Responses to reviewer #1 comments

Second review of the manuscript entitled "Long-term (2001-2012) trends of carbonaceous aerosols from remote island in the western North Pacific: an outflow region of Asian pollutants and dust". The revision is with significant improvement, but still some corrections are required before accepted for publication and I'm terming this again a minor revision. Some technical edits are offered as following and listed below with other comments.
Response: We appreciate for your decision on our manuscript and useful comments. We revised the manuscript following your comments. The responses are highlighted in yellow color in the revised manuscript as given below.

Specific comments:
1. Line 26: were associated
Response: Changed as suggested by the reviewer. Please see line 26 in the revised manuscript (ms).

2. Line 40: This point was
Response: Changed as suggested. See line 40 in the revised ms.

3. Line 78: (IPCC, 2013)
Response: Added comma as suggested. Please see line 77 in the revised ms.

4. Line 140: were low or
Response: Modified as suggested by the reviewer. See line 140 in the revised ms.

5. Line 141: which were analyzed….
Response: Changed as suggested. See line 141 in the revised ms.

6. Line 161: were corrected..
Response: Changed as suggested. See line 161 in the revised ms.

7. Line 162: were less than..
Response: Changed as suggested. See line 162 in the revised ms.

8. Line 167: equation was used
Response: Changed as suggested. See line 168 in the revised ms.

9. Line 167–168: all trends were assessed by using
Response: Changed as suggested. See line 169 in the revised ms.

10. Line 170: analyses are
Response: Changed as suggested. See line 171 in the revised ms.

11. Line 180: "over South and Southeast Asia" Also add "East Asia". Biomass burning is also more frequent in continental East Asia in winter. From BT and fire count analysis you are getting the intensity of biomass burning over all regions.
Response: Added as suggested. See line 181 in the revised ms.

12. Line 181: air masses were
Response: Changed as suggested. See line 187 in the revised ms.

13. Line 183: air masses were
Response: Changed as suggested. See line 189 in the revised ms.

14. Line 190: There was…
Response: Changed as suggested. See line 195 in the revised ms.

15. Line 198: All measured species (EC, OC, and WSOC) clearly showed……
Response: Added as suggested. See lines 202-203 in the revised ms.

16. Line 200: The seasonal variation in carbonaceous aerosols observed in this study was Found
Response: Modified as suggested. See lines 204-205 in the revised ms.

17. Line 204: In this version you're not discussing "synoptic wind circulation". Replace it with "air mass back trajectories".
Response: Replaced as suggested. See line 209 in the revised ms.

18. Line 206: Relatively higher
Response: Changed as suggested. See line 211 in the revised ms.

19. Line 207: were lower
Response: Changed as suggested. See line 212 in the revised ms.

20. Line 210: air masses were
Response: Changed as suggested. See line 215 in the revised ms.

21. Line 234–236: "The OC/EC ratios > 2.0 have been used to point out the presence of secondary organic aerosols (SOA) (Cao et al., 2003; Chow et al., 1996; Kunwar and Kawamura, 2014)". It is suggested to add one recent work on impact of Asian outflow over East Asia here as reference.
S. K. Pani, C. T. Lee, C. C. K. Chou, K. Shimada, S. Hatakeyama, A. Takami, S. H. Wang, and N. H. Lin (2017), Chemical Characterization of Wintertime Aerosols over Islands and Mountains in East Asia: Impacts of the Continental Asian Outflow, Aerosol and Air Quality Research, doi: 10.4209/aaqr.2017.03.0097.
Response: Added the above reference as suggested. Please see line 241 in the revised ms.

22. Line 245: are the tracers
Response: Changed as suggested. See line 254 in the revised ms.

23. Line 254–256: which clearly showed that air masses were occasionally coming from Southeast Asia (e.g., Indonesia, Malaysia, and New Guinea etc.)…
Response: Modified as suggested. Please see lines 264-265 in the revised ms.

24. Line 277: WSOC/OC ratios were….
Response: Changed as suggested. See line 286 in the revised ms.

25. Line 280: SOA formation was enhanced
Response: Changed as suggested. See line 289 in the revised ms.

26. Line 289: VOCs (Gilardoni et al., 2016; Youn et al., 2013) over continental East

Asia…….
Response: Modified. Please see line 299 in the revised ms.

27. Line 305: It was seen
Response: Rephrased. See line 332 in the revised ms.

28. Line 376–377: The RF of aerosol is generally estimated by using the aerosol optical depth (AOD), single scattering albedo (SSA), and asymmetry parameter (Pani et al., 2016).
Pani, S.K., Wang, S.H., Lin, N.H., Tsay, S.C., Lolli, S., Chuang, M.T., Lee, C.T., Chantara, S. and Yu, J.Y. (2016). Assessment of aerosol optical property and radiative effect for the layer decoupling cases over the northern South China Sea during the 7-SEAS/Dongsha Experiment. J. Geophys. Res. 121: 4894–4906. doi:10.1002/2015JD024601.
Response: Modified as suggested. Please see lines 402-403 in the revised ms.

29. Line 377–379: OC (except for brown carbon) and SO_4^{2-} mainly scatter the short-wave incoming solar radiation whereas EC strongly absorb the short-wave solar radiation as well as the long-wave outgoing terrestrial radiation in the atmosphere (Charlson et al., 1992; Ramanathan et al., 2001).
Charlson, R. J., S. E. Schwartz, J. M. Hales, R. D. Cess, J. D. Coakley, J. E. Hansen, and D. J. Hofmann (1992), Climate forcing by anthropogenic aerosols, Science, 255, 423–430.
Ramanathan, V., P. J. Crutzen, J. T. Kiehl, and D. Rosenfeld (2001), Aerosols, climate and the hydrological cycle, Science, 294, 2119–2124.
Response: Rephrased as"EC scatters the short-wave incoming solar radiation less than OC and that EC particles strongly absorb the short-wave solar radiation as well as long-wave outgoing terrestrial radiation in the atmosphere (Charlson et al., 1992;Ramanathan et al., 2001)." in the revised ms. Please see lines 403-405.

30. Line 918–920: Figure 3. Box-whisker plots of monthly variations of carbonaceous aerosol components (μg m^{-3}) and some specific mass ratios at Chichijima Island in the western North Pacific during 2001-2012.
Response: Modified as suggested. Please see the caption of Figure 3 in the revised ms.

31. Line 977–980: Figure 4. Annual trends (time series) in the concentrations (μg m^{-3}) of carbonaceous aerosol components, water-soluble ionic tracer compound (MSA^-), and some specific mass ratios during 2001-2012 over the western North Pacific. The liner trend equation (y = mx + c) is also shown for the each annual trend.
Response: Modified as suggested. Please see the caption of Figure 5 in the revised ms.

32. Line 999: Figure 5. Regression analysis between WSOC and MODIS-derived cloud condensation nuclei (CCN) concentrations over the western North Pacific.
Response: We rephrased this caption in the revised ms as "Regression analysis between (a) WSOC and MODIS-derived cloud condensation nuclei (CCN) concentrations, (b) sea salt and CCN, (c) seasalt+WSOC and CCN, and (d) WSOC and sea salt concentrations during July 2001- December 2012 over the western North Pacific". Please see the caption of Figure 6 in the revised ms.

33. The abscissa range of Fig. S1 and S3 should be consistent. Reposition the text (year) in X-axis to the middle and flip it to horizontal format as in Fig. S2. For Figure S3, please

do the same.
Response: Modified as suggested. Please see figure S1 and S3 in the revised ms.

34. Figure S2. Annual mean variations (μg m^{-3}) of carbonaceous species, water-soluble ionic tracer compound (MSA^-), and some specific mass ratios during 2001-2012 over the western North Pacific.
Response: Modified as suggested. Please see the caption of Figure S2 in the revised ms.

35. As biomass burning aerosol in SE and E Asia is concerned, a special issue (Nov., 2016) of the Seven South East Asian Studies (7-SEAS) on the journal of Aerosol and Air Quality Research gives the most updated information that can be included for comparison and discussion.
Response: We already discussed some of the studies (for example, Pani et al., 2017; 2016; Tsey et al., 2016; Lin et al., 2013) that belong to 7-SEAS program. Please see lines 101-102, 239, and 397-398 in the revised ms. We consider that this special issue is focused on biomass burning aerosols over the South and Southeast Asia for future studies. Thank you very much.

Responses to reviewer #2 comments

Overall, this paper has been improved by the revisions. The paper still contains grammatical mistakes and should be read through carefully and edited. The language should be toned down in some cases to be less definitive and more suggestive. The main conclusion is still that seasonal variations in wind patterns change the organic aerosol concentration. There is some discussion of decreasing particles from fossil fuel emissions. There is a small section on the contribution of marine aerosol, which is not complete, and the discussion of CCN at the end is still overreaching.
Response: Thank you for careful reading and suggestions on our revised manuscript (Ver. 1). Following your comments, we carefully revised the manuscript with English editing. We discussed more about the summer time marine emissions with appropriate supporting statements. We also modified discussion of CCN by following your comments. The responses are highlighted in yellow color in the revised manuscript as given below.

General Comments:
The OC/EC description has been improved, and Table 2 helps a lot in explaining the ratios measured in different sources. Based on Table 2, the split at OC/EC higher or lower than 2 may not be the best indicator (i.e. the first line with fossil fuel combustion has OC/EC of 4.0, 4.1, and 1.1). The authors could point out this range and then state that their values are much larger in the summer and still greater than the cutoff in the winter to spring, as shown.
Response: Following the reviewer's comment, we added following points in the revised ms.
"Based on Table 2, the split at OC/EC ratios higher or lower than 2 may not be the best indicator of SOA because fossil fuel combustion has OC/EC of 1.1 (Watson et al., 2001), 4.0 (Koch et al., 2001), and 4.1 (Cao et al., 2005). Monthly mean OC/EC ratios in this study are much larger in the summer and still greater than the cutoff (~ 4.0) in the winter-to-spring as shown in Table 1. This result suggests that the dominance of SOA in carbonaceous aerosol over the western North Pacific."
Please see lines 243-248 in the revised ms.

The part about the lower WSOC/OC ratio in the summer suggesting an ocean-derived source of organic carbon is still speculation. It is fine to include this paragraph with these references, but there is no concrete evidence here. This just says that other studies have measured OC in ocean-derived aerosol. Additionally, there is a wind-speed threshold required to produce breaking waves that in turn produce primary marine aerosol. The "low speed easterly winds" mentioned should include an actual wind speed and a reference to the speed needed for breaking waves, if the authors keep this discussion. The most that could be inferred from this data set, not including any correlations to sea salt, would be that air masses that originate over the ocean have lower concentrations of OC and are mixing and decreasing the total OC.

