

Response to anonymous Referee #1 comments

The manuscript titled “Long-term (2001-2012) trends of carbonaceous aerosols from remote island in the western North Pacific: an outflow region of Asian pollutants and dust”, is a well written paper. The methodology is sound and data analysis is convincing. The theme of the manuscript is well in accordance with the scope of the journal. The logic was explicit, and the content was comprehensive and integrated. However, some corrections are still needed before it can be published. Some grammatical errors as well as the wrong use of articles (a/an/the) are found and must be checked before resubmission.

Response: We thank the reviewer for careful reading and helpful comments on the manuscript. We revised the manuscript according to the reviewer’s comments. Our responses are indicated by the blue color. The changes in the revised manuscript are highlighted with yellow color. Please find the point-by-point responses.

Specific comments:

Line 24–25: It would be better to write the abbreviations just after to the name e.g. elemental carbon (EC)...

Response: Abbreviated as suggested. Please see lines 23-24 in the revised manuscript (MS).

Line 30: continental polluted air masses

Response: Modified as suggested. Please see line 29 in the revised MS.

Line 33: formation of secondary organic aerosols (SOAs)

Response: Modified as suggested. Please see line 33 in the revised MS.

Line 35: We found significant increase....

Response: Modified. Please see line 35 in the revised MS.

Line 36: biomass-burning-derived

Response: Modified as suggested. Please see line 36 in the revised MS.

Line 37: anthropogenic sources or anthropogenic aerosols?

Response: Modified as fossil fuel-derived aerosols in the revised MS. Please see line 37.

Line 38-39: The correlation between OC and MSA- can be shown here to strengthen the sentence.

Response: Based on the reviewer’s suggestion, we added the following sentence in the revised MS.

“This point is further supported by a moderate correlation ($r=0.40$) between WSOC and MSA⁻ concentrations.”

Please see lines 40-41 in the revised MS.

Line 40: significant increase in OC/TC and WSOC/TC ratios,

Response: Modified as suggested. Please see line 41 in the revised MS.

Line 40-42: Please rephrase the sentence.

Response: Rephrased in the revised MS as “We also found significant increase in OC/TC (total carbon) and WSOC/TC ratios, suggesting that the contribution of SOA to carbonaceous aerosols has significantly increased over the western North Pacific via long-range atmospheric transport from East Asian.” Please see lines 41-44 in the revised MS.

Line 42: long-range atmospheric transport? from?

Response: Please see above response.

Line 52: There should be a space after “;” in citation bracket throughout the ms e.g. (Zhang and Cao, 2015; Cui et al., 2015).

Response: Corrected as suggested in the revised manuscript.

Line 58: “cooling effect” It’s not necessarily always. It would be better to bring the term “brown carbon” also here and simply describe it.

Response: We rephrased this sentence in the revised manuscript as “However, the role of OC on cooling or warming has been a matter of debate (Chung et al., 2012; Cazorla et al., 2013) because some class of OC (so called brown carbon) may absorb sunlight (Feng et al., 2013; Lu et al., 2015; Laskin et al., 2015; Bahadur et al., 2012).” Please see lines 62-65 in the revised MS.

Line 60-61: This sentence is a complex one. It can be made simple by describing the above comment.

Response: Please see above response.

Line 62: estimation of net radiative forcing

Response: Modified as suggested. Please see line 66 in the revised MS.

Line 65: It would be better to write “radiative balance” in place of “climate”.

Response: Written as suggested. Please see line 68 in the revised MS.

Line 79: However, there is still large uncertainties exist in quantification of radiative impacts for carbonaceous aerosols....

Response: Modified as suggested. Please see lines 83-84 in the revised MS.

Line 88: Expand MEGAN and MOHYCAN

Response: Expanded. Please see lines 92-93 in the revised MS.

Line 109: Expand WSOC. It’s the first use of this term here.

Response: Expanded. Please see line 116 in the revised MS.

Line 175: Here the zero in ‘H0’ can be made subscript ‘H₀’.

Response: Corrected. We modified this section and moved some phrases to the supporting information (SI). Please see text S1 in the SI.

Line 189: Why 850 hPa pressure level has been used? Please brief the specific reason, if any? Why not 1000 hPa, as the study includes surface concentrations? 850 hPa level is roughly at 1.5 km, may be higher than the marine boundary layer over western Pacific irrespective of seasons. Have you also studied the seasonal variations in boundary layer height? Line 195-197: Some BT analysis can be added here from literatures

Response: Following the reviewer's comment, we modified this section and Figure 2 by replacing the NCEP wind circulation pattern with air mass backward trajectory analysis and corresponding Figure 2. Please see lines 174-186 and Figure 2 in the revises MS.

Line 204: The study period is 2001-2012, why authors have used the met data 2001-2013 in figure S1? Also the figure S1 is showing the year 2014. Please make it clear to easy go for readers.

Response: We modified Figure S1 in the revised manuscript and made consistent in sampling period (i.e., 2001-2012). Please see line 189 in the revised MS and also see Figure S1 in the revised SI.

Line 214: All measured species (Fig 3a–c).... and then again an increasing peak in autumn. It is suggested to discuss monthly variations instead of combine winter-spring season.

Response: Following the reviewer's comment, we modified the phrase in the revised MS as "All measured species clearly showed winter-to-spring maxima (highest concentration was in March) and summer minima (lowest in July) and then increase towards autumn." Please see lines 199-200.

Line 215: The seasonal pattern is found consistent with the typical....

Response: Written as suggested. Please see lines 200-201 in the revised MS.

Line 219: discussed in section 3.1.

Response: Modified as suggested. Please see line 205 in the revised MS.

Line 220: The highest concentration was clearly seen in March. It is suggested to discuss monthly variations wrt the figure 3 instead of combine winter-spring season.

Response: Modified as "Relatively high monthly average concentrations up to 0.28, 1.13 and 0.59 $\mu\text{g m}^{-3}$ were observed for EC, OC, and WSOC in March. In contrast, their monthly averages are lower in summer or early autumn months (July or September) with the concentrations of 0.04, 0.58, and 0.20 $\mu\text{g m}^{-3}$, respectively (Table 1)." Please see lines 206-209 in the revised MS.

Line 225: (Figure 2c)

Response: Written as Figure 2 in the revised MS. Please see line 211.

Line 232: were up to seven....

Response: Modified as suggested. Please see line 218 in the revised MS.

Line 233-234: suggested negligible contribution of local anthropogenic emissions as well as long-range influences over....

Response: Modified as suggested. Please see lines 219-220 in the revised MS.

Line 235: was found maximum in summer and minimum..

Response: Modified as suggested. Please see lines 239-240 in the revised MS.

Line 236: suggesting negligible.....No need of insert "a" in between.

Response: Based on the second reviewer's comment, we rephrased this line in the revised manuscript. Please see lines 217-220

Line 244: delete "over the sampling sites"

Response: Deleted as suggested.

Line 248: "observed in midsummer to early autumn"also write the name of months may in bracket for easy understanding.

Response: Written as suggested. Please see line 251 in the revised MS

Line 248-250: "suggesting an influence of biomass burning emissions from southeast Asian countries via long-range" How it suggests? Is it only an assumption? Otherwise provide some suitable references.

