. However, due to the relatively long period of sampling (one week), we consider that the artefacts may be minimal. We added the following sentences in the text "Quartz fibre filters may adsorb organic vapors, causing positive artefacts on OC measurements. However, due to the relatively long sampling period (one week), we consider that the artefacts may be minimal." Please see lines 96 to 98.

line 15. Specify procedure of the field blanks as the variety exists and may be interesting to a specialised reader.
Response: Thank you for the suggestion. We have added following sentences in the revised manuscript "Field blanks were also collected at the site. Blank filter was placed in the filter cartridge of sampler without pumping air. After 10 seconds, field blank filter was recovered from the cartridge." Please see lines 94 to 96.

Line 21. How carbonate carbon is considered negligible in the dust outflow? How

can Ca be soluble in the samples if not CaCO3 dissolved in acidic particles? Please reconsider/reword.
Response: In two spring samples, the extract of pH value is above 7.5. So these two samples may contain carbonate carbon. To make clear we have added following sentence "…..except for two spring samples, which showed that the pH of the filter extracts were alkaline." Please see lines 106 to 107.

P22065, line 14. Claiming "some degree of uncertainty" is not justified, more likely the results would be systematically biased high with higher than the actual minimum ratio. In would be more appropriate to use more conservative and rounded ratios of 3, 4, 5 and 3 for winter, spring, summer and autumn respectively.
Response: Thank you very much. Following the reviewer's comment, we took minimum rounded ratios of 3, 4, 5 and 3 for winter, spring, summer and autumn, respectively. Please see line 158 to 159 and Figures 4e and 4f.

Section 2.4 Good approach, but things become muddled in the text on whether nonsea-salt fraction or sea-salt fraction of the component is presented and discussed. I recommend authors split each relevant component into "nss" and "ss" fractions and redo correlation analysis with all implication re-discussed. That is especially applicable to correlation Tables. Some of the correlations are dubious to me and can be due to unspecified, not split fractions of e.g. SO4, Ca, etc.
Response: Thank you for your comments. We have split nss and ss fraction and remade correlation. We added following sentences in the revised manuscript "Throughout the year, we found strong correlations among $Na^+$, sea salt (ss)-$K^+$, ss-$Ca^{2+}$, ss-$Mg^{2+}$, ss-$SO_4^{2-}$ and $Cl^-$, indicating that these ions are derived from the sea spray. In winter, $NO_3^-$, a tracer of anthropogenic source, strongly correlates with $NH_4^+$, nss-$K^+$ and well correlates with nss-$Mg^{2+}$ (Table 4), suggesting that they are derived from anthropogenic sources in the Asian Continent. In spring, we did not find any significant correlation between $Na^+$ and $NO_3^-$ (Table 5). However, nss-$Ca^{2+}$, a tracer of crustal dust, was found to well correlate with nss-$K^+$ and nss-$Mg^{2+}$, indicating that they are derived from similar sources or reaction pathways. There is no correlation between nss-$Ca^{2+}$ and $Na^+$ in spring (Table 5). In summer, $NO_3^-$ showed a strong correlation with nss-$Mg^{2+}$ and nss-$SO_4^{2-}$ (Table 6), suggesting that they are formed from similar sources and/or reaction pathways. Both $NO_3^-$ and nss-$SO_4^{2-}$ are produced by photochemical reactions in the atmosphere (Pavuluri et al., 2011). It should be noted that ss-$SO_4^{2-}$ showed good correlations with $NH_4^+$ and $NO_3^-$ as well as other anthropogenic tracers (nss-$K^+$, nss-$Mg^{2+}$) during winter and spring (Tables 4 and 5). $NH_3$ and $HNO_3$ probably react with sea salt in the marine atmosphere." These points are briefly added in the revised MS. Please see lines 383 to 397 and Tables 4, 5, and 6.

Section 2.6 Air mass trajectories have an uncertainty of 15-30% of the distance at the start/end of it (check HYSPLIT model details on NOAA site) making their length above 120 hours unrealistic. For instance, 120hour trajectory length is of the order of 2000-3000km which introduces 300-1000km error at a backward starting point. Thus a longer trajectory of e.g 168 hours (7days) puts starting point essentially in random position. The sampling duration of 7 days does not require plotting 7day backward trajectory.
Response: Following the reviewer's comment, we redraw the trajectories to 5 days. Please see revised Figure 2.

Results

P22067, line 12. I already noted a problem of aerosol mass. How was it measured? Was it a sum of analysed components? In any event it has to be clearly stated.
Response: As we mentioned above, TSP mass was determined gravimetrically.

Line 22. My guess is of $CaCO_3$ as the particles become acidic. If the authors have other ideas please state, but provide explanation in any event.
Response: We did not agree with the reviewer's opinion. The most likely reason for Ca and TSP correlation is not the dissolution. $Ca^{2+}$ is already present in dust. We have added following sentence in the revised manuscript. "During spring, Asian dust is the source of $Ca^{2+}$." Please see lines 203 to 204.

P22068, line 17. The use of air parcels is inadequate given sample duration of 7days. Change to air masses.
Response: Following the reviewer's comment, we redraw trajectories to 5 days. Please see revised Figure 2.