Response: In light of the reviewer's comment, we discussed more about the ocean-derived organic matter in summer with suitable supporting evidences in the revised ms.
The following points are briefly noted in the revised ms.

"On the other hand, lower ratios of WSOC/OC in summer may suggest that the primary emission of OC from the ocean surface via sea-to-air flux due to the dominance of pristine marine air masses. Based on the gradient flux measurements, Ceburnis et al. (2008) found that water-insoluble organic matter (WIOM) exhibited an upward flux, whereas water-soluble organic matter (WSOM) exhibited a downward flux, suggesting a primary production for WIOM and a secondary formation for WSOM. In this study, WIOM/WSOM ratios were higher in summer (mean: 1.45±0.17) and autumn (0.35±0.57) than in winter (0.19±0.67) as shown in Figure 4a. Higher ratios of WIOM/WSOM in summer over the western North Pacific are consistent with an idea that the ocean-derived organic matter is emitted from the ocean surface via sea-to-air flux of a fresh (less aged) organic matter. This result is further supported by the study of Miyazaki et al. (2010), who reported a significant amount of WIOM in the western North Pacific during summer, which may be produced by bubble-bursting processes at the ocean surface. Similarly, Ovadnevaite et al. (2011) reported higher contributions of primary organic matter to marine aerosols over the Northeast Atlantic.

Further, laboratory studies have revealed a high abundance of primary organic matter dominated by WIOM in marine aerosols (Facchini et al., 2008;Keene et al., 2007). However, it should be noted that although bubble-bursting process is a common source for the both sea salt (sea salt = 3.2 × Na^+, where 3.2 is the conservative mass ratio of salinity to Na in seawater, data obtained from Boreddy and Kawamura (2015)) and WIOM in marine aerosols, we found a negative/no correlation (r= -0.22) between sea salt and WIOC concentrations in summer (Figure 4b). This inference suggests that an additional source of organic matter (completely independent of sea salt production and wind speed) which may be derived from the marine biota, which is further evidenced by the higher concentrations of azelaic acid (a specific photochemical oxidation product of biogenic unsaturated fatty acids emitted from the ocean surface (Kawamura and Sakaguchi, 1999)) during summer and autumn over the western North Pacific for the same study period (Boreddy et al., 2017)."
Please see lines 301-326 and Figure 4 in the revised ms.

The authors need to include references if they are going to state that OC particles "majorly scatter" solar radiation to the same degree that sulfate or other salts do. At the very least, this should be rephrased to state that EC scatters less than OC and that EC is more absorbing. That is well known, whereas the scattering efficiency of OC alone is not.

Response: Rephrased as suggested by the reviewer in the revised manuscript as "EC scatters the short-wave incoming solar radiation less than OC and that EC particles strongly absorb the short-wave solar radiation as well as long-wave outgoing terrestrial radiation in the atmosphere (Charlson et al., 1992;Ramanathan et al., 2001)."
Please see lines 403-405 in the revised ms.

The original comment on the "Atmospheric Implications" was not fully addressed. Figure 5 with one correlation between CCN and WSOC is not enough to show that "watersoluble organic matter also plays an important role in CCN formation." At the very least, this needs to be rephrased to state the uncertainty. There are many more factors that contribute to CCN activation, so a single correlation (and not showing the possible correlations between WSOC and salts or particle size, etc.) is not enough. Figure 5 does not show a direct link, and the new text is not enough.

Response:

"To better understand the impact of WSOC on cloud forming potential, we performed regression analyses between WSOC, sea salt and CCN concentrations as shown in Figure 6. CCN data were downloaded from the MODIS satellite over the region (140°–145° E, 25°–30° N) in the western North Pacific for the period of July 2002 to December 2012. The results show significantly good correlations ($r=0.61$ and 0.64, $p<0.05$) between WSOC versus CCN and sea salt versus CCN concentrations (Figure 6a and 6b), suggesting the importance of WSOC for the formation of CCN over the western North Pacific in addition to sea salt.

Further, the correlation coefficient between sea-salt and CCN concentrations was slightly increased ($r=0.69$; $p<0.05$) when WSOC was added to the sea salt as shown in Figure 6c. Likely, the slope of the regression line between sea-salt+WSOC and CCN was little higher (2.21E7) than the slope between sea-salt and CCN concentrations (2.19E7). These results indicate that WSOC may slightly enhance the cloud forming potential of sea-salts, although it has less concentration over the western North Pacific. All these results suggest that significant uncertainty exists in RF due to the contribution of water-soluble organic matter to cloud forming. Therefore, climate modellers should consider WSOC in addition to other factors (sea-salts sulfate, etc.), while calculating RF over the western North Pacific. This point is consistent with the previous studies, which explain the contribution of water-soluble organic matter to CCN (Matsumoto et al., 1997; Zhao et al., 2016)."

"It also should be clear that sea-salt is not a major source of WSOC in this study as inferred from Figure 6d, which showed a moderate correlation ($r=0.42$; $p>0.05$) between WSOC and sea salt concentrations during the study period. In this study, atmospheric processes or chemical aging makes OC more water-soluble during long-range transport over the western North Pacific as discussed in section 3.2."

The above points are briefly noted in the revised ms. Please see lines 429-447, 451-455 and Figure 6 (a-d).

Specific Comments:

Figure 2: The new figure is much better, but it still runs into the problem of 12 years of data overlapping in the same plot. The back trajectories show the general trends, and the fire data is interesting. Could both of those be colored by the year? Here, it is unclear if one year had a lot of fires and others had none or if there are always fires in the same area. Using a color bar for the years would be also useful since the back trajectories don't perfectly overlap. The MODIS data also stops at 80E – mention that in the caption to be clear.

Response: Although back trajectories do not perfectly overlap, fire spots are seriously overlapped and difficult to see year-to-year variations. We also found an overlap of back trajectories for some months (for example, winter months), particularly when they come closer to sampling site. Based on these issues, we decided to keep one year (2001) of fire spots to represent total period (2001-2012). However, we provided a reference of our previous study (Verma et al., 2015), which shows back trajectories and fire spots for each

year on monthly scale. We have also mentioned about the downloaded region of MODIS fire spots. We appreciate the reviewer's suggestion.

The following statements are mentioned in the revised ms.

"Fire spot data were downloaded from the MODIS website over the region (80°-150°E; -10-70°N) during the year 2001 as an example for all the years (2001-12) because of overlap issue (there is no much difference in the intensity and area of fire spots). More detailed information about the monthly air mass back trajectories and fire data for each year during 2001-2012 was described elsewhere (Verma et al., 2015)."
Please see lines 181-185 in the revised ms.

Line 248: Add numbers to the ratios to describe "higher" and "lower", especially since the higher and lower ratios are indicative of different sources.
Response: Added as suggested. Thank you. Please see lines 257-258 in the revised ms.

Line 338: Why would there have been higher ocean-derived OC emissions during 2007-2008? There is no evidence presented here supporting a one-year difference in marine aerosol emissions. This should be removed.
Response: Removed as reviewer suggested.

Technical Corrections:
These are examples of technical corrections in the abstract only. The whole paper should be checked for grammatical errors and corrected.
Response: Following the reviewer's comment we checked grammar carefully throughout the ms.

Line 32: Remove "that"
Response: Removed as suggested.

Line 35: Add "a" after "found"
Response: Added as suggested. Please see line 35 in the revised ms.

Line 36: Change to: "that the concentration of biomass-burning-derived carbonaceous aerosols has increased"
Response: This sentence was rephrased in the revised ms. Please see lines 35-38 in the revised ms.

Line 37: Change "are" to "has"
Response: See tha above response.

Line 40: Change "source" to "sources"
Response: Changed as suggested. Please see lines 40 in the revised ms.

Line 41: Add "a" after "found"
Response: Added as suggested. Please see lines 41 in the revised ms.

Lines 42-44: This is unclear.
Response: We rephrased in the revised ms as "We also found a significant increase in OC/TC (total carbon) and WSOC/TC ratios, suggesting that contributions of water-soluble

organic matter to total carbonaceous aerosols have significantly increased over the western North Pacific via long-range atmospheric transport from East Asia."
Please see lines 41-44 in the revised ms.

More examples of technical corrections:
Line 54: Remove "invisible"
Response: Removed as suggested.

Line 57: Remove "hence"
Response: Removed as suggested.

Line 59: This implies that EC is volatile – rephrase
Response: Rephrased as "They are traditionally divided into two fractions: organic carbon (OC), which contains less volatile and more reflective species, and elemental carbon (EC; alternatively referred as black carbon, BC), which is the least reflective and most light absorbing component (Pöschl, 2005)."
Please see lines 58-61 in the revised ms.

Line 60: Change "while" to "and"
Response: Changed as suggested. Please see line 59 in the revised ms.

Line 61: Add ", which" after "BC)"
Response: Added as suggested. Please see line 61 in the revised ms.

Line 63: Change "some" to "a" and remove "so called"
Response: Changed and removed as suggested. Please line 63 in the revised ms.

Line 67: Remove "about"; change "are" to "is"
Response: Removed and Changed as suggested. Please see line 67 in the revised ms.

Line 83: Change "exist" to "existing"
Response: Changed as suggested. Please see line 83 in the revised ms.

Line 91: Change to "dominating"
Response: Changed as suggested. Please see line 90 in the revised ms.

Line 96: Change "increased" to "increase in"
Response: Changed as suggested. Please see line 95 in the revised ms.

Line 119: Change "is" to "are"
Response: Changed as suggested. Please see line 118 in the revised ms.

Line 181: Fix "the air masses are stronger to transport"
Response: Fixed as "the air masses were stronger and carry ….". See lines 186-188 in the revised ms.

Line 184: Add "and" before "mostly"
Response: Added. Please see line 189 in the revised ms.

Line 226: Change to "EC particles are primary and predominately come"

Response: Changed. Please see line 231 in the revised ms.

Line 375: Add “and” before “thus”
Response: Added as suggested. Please see line 400 in the revised ms.