Response: This is not assumption. The provided picture (figure 2 in the revised MS), air mass backward trajectory analysis, clearly shows the influence of biomass burning influence from Southeast Asian countries. Considering the reviewer's comment, we added air mass backward trajectory analysis along with modis-derived fire spots and shown as Figure 2 in the revised MS. We also added the following phrases in the revised MS.

"This point is consistent with the air mass back trajectory analysis and MODIS-fire count data during summer months (Figure 2), which clearly show that air masses are occasionally coming from Southeast Asia including 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)." Please see lines 253-258 and Figure 2 in the revised MS.

Line 251-253: No. Figure 2c is not clearly showing dominant flow from SEA. Please maximize the axis scale in Figure 2. Moreover, enhanced BB over SEA is evident in February–April not common in June-August (summer) and Sept–Nov (autumn) as mentioned in this study. It may be only occasional. It is suggested to rephrase the sentences. In addition to the continental Asian outflow, western Pacific Ocean also receives biomass burning emissions from Southeast Asia particularly in spring (late February to mid-April) through westerlies. Ex: Tsay et al. (2016) Satellite-Surface Perspectives of Air Quality and Aerosol-Cloud Effects on the Environment: An Overview of 7-SEAS/BASELInE. Aerosol and Air Quality Research 16, 2581-2602. Lin et al. (2013). 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. *Atmos. Environ.* 78, 1–19.

Huang et al. (2013), *Impact assessment of biomass burning on air quality in Southeast and East Asia during BASE-ASIA*, *Atmospheric Environment*, 78, 291 – 302.

Response: Please see the above response. Further, we discussed above studies briefly in introduction section. Please see lines 102-104 in the revised MS.

Line 259: *an unique*

Response: Modified as suggested. Please see line 269 in the revised MS.

Line 283: *showed clear.....*

Response: Modified as suggested. Please see lines 306 in the revised MS.

Line 287: *EC showed a decreasing order,....continuously increasing.....*

Response: Modified as suggested. Please see lines 310-311 in the revised MS.

Line 336: *not necessarily OC always scatters the radiation. OC form BB mostly absorbs. Rephrase the sentence.*

Response: Rephrased as suggested as “OC (except for brown carbon) and SO_4^{2-} particles majorly scatter the solar radiation whereas EC particles strongly absorb the radiation in the atmosphere.” Please see lines 377-379 in the revised MS.

Line 338: *“extension” changes to “extinction”. It is suggested to use this reference.*

Pani et al. (2016). *Radiative effect of springtime biomass-burning aerosols over Northern Indochina during 7-SEAS/BASELInE 2013 campaign*. *Aerosol Air Qual. Res.* 16: 2802–2817.

Response: Corrected and added a reference as suggested. Please see line 380 in the revised MS.

Line: 341: *“OC/EC ratios can be used to understand the relative contributions of scattering or absorbing aerosols in the atmosphere (Ram and Sarin, 2015).” It can be but with much uncertainties and limitations. This is may not be true and enough for a marine boundary layer location where long-range transport of distinct air masses is the possible reason of carbons. OCs in this study may be more scatters only due to aging process.*

Response: We rephrased this sentence in the revised MS as “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 (Ram and Sarin, 2015).”

“In this study, atmospheric aging may be making OC more scatter during long-range transport over the western North Pacific.”

Please see lines 383-385 and 389-390 in the revised MS.

Line 351: *nss-sulfate (nss-SO₄²⁻) is a major contributor to the CCN,.....use reference..*

Response: Added a reference as suggested. Please see line 409 in the revised MS.

Line 352: also plays an.....

Response: Modified as suggested. Please see lines 410 in the revised MS.

Line 371: use “regional radiative balance” instead of “Earth’s radiative forcing”.

Response: Modified as suggested. Please see line 432 in the revised MS.

Responses to anonymous Referee #2 comments

This paper looks at measurements of organic carbon (OC), elemental carbon (EC), and water soluble OC (WSOC) from 2001-2013 collected on a remote island off the coast of Japan. While the timescale of the measurements is impressive, the paper lacks any suitable interpretation beyond the idea that polluted air masses come from Asia in the winter. The main conclusion is that seasonal variations in organic aerosol are based on the seasonal wind patterns. There is some discussion of ratios of the three main measurements, but their interpretations are not well explained. Some conclusions are not supported by the results of analysis. This paper could be interesting to the community, but it needs major revisions before publication.

Response: We thank the reviewer for careful reading and helpful comments on the manuscript. We revised the manuscript according to the reviewer's comments. Our responses are indicated by the blue color. The changes in the revised manuscript are highlighted with yellow color. Please find the point-by-point responses.

Major Comments.

The use of OC and EC and OC/EC to attribute air masses and emissions to local sources needs more explanation. For example, Lines 232-234 are not explained well. It is saying that because the EC concentrations are low, there is a negligible contribution of local emissions at the sampling site? Couldn't the concentrations of local emissions just be smaller than the concentrations from other sources? Low concentrations alone do not rule out contributions. Similarly in the following sentences, there needs to be more explanation on why a higher ratio of OC/EC in the summer indicates less local anthropogenic sources. Again, this could just mean that local sources have high OC/EC ratios. Other things like correlations with tracers and changes in time or correlations with wind direction, wind speed, or air mass back trajectories could be useful. Could the concentration of OC be controlling the trend in the ratio of OC/EC, since there is little variation in the total concentration of EC throughout the year (0.3 g/m³ for EC and more than 1 µg/m³ change for OC)? It would be useful to have a table with literature values of OC/EC for fossil fuel combustion, biomass burning, aged biomass burning, etc. for comparison to the results shown here. The authors could also show a map of forest fires or discuss anthropogenic fossil fuel burning sources in specific regions where the air masses originate.

Response: Following the reviewer's suggestion, we briefly added discussion about the OC/EC ratios and backward trajectory analysis along with modis-derived fire spots data. The following points are briefly added in the revised MS.

“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 is primary particle and predominantly comes 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 combustions. 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 (Cao et al., 2003; Chow et al., 1996; Kunwar and Kawamura, 2014). Table 2 summarizes OC/EC ratios reported for various sources of aerosol particles. Monthly mean OC/EC ratios in this study are greater than 2.0 for all months, suggesting the dominance of SOA in carbonaceous aerosol over the western North Pacific. The seasonal variation of OC/EC mass ratios was found maximum in summer (~21 to 33) and minimum 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 suggest that both biomass burning and fossil fuel combustion are important sources for carbonaceous aerosols over the western North Pacific.”

Please see lines 217-244 as well as Table 2 and Figure 2 in the revised MS.

More explanation is needed for the tracers and their sources. For example, why is WSOC a tracer for SOA? It is stated that as the organics are oxidized, they become more water soluble, but that does not necessarily make WSOC directly linked to SOA. There is plenty of primary OA that is water soluble. This argument needs to be more clearly laid out with references and explanations for other possibilities. The aging of organic aerosols and SOA are two different things, which are both represented by WSOC in this paper. Additionally, the attribution of low WSOC to OC ratios to primary marine OC is not justified (Lines 273 – 277). This is only one sentence with no discussion of emissions correlated to wind speed or OC correlated with any sea salt tracers. This should be removed or discussed in more detail.