P22069, line 1. I am curious why POC was highest in spring and not winter as it was primary anthropogenic. Were the emissions lower in winter? Probably not, but then the lack of precipitation in spring may have contribute to the observed maximum.
Response: Thank you very much for the comment. We checked the rainfall and wind speed data and concluded that wind speed is responsible for having the highest POC during spring. Hence, we added the following sentence in the revised manuscript "The higher wind speed during spring may be responsible for higher POC concentration." Please see lines 238 to 239.

Line 10-20. When was the maximum WSON of 2.2ug/m3 observed? Summer?
Response: Yes, it is. We found higher concentration of WSON during summer. We mentioned it in line 251.

P22070, line 2. Correlation coefficients are considered inconsistently in many parts of the paper. Correlation coefficient is either statistically significant or not statistically significant. If not significant then should not be even mentioned as the "null hypothesis" or spurious correlation cannot be reliably dismissed. ONLY if correlation was statistically significant can it be considered high or low. My estimate by the number of samples suggests that correlation of e.g. 0.22 is not statistically significant.
Response: Thank you, we have deleted the correlation that is statistically insignificant.

Line 3. The presence of EC must be accompanied by certain amount of OC; therefore, weak correlation does not exactly mean that sources are different, but rather the OC having at least two independent sources which distort correlation.
Response: Thank you very much for your suggestion. We deleted the correlation, which are not significant and added the following sentence in the text "…indicating that OC has at least two independent sources that distort the correlation." Please see line 264.

P22072, line 4. When claiming significance of marine carbon (it is relevant claim) the authors should consider marine carbon concentrations from literature and relate them to the observed percentages. Do things match and make sense? They may well do, but be more detailed and less speculative.
Response: Thank you very much. We tried to relate WSOC/OC ratios in literatures. We

found that the average summertime WSOC/OC ratio from Cape Hedo aerosols (28%) is slightly lower than average summertime WSOC/OC ratio from Delhi aerosols (36%). In summer, Delhi aerosols were influenced by marine sources (Aggarwal et al., 2013). Thus, we added following sentences in the revised text. "The average summertime WSOC/OC ratio from Cape Hedo aerosols (28%) is slightly lower than that from Delhi aerosols (36%). In summer, Delhi aerosols were also influenced by marine sources (Aggarwal et al., 2013)." Please see lines 322 to 324.

P22073, line 7-12. Consider and discuss numerous isotope studies for the presence of marine carbon in polluted air masses. Again consider absolute numbers as well, do they make sense?
Response: Thank you for your suggestion. This study focused only the OC, EC, WSOC and major ion. We are very sorry to say that we are not able to add isotope ratio in this manuscript.

Line 22. If you believe Ca coming from dissolved CaCO3 in dust when picking up acidic species during transport, state it.
Response: As we explained above, $Ca^{2+}$ is the source of crustal dust. See lines 203-204.

Section 3.4.1. NSS and SS fractions should be considered separately, otherwise discussion does not make sense. For instance, in continental air masses most of the Ca is nss while in marine air masses during summer most of it may be sea salt Ca.
Response: This time we have discussed nss and ss separately. Please see section 3.4.1.

P22075, line 13. Why Figure 10 presents 1:1 line when the ration in sea water is 1:1.16? 1:1 line doesn't make sense as sea water is not made of NaCl alone.
Response: Thank you, very much. We have made 1:1.6 instead of 1:1. Please see revised Figure 10.

Line 19. Indicate points by circle or arrow when the chlorine depletion was highest.
Response: Thank you very much. Following the reviewer's suggestion, we indicate the points by bracket when chlorine depletion was the highest. Please see revised Figure 10.

Line 24. How applicable is to consider 6% contribution of biogenic nssSO4 in this study when Savoie et al. (1994) study was made more than two decades ago and SO2 concentrations decreased dramatically over those two decades at least in Europe and North America? It is likely that the percentage of biogenic SO4 increased since the DMS source is the same while anthropogenic source decreased. Without considering SO2 decadal trend such claim is meaningless.
Response: Thank you very much. We deleted this sentence from the text.

P22078, line 4. Again which fractions are considered, nss or ss?
Response: nss fractions are considered here and clearly shown in equations. Please see lines 461 to 464.

Table 4-7. Redo the tables with separate nss and ss components. At the moment lack of correlation between e.g. SO4 and NH4 does not make sense as Ca amount is very small to neutralise significant fraction of nss sulphate and NH4 would more readily neutralise SO4 than NO3 due to acid strength.
Response: Thank you very much; we revised the tables by separating ss and nss

components. Please see revised Tables 4, 5 and 6.

Figure 5. I do not understand how the pie charts were constructed when aerosol mass measurements were not introduced.
Response: As mentioned above, TSP was measured gravimetrically.

Figure 10. Change 1:1 with 1:1.16. Indicate the points with highest Cl depletion clearly.
Response: As mentioned above, we have changed to 1:16 instead of 1:1 line. We indicated the highest chloride depletion points in bracket. Please see Figure 10.