Long-term (2001-2012) trends of carbonaceous aerosols from remote island in the western North Pacific: an outflow region of Asian pollutants and aging

Suresh K. R. Boreddy[1], Md. Mozammel Haque[1, 2], and Kimitaka Kawamura[1, 2*]

[1]Institute of Low Temperature Science, Hokkaido University, Sapporo 060-0819, Japan
[2]Now at Chubu Institute of Advanced Studies, Chubu University, Kasugai 487-8501, Japan

*Corresponding author
Kimitaka Kawamura
Email: kkawamura@isc.chubu.ac.jp

Abstract

The present study reports on long-term trends of carbonaceous aerosols in total suspended particulate (TSP) samples collected at Chichijima Island in the western North Pacific during 2001-2012. Seasonal variations of elemental carbon (EC), organic carbon (OC), and water-soluble organic carbon (WSOC) concentrations showed maxima in winter to spring and minima in summer. These seasonal differences in the concentrations of carbonaceous aerosols were associated with the outflows of polluted air masses from East Asia, which are clearly distinguishable from pristine air masses from the central Pacific. The higher concentrations of carbonaceous aerosols during winter to spring are associated with long-range atmospheric transport of East Asian continental polluted air masses, whereas lower concentrations may be due to pristine air masses from the central Pacific in summer. The annual trends of OC/EC (+0.46% yr^{-1}), WSOC (+0.18% yr^{-1}) and WSOC/OC (+0.08% yr^{-1}) showed significant ($p<0.05$) increases during the period of 2001-2012, suggesting an enhanced formation of secondary organic aerosols (SOAs) via photochemical oxidation of anthropogenic and biogenic volatile organic compounds (VOCs) during long-range atmospheric transport. We found a significant increase (+0.33% yr^{-1}) in nss-K^+/EC ratios, demonstrating that concentrations of biomass-burning-derived carbonaceous aerosols have increased, while those of fossil fuel-derived aerosols have decreased over the western North Pacific. Further, secondary biogenic emissions are also important over the western North Pacific as inferred from a significant increase (+0.14% yr^{-1}) in the concentrations of methanesulfonate (MSA^-, a tracer for biogenic sources). This point was further supported by a moderate correlation (r=0.40) between WSOC and MSA^-. We also found a significant increase in OC/TC (total carbon) and WSOC/TC ratios, suggesting that contributions of water-soluble organic matter to total carbonaceous aerosols have significantly increased over the western North Pacific via long-range atmospheric transport from East Asia.

Keywords: Carbonaceous aerosols, long-term trends, the western North Pacific, East Asia, biomass burning, biogenic emissions, long-range atmospheric transport, photochemical oxidation.

1. Introduction

Particulate air pollution is one of the most important environmental issues due to its severe impact on visibility and air quality, and has been a great issue over East Asia, particularly in China (Zhang and Cao, 2015; Cui et al., 2015). On the other hand, its impacts on not only climate but also public health may be more severe and intricate (Pöschl, 2005; Menon et al., 2002). Carbonaceous aerosols are ubiquitous in the Earth's atmosphere and potentially cause harmful effect on human health (Bond et al., 2013; Kanakidou et al., 2005; Ramanathan and Carmichael, 2008; Fatima et al., 2012; Chung and Seinfeld, 2002). They are traditionally divided into two fractions: organic carbon (OC), which contains less volatile and more reflective species, and elemental carbon (EC; alternatively referred as black carbon, BC), which is the least reflective and most light absorbing component (Pöschl, 2005). However, the role of OC on cooling or warming has been a matter of debate (Chung et al., 2012; Cazorla et al., 2013) because a class of OC (brown carbon) may absorb sunlight (Feng et al., 2013; Lu et al., 2015; Laskin et al., 2015; Bahadur et al., 2012). In the ambient atmosphere, however, these two fractions (EC and OC) are mixed and consequently complicate the estimation of net radiative forcing (Jacobson, 2001). Therefore, studying carbonaceous aerosols and their sources is essential to understand how the different sources of carbonaceous particles may influence the radiative balance on a regional and global scale.

The major sources of carbonaceous aerosols are fossil fuel and biomass burning in addition to the atmospheric oxidation of anthropogenic and biogenic volatile organic compounds (VOCs) (Chung et al., 2012; Szidat et al., 2006). The global emission of organic aerosols (OA) from biomass and fossil fuel sources has been estimated at 45-80 and 10-30 Tg/yr, respectively (Scholes and Andreae, 2000). Due to the presence of polar functional groups, particularly carboxylic acids, many organic compounds in OA are water-soluble (Boreddy et al., 2016) and hence aid in particles acting as cloud condensation nuclei (CCN) (Novakov and Penner, 1993; Matsumoto et al., 1997; Asa-Awuku et al., 2009). According to the recent report of the intergovernmental panel on climate change (IPCC, 2013), the radiative forcing of BC and OA associated with fossil fuel and biofuel combustions is in the range of +0.05 to +0.8 (mean: +0.4) W m^{-2} and -0.4 to -0.1 (-0.12) W m^{-2}, respectively. It is +0.0 (−0.2 to +0.2) W m^{-2} as a result of their change offset when BC and OA are emitted by biomass burning (Boucher et al., 2013). Therefore, carbonaceous aerosols have a net warming effect on the climate as per an IPCC 2013 report. However, there is still large uncertainties existing in quantification of radiative impacts for carbonaceous aerosols, particularly with regard to OA (Reddy and Boucher, 2004).

The atmosphere over East Asia is becoming worse due to not only the dense population, but also rapid urbanization/industrialization (Fu et al., 2012; Cao et al., 2007). On a global scale, China has the largest carbonaceous aerosol emissions from combustion with contributions about 24% and 30% for OC and BC, respectively (Bond et al., 2004). Recently, Wang et al. (2016) suggested that coal combustions and vehicular emissions are the dominating sources of carbonaceous aerosols in China (Kirillova et al., 2014). Using the emission Model of Emissions of Gases and Aerosols from Nature (MEGAN) combined with the MOdel of HYdrocarbon Emissions from the CANopy (MOHYCAN) model, Stavrakou et al. (2014) reported an increased emission of biogenic isoprene over Asia (0.16% yr^{-1}) with the more pronounced trend over China (0.52% yr^{-1}) during 1979-2012. Similarly, Zhang et al. (2016) reported an increase in biogenic isoprene emission (from 132000 to 175000t yr^{-1}) in northern China during 1982-2010. In contrast, SO_2 emissions over China have been declining after 2006 because of the wide usage of flue-gas desulfurization (FGD) equipment in power plants (Lu et al., 2010; Lu et al., 2011). All these East Asian pollutants along with soil dust are transported to the North Pacific via long-range atmospheric transport by westerly winds and perturb the remote marine background conditions and the ocean biogeochemistry by heterogeneous reactions (Boreddy et al., 2015; Matsumoto et al., 2004). In addition to East Asian pollutants, the western North Pacific also receives biomass burning emissions from Southeast Asia (Tsay et al., 2016; Lin et al., 2013; Huang et al., 2013)

To better understand the long-range transport of Asian pollutants and their atmospheric processing over the western North Pacific, we continuously collect total suspended particulate (TSP) samples since 1990 at Chichijima Island (Mochida et al., 2003; Kawamura et al., 2003; Boreddy and Kawamura, 2016). Chichijima is a remote marine island in the western North Pacific, which is located in the outflow region of East Asian pollutants and dust during the westerly wind season and in the pristine air masses under the wind regime of easterlies. This island is about 1000 km south of Tokyo, Japan and 2000 km from the East Asian countries (China) as shown in Figure 1. Therefore, the observation at Chichijima Island is useful for studying the long-range transport of East Asian pollutants and their heterogeneous chemistry over the western North Pacific (Boreddy et al., 2014; Verma et al., 2015; Chen et al., 2013). In this study, we discuss the long-term trends in the concentrations of carbonaceous aerosols (EC, OC, and water-soluble organic carbon (WSOC)) and their ratios during 2001-2012 in addition to seasonal variations. The role of photochemical oxidation of anthropogenic and biogenic VOCs on OC and WSOC and their relations to the CCN are also discussed.

2. Instrumentation and data analyses

2.1. Sampling site and aerosol collection

Figure 1 shows the location of the sampling site and its adjacent Asian countries in the western North Pacific. TSP samples were collected at the Satellite Tracking Centre of the Japan Aerospace Exploration Agency (JAXA, elevation: 254 m) in Chichijima Island (27°04′N; 142°13′E) on a weekly basis (Boreddy and Kawamura, 2015). Aerosol samples are collected on pre-combusted (450° C for 3-5 h) quartz filter (20 × 25 cm, Pallflex 2500QAT-UP) using a high volume air sampler (HVS) with a flow rate of 1 m^3 min^{-1}. The HVS was installed at a height of 5 m above the ground level. The filters were placed in a pre-baked (450°C for 6 h) glass jar (150 mL) with a Teflon-lined screw cap before sample collection. After aerosol collection, the filters were recovered into the glass jar, transported to the laboratory in Hokkaido University, Sapporo, and stored in a freezer room at −20 °C prior to analysis. A total of 545 aerosol samples and about 56 field blank samples were used for the analysis of carbonaceous components during 2001-2012.

2.2. Analyses of carbonaceous aerosols

Concentrations of OC and EC were determined using a Sunset Laboratory carbon analyzer following the IMPROVE (Interagency Monitoring of Protected Visual Environments) thermal/optical evolution protocol (Wang et al., 2005), assuming carbonate carbon (CC) in the aerosol samples to be insignificant (Chow and Watson, 2002). Previous studies have also shown that carbonate, particularly calcium carbonate, levels were low or negligible in most ambient samples, which were analyzed by IMPROVE protocol (Wang et al., 2005; Clarke and Karani, 1992; Chow et al., 2001). A filter cut of 1.54 cm^2 of each filter was placed in a quartz tube inside the thermal desorption chamber of the analyzer and then stepwise heating was applied. Helium (He) gas was applied in the first ramp and was switched to mixture of He/O_2 in the second ramp. The evolved CO_2 during the oxidation at each temperature step was measured by non dispersive infrared (NDIR) detector system. The calculated detection limits of OC and EC were 0.05 and 0.02 μgC m^{-3}, respectively. The sum of OC and EC was considered to as total carbon (TC) in this study.

To determine WSOC, a punch of 20 mm in diameter of each filter was extracted with 20 mL organic-free ultra pure water (>18.2 MΩ cm, Sartorius arium 611 UV) and ultrasonicated for 30 min. These extracts were passed through a disk filter (Millex-GV, 0.22 μm pore size, Millipore) to remove the filter debris and insoluble particles and analyzed using

a total organic carbon (TOC) analyzer (Shimadzu, TOC-Vcsh) equipped with a catalytic oxidation column and non-dispersive infrared detector (Miyazaki et al., 2011).

Concentrations of water-soluble methanesulfonate (MSA^-), non sea-salt sulfate (nss-SO_4^{2-}) and non sea-salt potassium (nss-K^+) were taken from the study of Boreddy and Kawamura (2015), in order to support the inferences related to carbonaceous species over the western North Pacific, which were determined using ion chromatography (761 Compact IC, Metrohm, Switzerland).

The analytical errors in the replicate analyses were less than 10% for OC, EC and WSOC in this study. The concentrations of carbonaceous aerosols reported in this study were corrected for field blanks. The levels of blanks were less than 5% for all the parameters in the real samples.