Response: Following the reviewer’s suggestion, we explained more about the WSOC and WSOC/OC ratios in the revised MS as follows.

“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 a 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; Boreddy et al., 2017). 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, monthly mean WSOC/OC ratios are >0.4 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 is 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 hydrogen peroxide 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 ($\sim 24^{\circ}\text{C}$) 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 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 because the low speed easterly winds originated from the central Pacific are dominant in summer over the western North Pacific (Figure 2). Miyazaki et al. (2010) reported the presence of significant water-insoluble organic matter 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 in sea-spray aerosols (Facchini et al., 2008; Keene et al., 2007).”

Please see lines 264-299 in the revised MS.

The discussion of the time series in Figure 4 is confusing. It is unclear why an increase in OC/EC and OC/TC (which are not shown) suggest an “enhanced formation of SOA” over the measurement time. An increase in OC/EC may suggest different sources, but not all OC is SOA. This needs a clearer explanation. Additionally, it may be clearer if the data was binned by year and/or just the first and last years were shown. With all of the variability in the time series, even the trends that are statistically significant do not appear to be actual trends.

Response: To better understand the discussion of the trends, we revised whole section 3.3 and Figure 4 in the revised MS. We quantified all the trends in this study and reported in the text where it is necessary and Figure 4. Following the reviewer’s comment, the annual mean variations of all chemical species and their ratios are shown as a Figure S2 in the supporting information.

Please see the text in section 3.3 as well as Figure 4 and Figure S2 in the revised MS.

OC is not purely “scattering” or “cooling” as suggested here. Brown carbon is OC that

can absorb solar radiation. More explanation is needed on how the ratio of OC/EC can be used to understand the relative contributions of scattering and absorbing of aerosols. Additionally, at line 341, there is no mention of radiative forcing by other types of aerosols. The ratio of OC/EC only applies to the organic fractions. And, the size of the particles plays a role as well as their morphology and composition. This needs to be included in the discussion.

Response: In light of the reviewer's comment, we briefly discussed following points in the revised MS.

“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, thus, radiative forcing (RF) (IPCC, 2013). The RF of aerosol is estimated based on the aerosol optical depth (AOD), absorption and scattering coefficients and asymmetry parameters. OC (except for brown carbon) and SO_4^{2-} particles majorly scatter the solar radiation whereas EC particles strongly absorb the radiation in the atmosphere. The single scattering albedo (SSA), defined as the ratio of scattering to the extinction coefficient of aerosols (Pani et al., 2016), is an important property for determining the direct RF (Gopal et al., 2017; He et al., 2009). 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 (Ram and Sarin, 2015). Further, 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.”

“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., 2008).”

Please see lines 374-392 and 413-416 in the revised MS.

Along these lines, the “Atmospheric implications” section is far reaching for the data shown and needs to be revised to reflect the actual measurements and analyses. The correlation between WSOC and CCN is very short and not fully explained. There needs to be much more discussion, if that is included. Figure 5 just shows a correlation between total particles activated (CCN) and the organic concentration. There is no description of initial particle sizes or compositions. It is possible that WSOC also correlates with NaCl in the particles, which are driving the CCN activity. No direct link can be shown with this correlation alone.

Response: Following the reviewer's comment, we revised this section 3.4 as follows.

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

(SO₄²⁻) and other inorganic compounds. Roberts et al. (2002) showed that biomass burning derived organic aerosol 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 SO₄²⁻ and sea-salts. To better understand the impact of WSOC on cloud forming potential, we performed regression analysis between WSOC and CCN concentrations as shown in Figure 5. 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 2002-2012. The results show a significantly good correlation ($r=0.69$, $p<0.001$) between WSOC and CCN concentrations. This result suggests that, although nss-sulfate is a major contributor to CCN activity (Mochida et al., 2011); water-soluble organic matter also plays an important role in CCN formation over the western North Pacific. This point is consistent with 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., 2008).”

Please lines 396-416 in the revised MS.

Specific Comments.

Lines 56-49: References are necessary for this statement. While it is true that OC may warm less than EC, it does not necessarily provide a “cooling effect” as written here. This is still a major topic of study and should be written to reflect that, along with the necessary references.

Response: Following the reviewer’s comment, we rephrased this sentence along with necessary references in the revised MS. Please see lines 62-65 in the revised MS.

Line 68: Check this reference.

Response: Checked as suggested. Please see line 72 in the revised MS.

Line 71: The particles are what act as CCN. Change “act” to “aid in particles acting”

Response: Changed as suggested. Please see line 76 in the revised MS.

Line 85: Contribution to what?

Response: Global contributions. We mentioned already in the manuscript as “on a global scale..” Please see lines 87-88 in the revised MS.

Line 92: Some general statements are made about increasing trends over time periods throughout the paper. These need to be rewritten or better explained. For example, at Line 92, it states “an increasing trend of biogenic emissions in northern China during 1982-2010.” It is unclear from this statement if the emissions were simply higher in 2010 than 1982 or if emissions increased every year during that period.

Response: Following the reviewer's comment, we quantified (increasing rate per year) all the trends in this study and reported in the text. Please see lines 96, 313-322, 325 etc., as an example.

Line 98: Is marine aerosol the main focus of this paper? It needs to be defined here. Just sampling at a remote island does not necessarily mean that the sampled air masses are marine in origin and can include polluted air masses, as the authors discuss.

Response: We rephrased this sentence in the revised MS as "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."

Please see lines 105-107 in the revised MS.

Figure 1: Why does this figure show the concentration of chlorophyll? Why is the winter 2008 chlorophyll map shown? That is not representative of the summer season. Is it representative of all of the years included in the study? That seems unnecessary to include. Also, the color bar is too small.

Response: We modified Figure 1 according to the reviewer's comment. Please see Figure 1 in the revised MS.

Line 133: How good of an assumption is it to assume that the carbonate carbon is insignificant. The IMPROVE network may be observing different sources and particle types that those in this study. Provide a reference to show that carbonate carbon is expected to be low in this region or with these sources.

Response: Provided a reference as suggested. We also briefly added the following sentence in the revised MS.

"Previous studies have also shown that carbonate, particularly calcium carbonate, levels are low or negligible in most ambient samples, which are analyzed by IMPROVE protocol (Wang et al., 2005; Clarke and Karani, 1992; Chow et al., 2001)."

Please see lines 139-142 in the revised MS.

Line 154: The whole section on statistical analysis should be condensed or moved to the supplement. Also, at line 163, this equation is unnecessary to list here.

Response: We modified this section in the revised MS. Please see lines 164-170 and also text in SI.

Figure 2: The text says 2001 to 2013, and the caption says 2001 to 2012. And an average over 11 years is not that interesting without some sort of error bars or something to show the lack of change with time. If this is the general trend during these four times of year, that is fine, but it seems unnecessary to show in a figure then. Additionally, there is no label on the color bar. The main point of this figure is to show that in the winter the air masses measured at the sampling site are from East Asia while the weaker winds in the summer transport air masses from the central Pacific. These figures and the wind show the general patterns, but it would be more relevant for this study to show the actual

air mass backtrajectories for the samples. The wind pattern does not show origin or destination but rather a general pattern. Additionally, the arrows in many regions are too small to actually determine their direction, and there is no scale for their size.

Response: Following the reviewer's comment, we replaced Figure 2 by air mass backtrajectories for each month and shown as Figure 2 in the revised MS. Please see Figure 2 in the revised MS.

Line 205: This is not new. Change "we found" to "there is" to be consistent. Figure 3: What are the small open, grey boxes (means?) and the X grey markers (outliers?)? So the EC is pollution and the OC is not?

Response: Changed as suggested. Please see line 190 in the revised MS. We also explained all symbols in Figure 3. Please see Figure 3 caption in the revised MS.

Line 268: Needs a reference.

Response: Provided references as suggested. Please see line 284 in the revised MS.

Lines 283-284: Panels d and e show the opposite trend.

Response: We rephrased this sentence in the revised MS as "It is seen that all the annual trends of chemical species and WSOC/OC ratios showed clear seasonal patterns with higher values in winter-spring and lower values in summer. In contrast, the OC/EC and nss-K⁺/EC ratios showed higher values in summer." Please see lines 305-307.

Line 289: Why are OC/EC and OC/TC not shown in Figure 4, especially since their trends are significant?

Response: Following the reviewer's comment, we included the OC/EC and OC/TC mass ratios in Figure 4. Please see Figure 4 in the revised MS.

Lines 292-293: How do these results show that "the contribution of combustion-derived sources to enhanced SOA seems to be decreased significantly"? This sentence is unclear. Is it possible that the EC concentration did not change?

Response: To make clearer, we rephrased this sentence in the revised MS as "These results further suggest that the contribution of fossil fuel combustion to carbonaceous aerosols has decreased during the sampling period." Please see lines 316-318.

Lines 297-300: Biomass burning is combustion. This sentence should be clarified if combustion is supposed to be anthropogenic or fossil fuel burning only.

Response: In this study, combustion means fossil fuel burning. However, based on the reviewer's comment, we clearly mentioned fossil fuel and biomass burning emissions in the revised MS. Please see lines 316-318 and 323-325 in the revised MS.

Lines 301-303: This conclusion is unwarranted for the results shown.

Response: Based on the reviewer's comment, we rephrased this sentence in the revised MS as "The annual trend of WSOC showed a significant increase ($p < 0.05$; $+0.18\% \text{ yr}^{-1}$) from 2001 to 2012 (Figure 4c), 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).” Please see lines 326-329 in the revised MS.

Line 305: Need more references.

Response: Provided as suggested. Please see lines 330-331 in the revised MS.

Line 307: There is also a significant decrease in WSOC/OC that is not discussed here. What is that cause of that decrease?

Response: Following the reviewer’s comment, we briefly added following points in the revised MS.

“We observed an abrupt decrease in the WSOC/OC ratios between 2007 and 2008, probably due to the enhanced OC that may be caused by the primary emissions from ocean surface. However, it should be noted that observed increase in the WSOC/OC ratios does not change the decadal trend even if those data are deleted.”

Please see lines 336-340 in the revised MS.

Line 310: What is the evidence that this is photochemical oxidation? These conclusions are all overreaching the data that is presented.

Response: Based on the reviewer’s comment, we rephrased this sentence in the revised MS as “A significant increasing trend of WSOC/TC ($p < 0.05$; $+0.15\% \text{ yr}^{-1}$; 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.”

Please see lines 340-342 in the revised MS.

Line 317: MSA can also be used as a tracer for ocean biogenic emissions. Is this referring to continental or oceanic biogenic emissions? Also, the trend line shows a slight increase, but the figure is not that convincing.

Response: Yes, MSA^- can also come from the oceanic biogenic emissions, however, in this study, to refer the continental transport of biogenic emissions over the western North Pacific, we briefly added following points in the revised MS.

“In our previous study (Boreddy and Kawamura, 2015), we reported that MSA^- significant 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 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 summer period, although it has less abundance compared to continental biogenic emissions over the western North Pacific.”

Please see lines 345-352 in the revised MS.

In addition to MSA^- concentrations, we also showed some biogenic tracer compounds such as methylglyoxal and pyruvic acid during the same sampling period over western North Pacific. Please see Figure S3 in SI.

Line 323: This is a correlation between land temperature and isoprene emitted from

land. It is unclear how much of an influence this would have on the data presented.

This needs more explanation and some analysis if it is included.

Response: This is a temperature from the above canopy not land and also isoprene emitted from the higher plants not from the land. Please see line 360.

To make much clear, we rephrased the sentence in Line 323 as “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.” Please see lines 361-365 and 367 in the revised MS.

At this moment, we are unable to do further analysis, however, we showed some tracers of isoprene biogenic emissions, which showed significant increase during the same period over the western North Pacific. Please Figure S3 in SI.

Line 329: Where is this data? It could be included in the supplement, if it is useful.

Response: Provided as Figure S3 in the revised MS.

Line 330: An value of $r = 0.40$ is not a significant correlation.

Response: We rephrased this line in the revised MS as “moderate correlation” Please see line 368.

Line 336: OC can also absorb solar radiation (i.e. brown carbon).

Response: Based on the reviewer’s comment, we rephrased this sentence in the revised MS as “OC (except for brown carbon) and SO_4^{2-} particles majorly scatter the solar radiation whereas EC particles strongly absorb the radiation in the atmosphere.” Please see lines 377-379 in the revised MS.

Technical Comments. This paper should be read through and edited for grammar. Some examples of necessary edits are below. The authors should be consistent with terminology (i.e. organic vs. carbonaceous, etc.) and write out all acronyms the first time they are used (i.e. MEGAN, MOHYCAN, etc.)

Response: Following the reviewer’s comment, the whole manuscript is edited for grammar and maintained consistent in terminology used in this study. We also abbreviated all acronyms in this study.

Line 62: Remove “ever”

Response: Removed as suggested.

Line 80: Awkward phrasing – “because of knowledge gap on”

Response: Rephrased. Please see lines 83-85 in the revised MS.

Line 82: Change “worst” to “worse”

Response: Changed as suggested. Please see line 86 in the revised MS.

Line 91: Remove “that”

Response: Removed as suggested.

Line 104: Remove “from the” and “away”

Response: Removed as suggested.

Lines 156-157: This sentence is a fragment.

Response: Rephrased this sentence in the revised MS. Please see lines 165-170.