2.3. Statistical analyses

Two statistical approaches were used to better conduct the trend analyses in time series of WSOC, EC, and OC and their ratios during 2001-2012. First, the tendency (linear trend) equation was used for each time series (Draper and Smith, 1966). Second, all trends were assessed by using the Mann-Kendall non-parametric test (Mann, 1945; Kendall, 1975), which is completely independent of the first approach. More detailed information about these statistical analyses are described in supporting information (SI).

3. Results and discussion

3.1 Air mass back trajectories and general meteorology

To better understand the influence of heterogeneity in air masses to carbonaceous aerosols, we computed daily 7-day isentropic air mass back trajectories at an altitude of 500 m for each month using the hybrid single particle Lagrangian-integrated trajectory (HYPLIT) model (Draxler and Rolph, 2013) during 2001-2012 as shown in Figure 2. We also investigated the MODerate resolution Imaging Spectroradiometer (MODIS) derived fire count data along with the back trajectories to understand the intensity of biomass burning over East Asia and South/Southeast Asia. Fire spot data were downloaded from the MODIS website over the region (80°-150°E; -10-70°N) during the year 2001 as an example for all the years (2001-12) because of overlapping (there is no much difference in the intensity and area of fire spots). More detailed information about the monthly air mass back trajectories and fire data for each year during 2001-2012 was described elsewhere (Verma et al., 2015). From Figure 2, it is obvious that from winter (December-February) to spring (March-May) the air

masses were stronger and carry continental air pollutants and dusts from East Asia to the sampling site in the Pacific by long-range atmospheric transport. The continental air masses were absent in summer (June to August) and mostly come from the central Pacific and carry pristine air masses to the observation site, whereas in autumn (September-November) the air mass pattern shifts from southeasterly to northwesterly and become stronger towards winter.

Figure S1 shows the temporal variations of meteorological parameters such as air temperature (°C), relative humidity (%), wind speed (m s^{-1}), and precipitation (mm) at Chichijima Island during the study period of 2001-2012. All the meteorological parameters were downloaded from the Japan Meteorological Agency (JMA). There was a clear seasonal variation in ambient temperature, relative humidity, and precipitation with summer maxima and winter minima. Wind speeds were higher in winter to spring and lower in summer.

3.2 Monthly/seasonal variations

Figure 3 (a-f) presents the monthly/seasonal variations in the concentrations of EC, OC, WSOC and their ratios at Chichijima Island in the western North Pacific during 2001-2012. The corresponding statistical data were reported in Table 1. All measured species (EC, OC, and WSOC) clearly showed winter-to-spring maxima (highest concentration was in March) and summer minima (lowest in July) and then increase towards autumn. The seasonal variation in carbonaceous aerosols observed in this study was found consistent with the typical seasonal pattern in ambient carbonaceous aerosols over China (Zhang et al., 2008b; Cao et al., 2006), indicating a common source for these components, which are long-range transported to the western North Pacific. This, of course, can also be influenced by seasonal meteorology and air mass back trajectories over the western North Pacific as discussed in section 3.1.

Relatively higher monthly average concentrations up to 0.28, 1.13 and 0.59 μg m^{-3} were observed for EC, OC, and WSOC in March. In contrast, their monthly averages were lower in summer or early autumn (July or September) with the concentrations of 0.04, 0.58, and 0.20 μg m^{-3}, respectively (Table 1). It is well documented that in summer, a maritime high-pressure wind dominated over the western North Pacific in which the air masses were pristine and less influenced by the continental outflow from East Asia (Figure 2). This observation is consistent with the fact that concentrations of anthropogenic nss-SO_4^{2-}, NO_3^-, NH_4^+, and nss-K^+ showed similar seasonal variations with winter and/or spring maxima and summer minima (Boreddy and Kawamura, 2015). On the other hand, continental air masses blow from the Asian continent in winter and spring; therefore, the maritime background

condition of the western North Pacific is often influenced by the continental outflow via long-range atmospheric transport (Duce et al., 1980). Very low concentrations of EC in summer, whose abundances were up to seven times lower than those in the continental outflow, suggested negligible contribution of local anthropogenic emissions as well as long-range influences over the sampling site. These results are consistent with previous studies, which reported that several times lower concentrations of organic compounds in summer compared to winter/spring over the same observation site (Kawamura et al., 2003; Mochida et al., 2003). Therefore, it is reasonable to believe that the sources of carbonaceous aerosols were transported from the adjacent Asian countries to the western North Pacific via long-range atmospheric transport.

As described earlier, EC particles are primary and predominately come from biomass and fossil fuel combustion sources. On the contrary, OC is of either primary origin or secondary formation via gas-to-particle conversion in the atmosphere. The precursors of secondary OC may also come from biogenic sources in addition to fossil fuel and biomass burning emissions. The OC/EC ratios often used to distinguish the relative contribution of primary vs. secondary sources as well as biomass vs. fossil fuel burning sources (Turpin and Huntzicker, 1995; Castro et al., 1999; Rastogi et al., 2016). Atmospheric aerosols emitted from fossil fuel combustion are characterized by lower OC/EC ratios (<2.0) whereas higher OC/EC ratios (>5.0) are characteristic of biomass burning aerosols. The OC/EC ratios > 2.0 have been used to point out the presence of secondary organic aerosols (SOA) (Cao et al., 2003; Chow et al., 1996; Kunwar and Kawamura, 2014; Pani et al., 2017).

Table 2 summarizes OC/EC ratios reported for various sources of aerosol particles. Based on Table 2, the split at OC/EC ratios higher or lower than 2 may not be the best indicator of SOA because fossil fuel combustion has OC/EC of 1.1 (Watson et al., 2001), 4.0 (Koch et al., 2001), and 4.1 (Cao et al., 2005). Monthly mean OC/EC ratios in this study are much larger in the summer and still greater than the cutoff (~ 4.0) in the winter-to-spring as shown in Table 1. This result suggests that the dominance of SOA in carbonaceous aerosol over the western North Pacific. The seasonal variation of OC/EC mass ratios showed maxima in summer (~21 to 33) and minima in winter-to-spring (3.9 to 7.7). The extremely high OC/EC ratios in summer indicate the secondary formation of OC via oxidation processes, while low OC/EC ratios in winter-to-spring suggests that both biomass burning and fossil fuel combustion are important sources for carbonaceous aerosols over the western North Pacific.

It is well documented that nss-K^+ and EC are the tracers for biomass burning and fossil fuel combustion emissions, respectively. Therefore, nss-K^+/EC ratios were widely used to better identify major sources of carbonaceous aerosols (Wang et al., 2005; Rastogi et al., 2016; Ram and Sarin, 2011). The higher nss-K^+/EC ratios (>0.20) indicate the dominance of biomass burning emissions, whereas lower ratios (<0.10) suggest the prevalence of fossil fuel combustion emissions. In this study, higher nss-K^+/EC mass ratios were observed in midsummer (July) to early autumn (September) (Figure 3e), suggesting an influence of biomass burning emissions from southeast Asian countries via long-range atmospheric transport over the western North Pacific. This point is consistent with the air mass back trajectory analysis and MODIS-fire count data during summer months (Figure 2), which clearly showed that air masses were occasionally coming from Southeast Asia (Indonesia, Malaysia and New Guinea, etc.) where biomass burning is a common phenomena during summer to early autumn. Biomass burning products were transported to the western North Pacific (Figure 2). In this context, Verma et al. (2015) reported significant concentrations of levoglucosan during summer in Chichijima (in the absence of East Asian outflows), which were attributed to the occasional transport of biomass burning influenced air masses from southeast Asia, as inferred from the air mass trajectories and fire spot data during 2001-2013. Therefore, carbonaceous aerosols over Chichijima strictly follow the seasonal wind patterns in the western North Pacific.

Previous studies have shown that SOA is largely composed of oxygenated compounds that are highly water-soluble (Kanakidou et al., 2005; Kondo et al., 2007) and references therein). Thus, measurements of WSOC have been used to estimate the SOA in ambient aerosols (Weber et al., 2007; Snyder et al., 2009; Sudheer et al., 2015; Decesari et al., 2001; Docherty et al., 2008). Because major fraction of biomass burning products is highly water-soluble (Sannigrahi et al., 2006; Saarikoski et al., 2008), WSOC/OC ratio has been used as an unique tracer to better understand the photochemical activity and/or aging of aerosols and to discuss SOA formation mechanism in the atmosphere during long-range transport (Miyazaki et al., 2007; Ram et al., 2010b; Ram and Sarin, 2011; Kondo et al., 2007; Weber et al., 2007; Gilardoni et al., 2016). The WSOC/OC ratios exceeding 0.4 have been used to indicate the significant contribution of SOA (Ram et al., 2010a) and aged aerosols. The WSOC/OC ratios ranged from 0.06 to 0.19 in diesel particles (Cheung et al., 2009) and 0.27 for vehicular emissions (Saarikoski et al., 2008).

In this study, we found that monthly mean WSOC/OC ratios were >4.0 for all months except for September, indicating a significant contribution from SOA over the western North

Pacific. The seasonal variation of WSOC/OC showed higher values (monthly mean: 0.44 to 0.62) during winter-spring months (Figure 3f), implying that the SOA formation was enhanced due to increased photochemical activity and/or aging of East Asian polluted aerosols during long-range atmospheric transport. The high WSOC/OC ratios are traditionally attributed to the atmospheric oxidation of various VOCs in the presence of oxidants such as ozone and hydroxyl radicals via gas and/or aqueous phase reactions in the atmosphere (Miyazaki et al., 2007; Ram and Sarin, 2012). However, the atmosphere over the western North Pacific is always characterized by high relative humidity (>80%) and air temperature (~24°C) during the whole year (Figure S1). Therefore, higher WSOC concentrations in winter-to-spring over the western North Pacific were largely attributed to the aqueous-phase oxidation of anthropogenic and/or biogenic VOCs (Gilardoni et al., 2016; Youn et al., 2013), which are emitted over continental East Asia and long-range transported to the western North Pacific.

On the other hand, lower ratios of WSOC/OC in summer may suggest that the primary emission of OC from the ocean surface via sea-to-air flux due to the dominance of pristine marine air masses. Based on the gradient flux measurements, Ceburnis et al. (2008) found that water-insoluble organic matter (WIOM) exhibited an upward flux, whereas water-soluble organic matter (WSOM) exhibited a downward flux, suggesting a primary production for WIOM and a secondary formation for WSOM. In this study, WIOM/WSOM ratios were higher in summer (mean: 1.45±0.17) and autumn (0.35±0.57) than in winter (0.19±0.67) as shown in Figure 4a. Higher ratios of WIOM/WSOM in summer over the western North Pacific are consistent with an idea that the ocean-derived organic matter is emitted from the ocean surface via sea-to-air flux as a fresh (less aged) organic matter. This result is further supported by the study of Miyazaki et al. (2010), who reported a significant amount of WIOM in the western North Pacific during summer, which may be produced by bubble-bursting processes at the ocean surface. Similarly, Ovadnevaite et al. (2011) reported higher contributions of primary organic matter to marine aerosols over the Northeast Atlantic.