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

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4
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20 Abstract

21 The present study reports on long-term trends of carbonaceous aerosols in total
22 suspended particulate (TSP) samples collected at Chichijima Island in the western North
23 Pacific during 2001-2012. Seasonal variations of elemental carbon (EC), organic carbon
24 (OC), and water-soluble organic carbon (WSOC) concentrations showed maxima in winter to
25 spring and minima in summer. These seasonal differences in the concentrations of
26 carbonaceous aerosols are associated with the outflows of polluted air masses from East Asia,
27 which are clearly distinguishable from pristine air masses from the central Pacific. The higher
28 concentrations of carbonaceous aerosols during winter to spring are associated with long-
29 range atmospheric transport of East Asian continental polluted air masses, whereas lower
30 concentrations may be due to pristine air masses from the central Pacific in summer. The
31 annual trends of OC/EC (+0.46% yr⁻¹), WSOC (+0.18% yr⁻¹) and WSOC/OC (+0.08% yr⁻¹)
32 showed significant (p<0.05) increases during the period of 2001-2012, suggesting that an
33 enhanced formation of secondary organic aerosols (SOAs) via photochemical oxidation of
34 anthropogenic and biogenic volatile organic compounds (VOCs) during long-range
35 atmospheric transport. We found significant increase (+0.33% yr⁻¹) in nss-K⁺/EC ratios,
36 demonstrating that biomass-burning-derived carbonaceous aerosols are increased, while
37 fossil fuel-derived aerosols are decreased over the western North Pacific. Further, secondary
38 biogenic emissions are also important over the western North Pacific as inferred from a
39 significant increase (+0.14% yr⁻¹) in the concentrations of methanesulfonate (MSA⁻, a tracer
40 for biogenic source). This point is further supported by a moderate correlation (r=0.40)
41 between WSOC and MSA⁻. We also found significant increase in OC/TC (total carbon) and
42 WSOC/TC ratios, suggesting that the contribution of SOA to carbonaceous aerosols has
43 significantly increased over the western North Pacific via long-range atmospheric transport
44 from East Asia.

45

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

49

50

51 1. Introduction

52 Particulate air pollution is one of the most important environmental issues due to its
53 severe impact on visibility and air quality, and has been a great issue over East Asia,
54 particularly in China (Zhang and Cao, 2015; Cui et al., 2015). On the other hand, its invisible
55 impacts on not only climate but also public health may be more severe and intricate (Pöschl,
56 2005; Menon et al., 2002). Carbonaceous aerosols are ubiquitous in the Earth's atmosphere
57 and hence potentially cause harmful effect on human health (Bond et al., 2013; Kanakidou et
58 al., 2005; Ramanathan and Carmichael, 2008; Fatima et al., 2012; Chung and Seinfeld, 2002).
59 They are traditionally divided into two fractions: organic carbon (OC), which contains less
60 volatile and more reflective carbonaceous species, while elemental carbon (EC; alternatively
61 referred as black carbon, BC) encompasses the most refractory and most light absorbing
62 species (Pöschl, 2005). However, the role of OC on cooling or warming has been a matter of
63 debate (Chung et al., 2012; Cazorla et al., 2013) because some class of OC (so called brown
64 carbon) may absorb sunlight (Feng et al., 2013; Lu et al., 2015; Laskin et al., 2015; Bahadur
65 et al., 2012). In the ambient atmosphere, however, these two fractions (EC and OC) are
66 mixed and consequently complicate the estimation of net radiative forcing (Jacobson, 2001).
67 Therefore, studying about carbonaceous aerosols and their sources are essential to understand
68 how the different sources of carbonaceous particles may influence the radiative balance on a
69 regional and global scale.

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

84 **quantification of radiative impacts for carbonaceous aerosols**, particularly with regard to OA
85 (Reddy and Boucher, 2004).

86 The atmosphere over East Asia is becoming **worse** due to not only the dense
87 population, but also rapid urbanization/industrialization (Fu et al., 2012; Cao et al., 2007). **On**
88 **a global scale**, China has the largest carbonaceous aerosol emissions from combustion with
89 contributions about 24% and 30% for OC and BC, respectively (Bond et al., 2004). Recently,
90 Wang et al. (2016) suggested that coal combustions and vehicular emissions are the
91 dominated sources of carbonaceous aerosols in China (Kirillova et al., 2014). Using the
92 emission **Model of Emissions of Gases and Aerosols from Nature** (MEGAN) combined with
93 the **MOdel of HYdrocarbon Emissions from the CANopy** (MOHYCAN) model, Stavrakou et
94 al. (2014) reported an increased emission of biogenic isoprene over Asia ($0.16\% \text{ yr}^{-1}$) with
95 the more pronounced trend over China ($0.52\% \text{ yr}^{-1}$) during 1979-2012. Similarly, Zhang et al.
96 (2016) **reported an increased** biogenic isoprene emission **(from 132000 to 175000t yr^{-1})** in
97 northern China during 1982-2010. In contrast, SO_2 emissions over China have been declining
98 after 2006 because of the wide usage of flue-gas desulfurization (FGD) equipment in power
99 plants (Lu et al., 2010; Lu et al., 2011). All these East Asian pollutants along with soil dust
100 are transported to the North Pacific via long-range atmospheric transport by westerly winds
101 and perturb the remote marine background conditions and the ocean biogeochemistry by
102 heterogeneous reactions (Boreddy et al., 2015; Matsumoto et al., 2004). In addition to East
103 Asian pollutants, western North Pacific also receives biomass burning emissions from
104 Southeast Asia (Tsay et al., 2016; Lin et al., 2013; Huang et al., 2013)

105 **To better understand the long-range transport of Asian pollutants and their**
106 **atmospheric processing over the western North Pacific, we continuously collect total**
107 **suspended particulate (TSP) samples since 1990 at Chichijima Island.** (Mochida et al., 2003;
108 Kawamura et al., 2003; Boreddy and Kawamura, 2016). Chichijima is a remote marine island
109 in the western North Pacific, which is located in the outflow region of East Asian pollutants
110 and dust during the westerly wind season and in the pristine air masses under the wind regime
111 of easterlies. This island is about 1000 km south of Tokyo, Japan and 2000 km from the East
112 Asian countries (China) as shown in Figure 1. Therefore, the observation at Chichijima Island
113 is useful for studying the long-range transport of East Asian pollutants and their
114 heterogeneous chemistry over the western North Pacific (Boreddy et al., 2014; Verma et al.,
115 2015; Chen et al., 2013). In this study, we discuss the long-term trends in the concentrations
116 of carbonaceous aerosols (EC, OC, and **water-soluble organic carbon** (WSOC)) and their
117 ratios during 2001-2012 in addition to seasonal variations. The role of photochemical

118 oxidation of anthropogenic and biogenic VOCs on OC and WSOC and their relations to the
119 CCN is also discussed.

120

121 **2. Instrumentation and data analyses**

122 **2.1. Sampling site and aerosol collection**

123 Figure 1 shows the location of the sampling site and its adjacent Asian countries in
124 the western North Pacific. TSP samples were collected at the Satellite Tracking Centre of the
125 Japan Aerospace Exploration Agency (JAXA, elevation: 254 m) in Chichijima Island
126 (27°04'N; 142°13'E) on a weekly basis (Chen et al., 2013; Boreddy and Kawamura, 2015).
127 Aerosol samples are collected on pre-combusted (450° C for 3-5 h) quartz filter (20 × 25 cm,
128 Pallflex 2500QAT-UP) using a high volume air sampler (HVS) with a flow rate of 1 m³ min⁻¹
129 ¹. The HVS was installed at a height of 5 m above the ground level. The filters were placed in
130 a pre-baked (450°C for 6 h) glass jar (150 mL) with a Teflon-lined screw cap before sample
131 collection. After aerosol collection, the filters were recovered into the glass jar, transported to
132 the laboratory in Hokkaido University, Sapporo, and stored in a freezer room at -20 °C prior
133 to analysis. A total of 545 aerosol samples and about 56 field blank samples were used for the
134 analysis of carbonaceous components during 2001-2012.

135 **2.2. Analyses of carbonaceous aerosols**

136 Concentrations of OC and EC were determined using a Sunset Laboratory carbon
137 analyzer following the IMPROVE (Interagency Monitoring of Protected Visual
138 Environments) thermal/optical evolution protocol (Wang et al., 2005), assuming carbonate
139 carbon (CC) in the aerosol samples to be insignificant (Chow and Watson, 2002). Previous
140 studies have also shown that carbonate, particularly calcium carbonate, levels are low or
141 negligible in most ambient samples, which are analyzed by IMPROVE protocol (Wang et al.,
142 2005; Clarke and Karani, 1992; Chow et al., 2001). A filter cut of 1.54 cm² of each filter was
143 placed in a quartz tube inside the thermal desorption chamber of the analyzer and then
144 stepwise heating was applied. Helium (He) gas is applied in the first ramp and is switched to
145 mixture of He/O₂ in the second ramp. The evolved CO₂ during the oxidation at each
146 temperature step was measured by non dispersive infrared (NDIR) detector system. The
147 calculated detection limits of OC and EC were 0.05 and 0.02 µgC m⁻³, respectively. The sum
148 of OC and EC was considered to as total carbon (TC) in this study.

149 To determine WSOC, a punch of 20 mm in diameter of each filter was extracted with
150 20 mL organic-free ultra pure water (>18.2 MΩ cm, Sartorius arium 611 UV) and
151 ultrasonicated for 30 min. These extracts were passed through a disk filter (Millex-GV, 0.22

152 μm pore size, Millipore) to remove the filter debris and insoluble particles and analyzed using
153 a total organic carbon (TOC) analyzer (Shimadzu, TOC-Vcsh) equipped with a catalytic
154 oxidation column and non-dispersive infrared detector (Miyazaki et al., 2011).

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

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

164 **2.3. Statistical analyses**

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

171

172 **3. Results and discussion**

173 **3.1 Air mass back trajectories and general meteorology**

174 To better understand the influence of heterogeneity in air masses to carbonaceous
175 aerosols, we computed daily 7-day isentropic air mass back trajectories at an altitude of 500
176 m for each month using the hybrid single particle Lagrangian-integrated trajectory (HYPLIT)
177 model (Draxler and Rolph, 2013) during 2001-2012 as shown in Figure 2. We also
178 investigated the MODerate resolution Imaging Spectroradiometer (MODIS) derived fire
179 count data along with the back trajectories to understand the intensity of biomass burning
180 over South and Southeast Asia. From Figure 2, it is obvious that from winter (December-
181 February) to spring (March-May) the air masses are stronger to transport continental air
182 pollutants and dusts from East Asia to the sampling site in the Pacific by long-range
183 atmospheric transport. The continental air masses are absent in summer (June to August),
184 mostly come from the central Pacific and carry pristine air masses to the observation site,

185 whereas in autumn (September-November) the air mass pattern shifts from southeasterly to
186 northwesterly and become stronger towards winter.

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

194

195 3.2 Monthly/seasonal variations

196 Figure 3 (a-f) presents the monthly/seasonal variations in the concentrations of EC,
197 OC, WSOC and their ratios at Chichijima Island in the western North Pacific during 2001-
198 2012. The corresponding statistical data were reported in Table 1. All measured species
199 clearly showed winter-to-spring maxima (highest concentration was in March) and summer
200 minima (lowest in July) and then increase towards autumn. The seasonal pattern is found
201 consistent with the typical seasonal pattern in ambient carbonaceous aerosols over China
202 (Zhang et al., 2008; Cao et al., 2006), indicating a common source for these components,
203 which are long-range transported to the western North Pacific. This, of course, can also be
204 influenced by seasonal meteorology and synoptic wind circulation over the western North
205 Pacific as discussed in section 3.1.

206 Relatively high monthly average concentrations up to 0.28, 1.13 and $0.59 \mu\text{g m}^{-3}$ were
207 observed for EC, OC, and WSOC in March. In contrast, their monthly averages are lower in
208 summer or early autumn months (July or September) with the concentrations of 0.04, 0.58,
209 and $0.20 \mu\text{g m}^{-3}$, respectively (Table 1). It is well documented that in summer, a maritime
210 high-pressure wind dominated over the western North Pacific in which the air masses are
211 pristine and less influenced by the continental outflow from East Asia (Figure 2). This
212 observation is consistent with the fact that concentrations of anthropogenic nss-SO_4^{2-} , NO_3^- ,
213 NH_4^+ , and nss-K^+ showed similar seasonal variations with winter and/or spring maxima and
214 summer minima (Boreddy and Kawamura, 2015). On the other hand, continental air masses
215 blow from the Asian continent in winter and spring; therefore, the maritime background
216 condition of western North Pacific is often influenced by the continental outflow via long-
217 range atmospheric transport (Duce et al., 1980). Very low concentrations of EC in summer,
218 whose abundances were up to seven times lower than those in the continental outflow,

219 suggested negligible contribution of local anthropogenic emissions as well as long-range
220 influences over the sampling site. These results are consistent with previous studies, which
221 reported that several times lower concentrations of organic compounds in summer compared
222 to winter/spring over the same observation site (Kawamura et al., 2003; Mochida et al.,
223 2003). Therefore, it is reasonable to believe that the sources of carbonaceous aerosols were
224 transported from the adjacent Asian countries to the western North Pacific via long-range
225 atmospheric transport.

226 As described earlier, EC is primary particle and predominantly comes from biomass
227 and fossil fuel combustion sources. On the contrary, OC is of either primary origin or
228 secondary formation via gas-to-particle conversion in the atmosphere. The precursors of
229 secondary OC may also come from biogenic sources in addition to fossil fuel and biomass
230 burning emissions. The OC/EC ratios often used to distinguish the relative contribution of
231 primary vs. secondary sources as well as biomass vs. fossil fuel burning sources (Turpin and
232 Huntzicker, 1995; Castro et al., 1999; Rastogi et al., 2016). Atmospheric aerosols emitted
233 from fossil fuel combustion are characterized by lower OC/EC ratios (<2.0) whereas higher
234 OC/EC ratios (>5.0) are characteristic of biomass burning aerosols. The OC/EC ratios > 2.0
235 have been used to point out the presence of secondary organic aerosols (SOA) (Cao et al.,
236 2003; Chow et al., 1996; Kunwar and Kawamura, 2014). Table 2 summarizes OC/EC ratios
237 reported for various sources of aerosol particles. Monthly mean OC/EC ratios in this study
238 are greater than 2.0 for all months, suggesting the dominance of SOA in carbonaceous
239 aerosol over the western North Pacific. The seasonal variation of OC/EC mass ratios was
240 found maximum in summer (~21 to 33) and minimum in winter-to-spring (3.9 to 7.7). The
241 extremely high OC/EC ratios in summer indicate the secondary formation of OC via
242 oxidation processes, while low OC/EC ratios in winter-to-spring suggests that both biomass
243 burning and fossil fuel combustion are important sources for carbonaceous aerosols over the
244 western North Pacific.