Further, laboratory studies have revealed a high abundance of primary organic matter dominated by WIOM in marine aerosols (Facchini et al., 2008; Keene et al., 2007). However, it should be noted that although bubble-bursting process is a common source for the both sea salt (sea salt = 3.2 × Na^+, where 3.2 is the conservative mass ratio of salinity to Na in seawater, data obtained from Boreddy and Kawamura (2015)) and WIOM in marine aerosols, we found a negative/no correlation (r= -0.22) between sea salt and WIOC concentrations in summer (Figure 4b). This inference suggests that an additional source of organic matter

(completely independent of sea salt production and wind speed) which may be derived from the marine biota, which is further evidenced by the higher concentrations of azelaic acid (a specific photochemical oxidation product of biogenic unsaturated fatty acids emitted from the ocean surface (Kawamura and Sakaguchi, 1999)) during summer and autumn over the western North Pacifc for the same study period (Boreddy et al., 2017).

3.3 Annual trends

Figure 5 shows the annual trends in the concentrations of EC, OC, TC (EC+OC), WSOC, and WSOC/OC ratios during the period of 2001-2012 over the western North Pacific (see Figure S2 for annual mean variations). Table 3 summarizes the results of the statistical analyses. All the annual trends of chemical species and WSOC/OC ratios seem to present clear seasonal patterns with higher values in winter-spring and lower values in summer. On the other hand, seasonal variations of the OC/EC and nss-K^+/EC ratios showed higher values in summer.

As seen from Figure 4a-c, concentrations of EC, OC, and TC during 2001-2012 ranged from 0.001 to 0.36 μg m^{-3} (mean: 0.142 μg m^{-3}), 0.25 to 1.7 μg m^{-3} (0.76 μg m^{-3}) and 0.28 to 2.01 μg m^{-3} (0.90 μg m^{-3}), respectively. The annual variations of EC showed a decreasing trend (-0.007% yr^{-1}), while OC and TC trends are continuously increasing (+0.16% yr^{-1} and +0.11% yr^{-1}, respectively) from 2001 to 2012 although the rates were not significant ($p>0.05$). However, the annual trends of OC/EC and OC/TC ratios increased significantly ($p<0.05$; +0.46% yr^{-1} and +0.06% yr^{-1}) from 2001 to 2012 (Figure 5d and 5e), suggesting that the secondary formation of OA and its contribution to carbonaceous aerosols have continually increased over the western North Pacific. These results further suggest that the contribution of fossil fuel combustion to carbonaceous aerosols has declined during the sampling period. This point is supported by the annual trend of nss-K^+/EC mass ratios, which showed a significant increase ($p<0.05$; +0.33% yr^{-1}) during the sampling period (Figure 5g). This observation is consistent with the study of Verma et al. (2015), who observed a significant enhancement of levoglucosan (a good biomass burning tracer, e.g., Simoneit, 2002) during 2006-2013 over the sampling site. Therefore, all these results demonstrate that the contributions of biomass burning emissions to carbonaceous aerosols have increased significantly over the western North Pacific whereas the contributions of fossil fuel combustion have decreased.

The annual trend of WSOC showed a significant increase ($p<0.05$; +0.18% yr^{-1}) from 2001 to 2012 (Figure 5c), implying an important SOA formation over the western North

Pacific because SOA largely consists of water-soluble matter (Weber et al., 2007; Kondo et al., 2007). Generally, atmospheric aging makes aerosols more water-soluble during long-range transport (Aggarwal and Kawamura, 2009; Rudich et al., 2007; Robinson et al., 2007; Jimenez et al., 2009; Kawamura et al., 2010), especially in the remote marine atmosphere (Kawamura et al., 2003). This point is further supported by a decadal increase (+0.08% yr^{-1}) in the WSOC/OC ratios (Figure 5f). These results may demonstrate that the formation of WSOC (or OC) over the western North Pacific is significantly linked with photochemical aging of aerosols and oxidation of various VOCs during long-range atmospheric transport (Zhang et al., 2007; Decesari et al., 2010). A significant increasing trend of WSOC/TC ($p<0.05$; +0.15% yr^{-1}; Table 2) again suggests that formation of SOA and its contributions to carbonaceous aerosols have significantly increased over the western North Pacific during 2001-2012.

To better understand the contributions of photochemical oxidation of biogenic VOCs to WSOC during long-range atmospheric transport, we showed the annual trend of water-soluble organic ion such as MSA^- (a biogenic tracer; see Figure 4g). In our previous study (Boreddy and Kawamura, 2015), we reported that MSA^- significantly correlates with continental pollutants such as NH_4^+ (r=0.56), nss-K^+(0.52) and nss-SO_4^{2-} (0.50) and no correlation with Na^+, suggesting that continentally derived MSA^- may be associated with the terrestrial higher plants and other biogenic sources along with Asian pollutants during the long-range transport. However, we should not ignore the oceanic biogenic emissions, especially in the summer period (Bikkina et al., 2014), although it has less abundance compared to continental biogenic emissions over the western North Pacific. In this study, the annual trend of MSA^- showed a significant increase ($p<0.05$; +0.14% yr^{-1}) during 2001-2012, implying that continental transport of biogenic VOCs (BVOCs) over the western North Pacific have increased significantly during 2001-2012.

Zhang et al. (2016) have reported an increase (from 132000 to 175000t yr^{-1}) in the emission of isoprene in northern China during 1982-2010 using an emission model. Consistently, Stavrakou et al. (2014) reported that an increased isoprene emission (+0.52% yr^{-1}) over Asia, especially China during 1979-2012. Based on strong correlations ($r>0.90$) between isoprene and above-canopy temperature, they suggested that oxidations of biogenic BVOCs from the terrestrial higher plants are important in Asia (especially in China). Since Chichijima is an outflow region of East Asia, long-range atmospheric transport of BVOCs may be possible from terrestrial higher plants in Asia/China to the western North Pacific by westerly winds, which may significantly contribute to the enhanced trends of OC and WSOC

during 2001-2012. We found significant ($p<0.05$) increases in the annual trends of methylglyoxal and pyruvic acid, which are tracers of aqueous-phase oxidation of biogenic isoprene (Carlton et al., 2009), over the western North Pacific as shown in Figure S3. We also found a moderate correlation ($r=0.40$, $p<0.01$) between of MSA^- and WSOC concentrations (not shown as a figure). These results demonstrate that increase of WSOC is likely due to the increased photochemical oxidation of BVOCs during long-range transport over the western North Pacific in addition to the other emissions such as biomass burning.

3.4 Atmospheric implications

It is well known that atmospheric aerosols play a key role in the climate system as they can act as cloud condensation nuclei (CCN) and impact cloud formation and thus, radiative forcing (RF) (IPCC, 2013). The RF of aerosol is generally estimated by using the aerosol optical depth (AOD), single scattering albedo (SSA) and asymmetry parameter (Pani et al., 2016). EC scatters the short-wave incoming solar radiation less than OC and that EC particles strongly absorb the short-wave solar radiation as well as long-wave outgoing terrestrial radiation in the atmosphere (Charlson et al., 1992; Ramanathan et al., 2001). The single scattering albedo (SSA), defined as the ratio of scattering to the extinction coefficient of aerosols, is an important property for determining the direct RF (Pani et al., 2016). The SSA is highly sensitive to the nature (scattering and/or absorption) of aerosols in the atmosphere. Therefore, although OC has certain uncertainty because of light absorbing brown carbon, the OC/EC ratios can be used to understand the relative contributions of scattering or absorbing aerosols in the atmosphere.

Further, a good knowledge of the OC/EC ratios in aerosols (for example, biomass burning) may also help to improve model representation of the absorption caused by organic compounds constituting the so called brown carbon, which contributes to the aerosol RF (Chung et al., 2012; Saleh et al., 2014; Kirchstetter and Thatcher, 2012). In this study, atmospheric aging may make OC more scattering during long-range transport over the western North Pacific. A significant increasing trend of OC/EC ratios suggests that scattering aerosols are increased significantly over the western North Pacific. In contrast, absorbing aerosols may be decreased during the study period. This result may provide an important implication for radiative forcing because scattering and absorption coefficients are playing crucial role in the radiative forcing calculations as mentioned above.

Novakov and Corrigan (1996) found that pure organic components from biomass smoke emissions can form cloud condensation nuclei (CCN) without the presence of sulfate

(SO_4^{2-}) and other inorganic compounds. Roberts et al. (2002) showed that biomass burning derived organic aerosols does serve as CCN. Further, large loadings of CCN in continental air masses were observed over the western North Pacific (Matsumoto et al., 1997; Boreddy et al., 2015). In this study, the enhanced WSOC concentrations and WSOC/OC ratios in continental air masses suggest an important role of WSOC in CCN activity over the western North Pacific in addition to other particles such as SO_4^{2-} and sea-salts. To better understand the impact of WSOC on cloud forming potential, we performed regression analyses between WSOC, sea salt and CCN concentrations as shown in Figure 6. CCN data were downloaded from the MODIS satellite over the region (140°–145° E, 25°–30° N) in the western North Pacific for the period of July 2002 to December 2012. The results show significantly good correlations ($r=0.61$ and 0.64, $p<0.05$) between WSOC versus CCN and sea salt versus CCN concentrations (Figure 6a and 6b), suggesting the importance of WSOC for the formation of CCN over the western North Pacific in addition to sea salt. Further, the correlation coefficient between sea salt and CCN concentrations was slightly increased ($r=0.69$; $p<0.05$) when WSOC was added to the sea salt as shown in Figure 6c. Likely, the slope of the regression line between WSOC+sea salt and CCN concentrations was little higher (2.21E7) than the slope between sea salt and CCN concentrations (2.19E7). These results indicate that WSOC may slightly enhance the cloud forming potential of sea salt, although it has less concentration over the western North Pacific. All these results suggest that significant uncertainty exists in RF due to the contribution of water-soluble organic matter to cloud forming. Therefore, climate modelers should consider WSOC in addition to other factors (sea-salts, sulfate, etc.,), while calculating RF over the western North Pacific. This point is consistent with the previous studies, which explain the contribution of water-soluble organic matter to CCN (Matsumoto et al., 1997; Zhao et al., 2016).