245 It is well documented that nss-K^+ and EC are tracers for biomass and fossil fuel
246 burning emissions, respectively. Therefore, $\text{nss-K}^+/\text{EC}$ ratios were widely used to better
247 identify major sources of carbonaceous aerosols (Wang et al., 2005; Rastogi et al., 2016;
248 Srinivas and Sarin, 2014; Ram and Sarin, 2011). The higher $\text{nss-K}^+/\text{EC}$ ratios indicate the
249 dominance of biomass burning emissions, whereas lower ratios suggest the prevalence of
250 fossil fuel burning emissions. In this study, higher $\text{nss-K}^+/\text{EC}$ mass ratios were observed in
251 midsummer (July) to early autumn (September) (Figure 3e), suggesting an influence of
252 biomass burning emissions from southeast Asian countries via long-range atmospheric

253 transport over the western North Pacific. This point is consistent with the air mass back
254 trajectory analysis and MODIS-fire count data during summer months (Figure 2), which
255 clearly show that air masses are occasionally coming from Southeast Asia, including
256 Indonesia, Malaysia and New Guinea etc., where biomass burning is a common phenomena
257 during summer to early autumn. Biomass burning products were transported to the western
258 North Pacific (Figure 2). In this context, Verma et al. (2015) reported significant
259 concentrations of levoglucosan during summer in Chichijima (in the absence of East Asian
260 outflows), which were attributed to the occasional transport of biomass burning influenced air
261 masses from southeast Asia, as inferred from the air mass trajectories and fire spot data
262 during 2001-2013. Therefore, carbonaceous aerosols over Chichijima strictly follow the
263 seasonal wind patterns in the western North Pacific.

264 Previous studies have shown that SOA is largely composed of oxygenated compounds
265 that are highly water-soluble (Kanakidou et al., 2005; Kondo et al., 2007 and references
266 therein). Thus, measurements of WSOC have been used to estimate the SOA in ambient
267 aerosols (Weber et al., 2007; Snyder et al., 2009; Sudheer et al., 2015; Decesari et al., 2001;
268 Docherty et al., 2008). Because major fraction of biomass burning products is highly water-
269 soluble (Sannigrahi et al., 2006; Saarikoski et al., 2008), WSOC/OC ratio has been used as an
270 unique tracer to better understand the photochemical activity and/or aging of aerosols and to
271 discuss SOA formation mechanism in the atmosphere during long-range transport (Miyazaki
272 et al., 2007; Ram et al., 2010b; Ram and Sarin, 2011; Kondo et al., 2007; Weber et al., 2007;
273 Gilardoni et al., 2016; Boreddy et al., 2017). The WSOC/OC ratios exceeding 0.4 have been
274 used to indicate the significant contribution of SOA (Ram et al., 2010a) and aged aerosols.
275 The WSOC/OC ratios ranged from 0.06 to 0.19 in diesel particles (Cheung et al., 2009) and
276 0.27 for vehicular emissions (Saarikoski et al., 2008). In this study, monthly mean
277 WSOC/OC ratios are >4.0 for all months except for September, indicating a significant
278 contribution from SOA over the western North Pacific. The seasonal variation of WSOC/OC
279 showed higher values (monthly mean: 0.44 to 0.62) during winter-spring months (Figure 3f),
280 implying that the SOA formation is enhanced due to increased photochemical activity and/or
281 aging of East Asian polluted aerosols during long-range atmospheric transport. The high
282 WSOC/OC ratios are traditionally attributed to the atmospheric oxidation of various VOCs in
283 the presence of oxidants such as ozone and hydrogen peroxide radicals via gas and/or
284 aqueous phase reactions in the atmosphere (Miyazaki et al., 2007; Ram and Sarin, 2012).
285 However, the atmosphere over the western North Pacific is always characterized by high
286 relative humidity (>80%) and air temperature (~24°C) during the whole year (Figure S1).

287 Therefore, higher WSOC concentrations in winter-to-spring over the western North Pacific
288 were largely attributed to the aqueous-phase oxidation of anthropogenic and/or biogenic
289 VOCs (Gilardoni et al., 2016; Youn et al., 2013), which are emitted over East Asia and long-
290 range transported to the western North Pacific.

291 On the other hand, lower ratios of WSOC/OC in summer may suggest that the
292 primary emission of OC from the ocean surface via sea-to-air flux because the low speed
293 easterly winds originated from the central Pacific are dominant in summer over the western
294 North Pacific (Figure 2). Miyazaki et al. (2010) reported the presence of significant water-
295 insoluble organic matter in the western North Pacific during summer, which may be produced
296 by bubble-bursting processes at the ocean surface. Similarly, Ovadnevaite et al. (2011)
297 reported higher contributions of primary organic matter to marine aerosols over the Northeast
298 Atlantic. Further, laboratory studies have revealed a high abundance of primary organic
299 matter in sea-spray aerosols (Facchini et al., 2008; Keene et al., 2007).

300

301 3.3 Annual trends

302 Figure 4 shows the annual trends in the concentrations of EC, OC, TC (EC+OC),
303 WSOC, and WSOC/OC ratios during the period of 2001-2012 over the western North Pacific
304 (see Figure S2 for annual mean variations). Table 3 summarizes the results of the statistical
305 analyses. It is seen that all the annual trends of chemical species and WSOC/OC ratios
306 showed clear seasonal patterns with higher values in winter-spring and lower values in
307 summer. In contrast, the OC/EC and nss-K⁺/EC ratios showed higher values in summer.

308 As seen from Figure 4a-c, concentrations of EC, OC, and TC during 2001-2012
309 ranged from 0.001 to 0.36 $\mu\text{g m}^{-3}$ (mean: 0.142 $\mu\text{g m}^{-3}$), 0.25 to 1.7 $\mu\text{g m}^{-3}$ (0.76 $\mu\text{g m}^{-3}$) and
310 0.28 to 2.01 $\mu\text{g m}^{-3}$ (0.90 $\mu\text{g m}^{-3}$), respectively. The annual trend of EC showed a decreasing
311 order (-0.007% yr^{-1}), while OC and TC trends are continuously increasing (+0.16% yr^{-1} and
312 +0.11% yr^{-1} , respectively) from 2001 to 2012 although the trends were not significant
313 ($p>0.05$). However, the annual trends of OC/EC and OC/TC ratios increased significantly
314 ($p<0.05$; +0.46% yr^{-1} and +0.06% yr^{-1}) from 2001 to 2012 (Figure 4d and 4e), suggesting that
315 the secondary formation of OA and its contribution to carbonaceous aerosols have
316 continually increased over the western North Pacific. These results further suggest that the
317 contribution of fossil fuel combustion to carbonaceous aerosols has decreased during the
318 sampling period. This point is supported by the annual trend of nss-K⁺/EC mass ratios, which
319 showed a significant increase ($p<0.05$; +0.33% yr^{-1}) during the sampling period (Figure 4g).
320 This observation is consistent with the study of Verma et al. (2015), who observed a

321 significant enhancement of levoglucosan (a good biomass burning tracer, e.g., Simoneit,
322 2002) during 2006-2013 over the sample sampling site. Therefore, all these results
323 demonstrate that the contributions of biomass burning emissions to carbonaceous aerosols
324 have increased significantly over the western North Pacific whereas the contributions of
325 fossil fuel combustion have decreased.