It should be noted that all these ratios are applicable to organic fractions that are derived from the bulk measurements only; however, the size of the particle also plays a role on RF as well as their morphology, chemical composition and mixing state (Jacobson, 2001; Lohmann and Feichter, 2005; Zhang et al., 2008a). It also should be clear that sea salt is not a major source of WSOC in this study as inferred from Figure 6d, which showed a moderate correlation ($r=0.42$; $p>0.05$) between WSOC and sea salt concentrations during the study period. In this study, atmospheric processes or chemical aging makes OC more water-soluble during long-range transport over the western North Pacific as discussed in section 3.2.

4. Conclusions

Based on the long-term (2001-2012) trends of carbonaceous aerosols from Chichijima Island in the western North Pacific, we conclude that the seasonal variations of carbonaceous aerosols strictly followed seasonal trends of wind pattern at Chichijima in the western North Pacific. The annual trends of OC and WSOC with significant increases over the western North Pacific are probably due to the enhanced photochemical oxidation of biomass burning- and biogenic-derived VOCs during long-range atmospheric transport over the western North Pacific. This inference is supported by significant increases in the annual trends of OC/EC, WSOC/OC, OC/TC, WSOC/TC, nss-K^+/EC mass ratios and MSA^- concentrations. On the other hand, a decrease in the concentrations of EC during 2001-2012 suggests that the contribution of fossil fuel-derived sources to carbonaceous aerosols may be decreased over the western North Pacific. Further, a good correlation (r=0.69) between WSOC and CCN concentrations suggests that not only sea salt and nss-SO_4^{2-} but also water-soluble organic aerosols play a role in CCN formation. Therefore, the results from our study have important implications toward the regional radiative balance, especially over the North Pacific.

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Table 1. Monthly mean (± standard deviation) values of EC, OC, WSOC concentrations and their ratios during 2001-2012 over the western North Pacific.

Month	EC ($\mu g\ m^{-3}$)	OC ($\mu g\ m^{-3}$)	WSOC ($\mu g\ m^{-3}$)	OC/EC	WSOC/OC	nss-K^+/EC
January	0.18±0.07	0.80±0.41	0.54±0.28	4.85±2.01	0.69±0.14	0.29±0.16
February	0.25±0.07	0.95±0.36	0.55±0.17	3.95±1.31	0.63±0.22	0.35±0.39
March	0.28±0.05	1.13±0.37	0.59±0.22	4.11±1.19	0.56±0.19	0.22±0.09
April	0.22±0.10	0.77±0.32	0.48±0.28	3.89±1.37	0.62±0.20	0.26±0.12
May	0.14±0.08	0.80±0.31	0.35±0.19	7.68±4.11	0.44±0.19	0.40±0.27
June	0.08±0.07	0.74±0.35	0.30±0.18	21.1±30.4	0.44±0.17	0.54±0.36
July	0.06±0.06	0.58±0.35	0.22±0.07	19.0±16.7	0.44±0.17	0.97±0.94
August	0.04±0.03	0.63±0.27	0.27±0.16	33.2±52.5	0.46±0.23	0.70±0.69
September	0.05±0.04	0.60±0.26	0.20±0.10	22.3±17.3	0.38±0.19	1.02±0.82
October	0.08±0.04	0.62±0.18	0.27±0.12	12.2±9.07	0.45±0.19	0.50±0.43
November	0.15±0.10	0.75±0.39	0.42±0.20	6.68±4.89	0.61±0.20	0.44±0.26
December	0.18±0.09	0.73±0.29	0.39±0.08	4.63±1.65	0.59±0.18	0.21±0.12

Table 2. Literature values of OC/EC ratios for various sources of aerosol.

Source of aerosol	OC/EC ratio	References
Fossil fuel combustion	4.0, 4.1, *1.1*	Koch (2001), Cao et al. (2005), *Watson et al. (2001)*
Coal combustion	*2.7*, 12.0	*Watson et al. (2001)*, Cao et al. (2005)
Biomass burning	9.0, 60.3, *5-8*	Cachier et al. (1989), Cao et al. (2005), *Andreae and Merlet (2001)*
Forest fire	~16.0	Watson et al. (2001)
Diesel truck plume	0.06, *0.8*,0.3	Dallmann et al. (2014), *Na et al. (2004)*, Turpin and Huntzicker (1995)
Gasoline vehicle	0.02, *2.2*	Dallmann et al. (2014), *Na et al. (2004)*
Secondary organic carbon	3.3	Saarikoski et al. (2008)
Long-rage transported/aged	12.0	Saarikoski et al. (2008)
Traffic	0.7	Saarikoski et al. (2008)
Cooking emissions	4.3-7.7	See and Balasubramanian (2008)

Table 3. Statistical report on the annual trends in carbonaceous aerosols and their ratios during 2001-2012 at Chichijima Island in the western North Pacific. '*' indicates that the trends are significant at $p<0.05$ level.

Species	Concentrations (μg m^{-3})				Mann-Kendall non-parametric test		
	Min	Max	Mean	SD	Kendall's tau (τ)	*p*-value	Sen's slope
EC	0.00	0.36	0.14	0.10	-0.06	>0.05	-0.0002
OC	0.26	1.70	0.76	0.36	0.07	>0.05	0.0008
TC	0.28	2.01	0.90	0.43	0.05	>0.05	0.0007
WSOC	0.08	1.30	0.38	0.22	0.09*	<0.05	0.0006
OC/EC	1.91	67	9.74	21.9	0.21*	<0.05	0.0240
WSOC/OC	0.06	0.94	0.53	0.21	0.09*	<0.05	0.0007
OC/TC	0.66	1.00	0.85	0.08	0.21*	<0.05	0.0007
EC/TC	0.00	0.34	0.15	0.08	-0.21	>0.05	-0.0007
WSOC/TC	0.06	0.86	0.44	0.17	0.14*	<0.05	0.0009
MSA^-	0.00	0.05	0.02	0.01	0.08*	<0.05	0.00002
nss-K^+/EC	0.02	2.97	0.51	0.40	0.09*	<0.05	0.0009

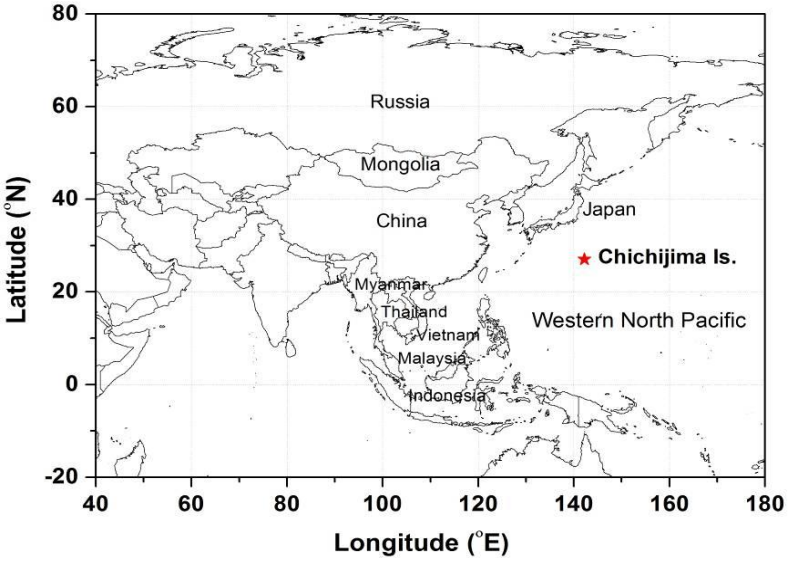

Figure 1. Location of sampling site (indicated by red colored '*') in the western North Pacific and its adjacent Asian countries.

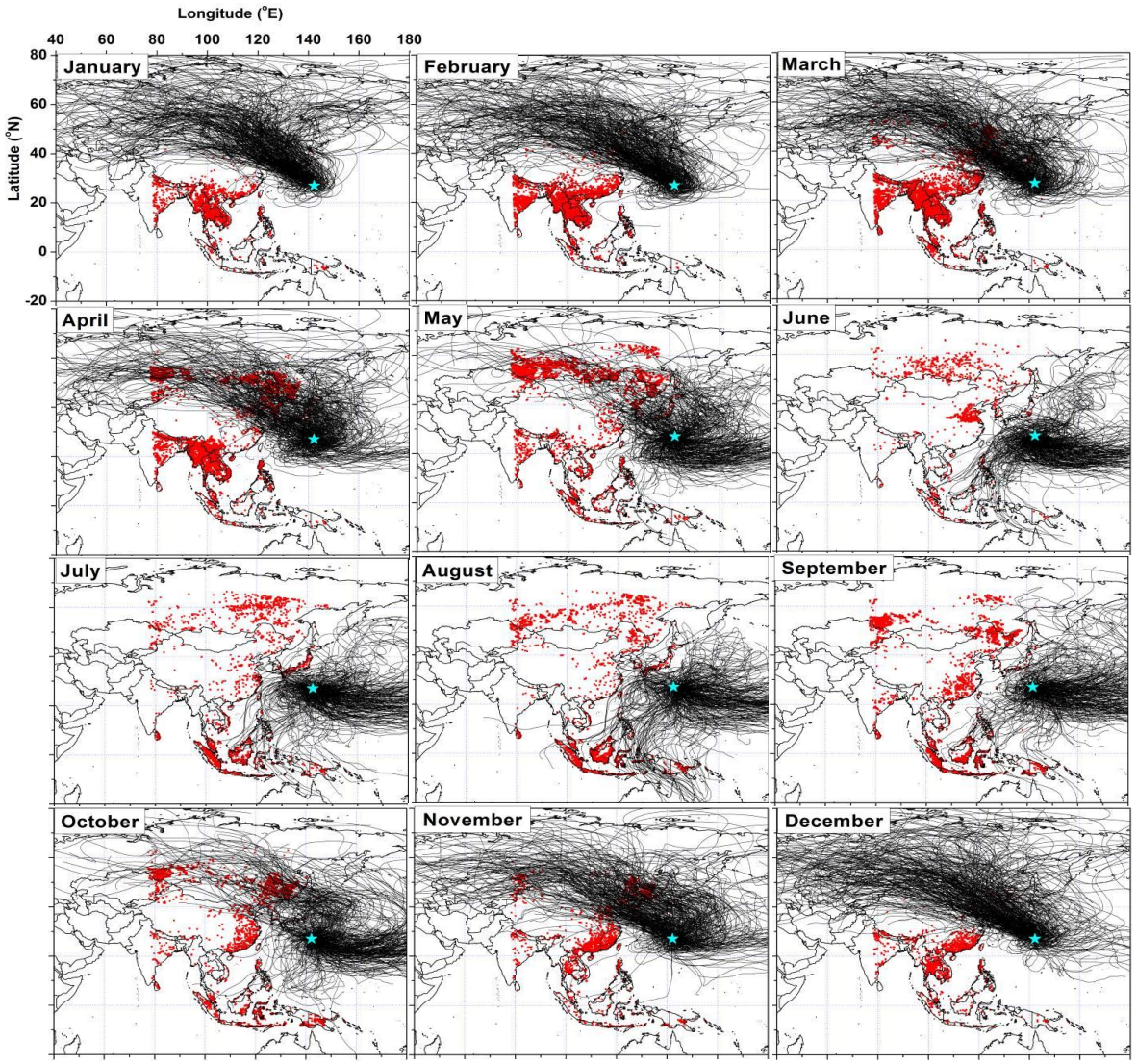

Figure 2. 7-day daily air mass back trajectories at 500 m a.g.l. computed using HYPLIT model for each month during 2001-2012 at Chichijima Island in the western North Pacific. The symbol '*' indicates the sampling site and red dots represent the MODIS inferred fire spots. Fire spots were downloaded for region (80°-150°E; -10-70°N) during the year 2001.

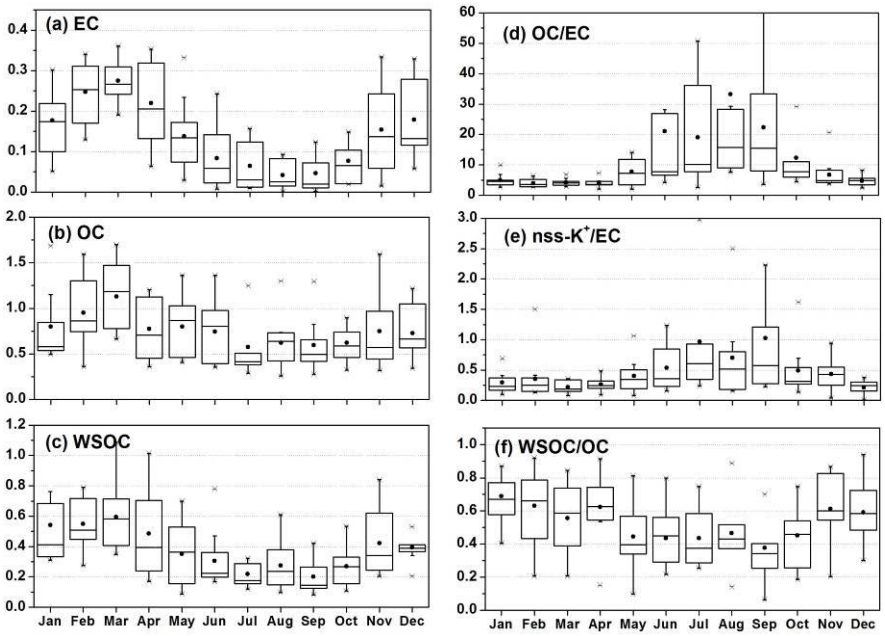

Figure 3. Box-whisker plots of monthly variations of carbonaceous aerosol components (μg m^{-3}) and some specific mass ratios at Chichijima Island in the western North Pacific during 2001-2012. The horizontal line and small dot inside the box indicate maiden and mean, respectively. The vertical hinges represent data points from the lower to the upper quartile (i.e., 25th and 75th percentiles). The whiskers represent data points from the 1st to 99th percentiles.

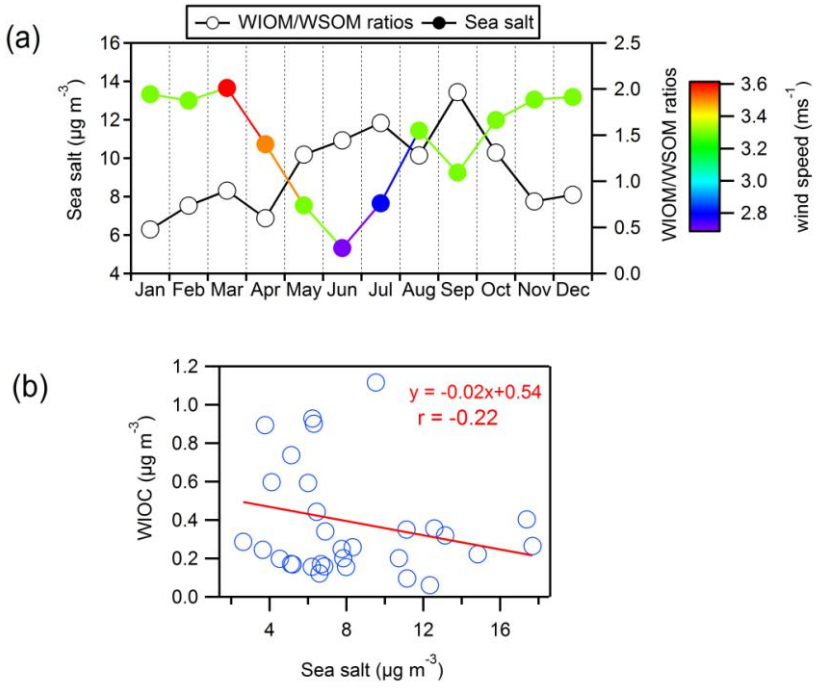

Figure 4. Monthly variations (a) WSIM/WSOM mass ratios and sea salt concentrations and (b) regression analysis between WIOC and sea salt concentrations. The color scale in the Figure 4(a) indicates the wind speed over the western North Pacific.

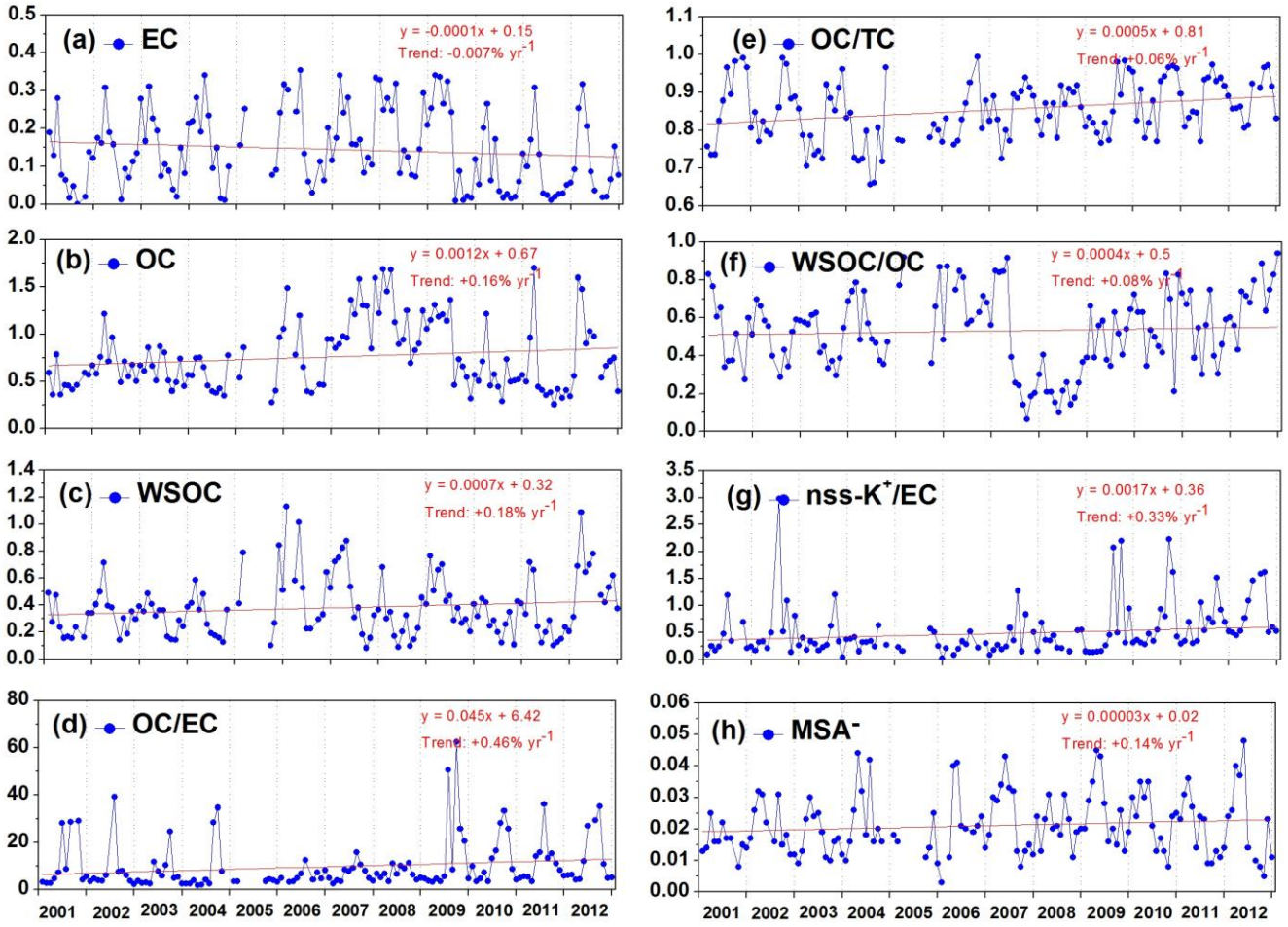

Figure 5. Annual trends (time series) in the concentrations (μg m^{-3}) of carbonaceous aerosol components, water-soluble ionic tracer compound (MSA^-) and some specific mass ratios during 2001-2012 over the western North Pacific. The liner trend equation (y=mx+c) is also shown for the each annual trend.

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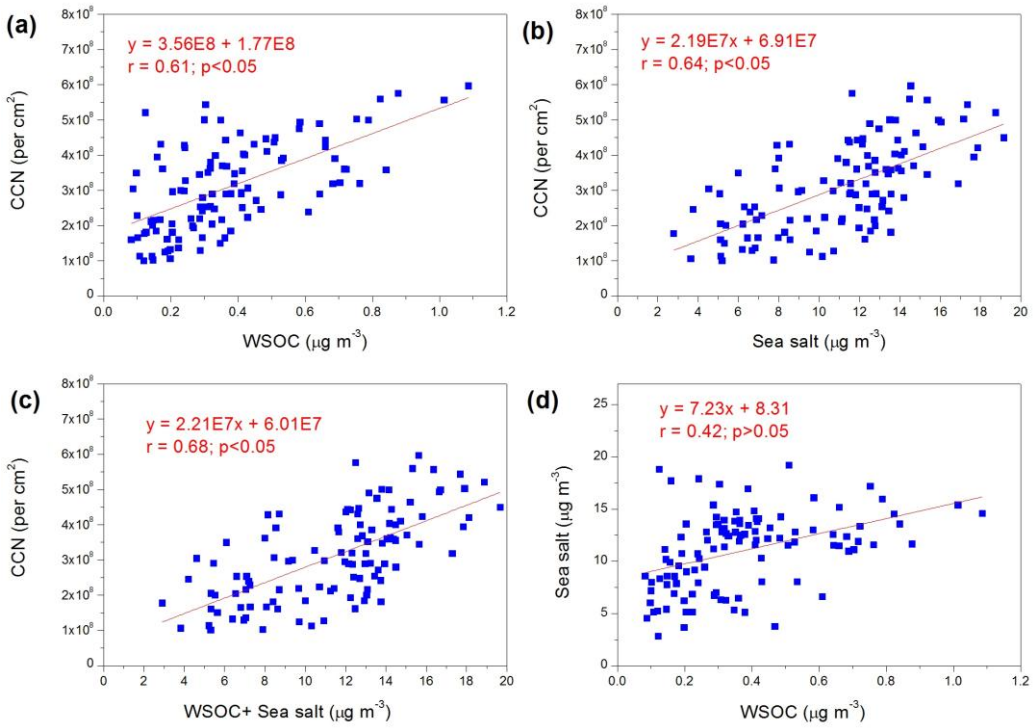

Figure 6. Regression analyses between (a) WSOC and MODIS-derived cloud condensation nuclei (CCN), (b) sea salt and CCN, (c) WSOC+seasalt and CCN, and (d) WSOC and sea salt concentrations over the western North Pacific.

Supporting information for

Long-term (2001-2012) trends of carbonaceous aerosols from remote island in the western North Pacific: an outflow region of Asian pollutants and aging

Suresh K. R. Boreddy[1], Mozammel Haque[1,2], and Kimitaka Kawamura[1,2*]

[1]Institute of Low Temperature Science, Hokkaido University, Sapporo 060-0819, Japan
[2]Now at Chubu Institute of Advanced Studies, Chubu University, Kasugai 487-8501, Japan

1. Statistical analyses

1.1. The linear trend equation

The linear trend equation was used to calculate the trend equation of all chemical species and their ratios using linear regression analysis, as

$$y = ax+b \qquad (1)$$

where *y* is the concentrations in μg m^{-3}, *a* is the slope, *x* is the time in years, and *b* is concentrations at the beginning of the period (intercept).

This approach gives results which are simple to interpret; both analytically and graphically on the basis of the shape and parameters of the trend equation For example, the sign of the concentration trend depends on the value of the slope. In this kind of interpretation when the slope is greater than zero, less than zero, or equal to zero, the sign of the trend is positive (increase), negative (decrease), or there is no trend (no change), respectively.

1.2. The Mann-Kendall test

This statistical approach is simple, robust and widely used non-parametric tests to detect the significant trends in time series. According to this approach, two hypotheses were tested: the null hypothesis, H_0, that there is no trend in the time series; and the alternative hypothesis, H_a, that there is a significant trend in the series, for a given α significance level. Probability (*p* value) was calculated to determine the level of confidence in the hypothesis. If the *p* value is lower than the chosen significance level α (α=5% or 0.05), the H_0 should be rejected, and H_a should be accepted (means there is a trend). In case, the *p* value is greater than the significance level α, the H_0 cannot be rejected (there is no trend). In this study, we used XLSTAT software (http://www.xlstat.com/en/) for Mann-Kendall test analysis. The absolute value of Kendall *tou* (*τ*) is compared to the standard normal cumulative distribution to define if there is a trend or not at the chosen α (0.05) of significance. A positive and negative value of *τ* indicates an increase and decrease in the trends, respectively.

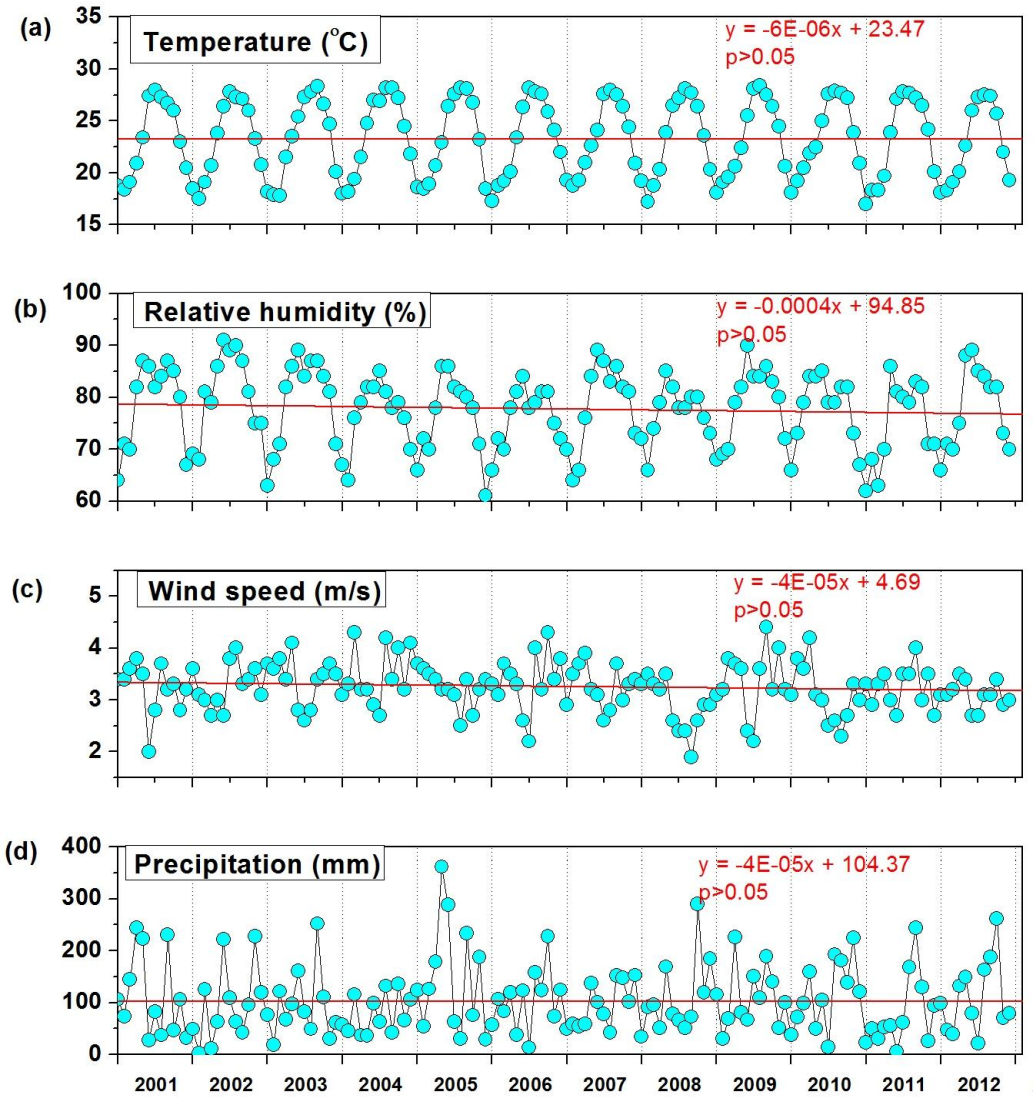

Figure S1. Temporal variations of meteorological parameters such as (a) air temperature (°C), (b) relative humidity (%), (c) wind speed (ms^{-1}), and (d) precipitation (mm) at Chichijima Island during the study period from 2001 to 2012.

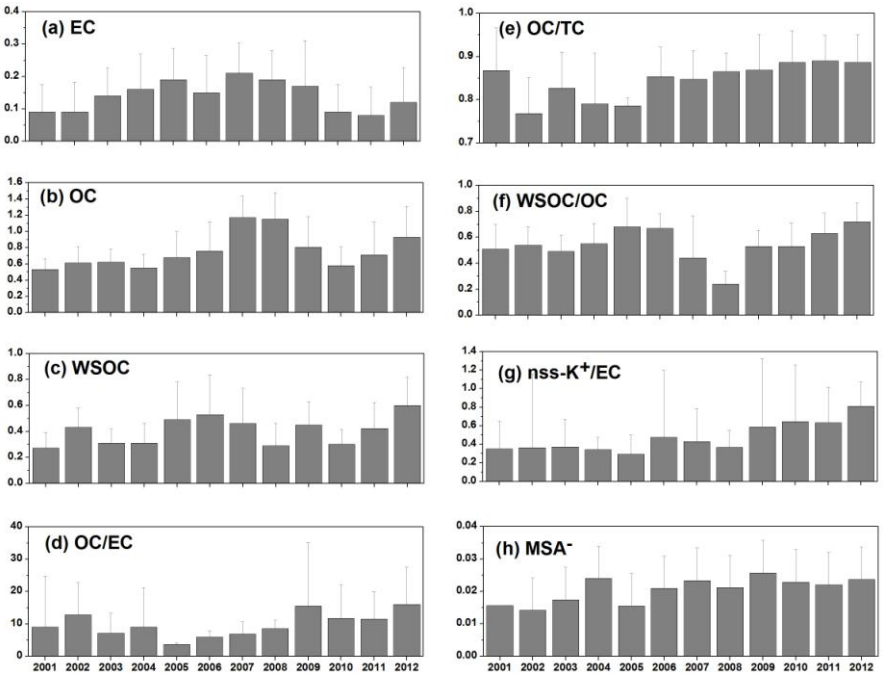

Figure S2. Annual mean variations (μg m^{-3}) of carbonaceous species, water-soluble ionic tracer compound (MSA^-) and some specific mass ratios during 2001-2012 over the western North Pacific.

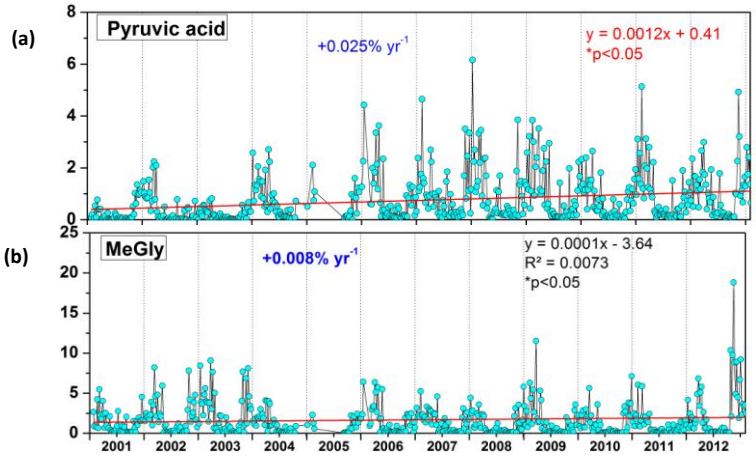

Figure S3. Annual trends in the concentrations (ng m^{-3}) of aqueous-phase photooxidations of biogenic isoprene tracer compounds (a) puruvic acid and (b) methylglyoxal during 2001-2012 over the western North Pacific (Boreddy et al., 2017).