326 The annual trend of WSOC showed a significant increase ($p < 0.05$; $+0.18\% \text{ yr}^{-1}$) from
327 2001 to 2012 (Figure 4c), implying an important SOA formation over the western North
328 Pacific because SOA largely consists of water-soluble matter (Weber et al., 2007; Kondo et
329 al., 2007). Generally, atmospheric aging makes aerosols more water-soluble during long-
330 range transport (Aggarwal and Kawamura, 2009; Rudich et al., 2007; Robinson et al., 2007;
331 Jimenez et al., 2009; Kawamura et al., 2010), especially in the remote marine atmosphere
332 (Kawamura et al., 2003). This point is further supported by an increase ($+0.08\% \text{ yr}^{-1}$) in the
333 decadal trend of WSOC/OC ratios (Figure 4f). These results may demonstrate that the
334 formation of WSOC (or OC) over the western North Pacific is significantly linked with
335 photochemical aging of aerosols and oxidation of various VOCs during long-range
336 atmospheric transport (Zhang et al., 2007; Decesari et al., 2010). We observed an abrupt
337 decrease in the WSOC/OC ratios between 2007 and 2008, probably due to the enhanced OC
338 that may be caused by the primary emissions from the ocean surface. However, it should be
339 noted that the observed increase in the WSOC/OC ratios does not change the decadal trend
340 even if those data are deleted. A significant increasing trend of WSOC/TC ($p < 0.05$; $+0.15\%$
341 yr^{-1} ; Table 2) again suggests that formation of SOA and its contributions to carbonaceous
342 aerosols have significantly increased over the western North Pacific during 2001-2012.

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

354 continental transport of biogenic VOCs (BVOCs) over the western North Pacific have
355 increased significantly during 2001-2012.

356 Zhang et al. (2016) have reported an increase (from 132000 to 175000t yr⁻¹) in the
357 emission of isoprene in northern China during 1982-2010 using an emission model.
358 Consistently, Stavrou et al. (2014) reported that an increased isoprene emission (+0.52%
359 yr⁻¹) over Asia, especially China during 1979-2012. Based on strong correlations ($r > 0.90$)
360 between isoprene and above-canopy temperature, they suggested that oxidations of biogenic
361 BVOCs from the terrestrial higher plants are important in Asia (especially in China). Since
362 Chichijima is an outflow region of East Asia, long-range atmospheric transport of BVOCs
363 may be possible from terrestrial higher plants in Asia/China to the western North Pacific by
364 westerly winds, which may significantly contribute to the enhanced trends of OC and WSOC
365 during 2001-2012. We found significant ($p < 0.05$) increases in the annual trends of
366 methylglyoxal and pyruvic acid, which are tracers of aqueous-phase oxidation of biogenic
367 isoprene (Carlton et al., 2009), over the western North Pacific as shown in Figure S3. We also
368 found a moderate correlation ($r = 0.40$, $p < 0.01$) between of MSA⁻ and WSOC concentrations
369 (not shown as a figure). These results demonstrate that increase of WSOC is likely due to the
370 increased photochemical oxidation of BVOCs during long-range transport over the western
371 North Pacific in addition to the other emissions such as biomass burning.

372

373 3.4 Atmospheric implications

374 It is well known that atmospheric aerosols play a key role in the climate system as
375 they can act as cloud condensation nuclei (CCN) and impact cloud formation, thus, radiative
376 forcing (RF) (IPCC, 2013). The RF of aerosol is estimated based on the aerosol optical depth
377 (AOD), absorption and scattering coefficients and asymmetry parameters. OC (except for
378 brown carbon) and SO₄²⁻ particles majorly scatter the solar radiation whereas EC particles
379 strongly absorb the solar radiation in the atmosphere. The single scattering albedo (SSA),
380 defined as the ratio of scattering to the extinction coefficient of aerosols (Pani et al., 2016), is
381 an important property for determining the direct RF (Gopal et al., 2017; He et al., 2009). The
382 SSA is highly sensitive to the nature (scattering and/or absorption) of aerosols in the
383 atmosphere. Therefore, although OC has certain uncertainty because of light absorbing brown
384 carbon, the OC/EC ratios can be used to understand the relative contributions of scattering or
385 absorbing aerosols in the atmosphere (Ram and Sarin, 2015). Further, a good knowledge of
386 the OC/EC ratios in aerosols (for example, biomass burning) may also help to improve model
387 representation of the absorption caused by organic compounds constituting the so called

388 brown carbon, which contributes to the aerosol RF (Chung et al., 2012; Saleh et al., 2014;
389 Kirchstetter and Thatcher, 2012). In this study, atmospheric aging may make OC more
390 scattering during long-range transport over the western North Pacific. A significant
391 increasing trend of OC/EC ratios suggests that scattering aerosols are increased significantly
392 over the western North Pacific. In contrast, absorbing aerosols may be decreased during the
393 study period. This result may provide an important implication for radiative forcing because
394 scattering and absorption coefficients are playing crucial role in the radiative forcing
395 calculations as mentioned above.

396 Novakov and Corrigan (1996) found that pure organic components from biomass
397 smoke emissions can form cloud condensation nuclei (CCN) without the presence of sulfate
398 (SO_4^{2-}) and other inorganic compounds. Roberts et al. (2002) showed that biomass burning
399 derived organic aerosol does serve as CCN. Further, large loadings of CCN in continental air
400 masses were observed over the western North Pacific (Matsumoto et al., 1997; Boreddy et al.,
401 2015). In this study, the enhanced WSOC concentrations and WSOC/OC ratios in continental
402 air masses suggest an important role of WSOC in CCN activity over the western North
403 Pacific in addition to other particles such as SO_4^{2-} and sea-salts. To better understand the
404 impact of WSOC on cloud forming potential, we performed regression analysis between
405 WSOC and CCN concentrations as shown in Figure 5. CCN data were downloaded from the
406 MODIS satellite over the region (140° – 145° E, 25° – 30° N) in the western North Pacific for
407 the period 2002-2012. The results show a significantly good correlation ($r=0.69$, $p<0.001$)
408 between WSOC and CCN concentrations. This result suggests that, although nss-sulfate is a
409 major contributor to CCN activity (Mochida et al., 2011) water-soluble organic matter also
410 plays an important role in CCN formation over the western North Pacific. This point is
411 consistent with previous studies, which explain the contribution of water-soluble organic
412 matter to CCN (Matsumoto et al., 1997; Zhao et al., 2016).

413 It should be noted that all these ratios are applicable to organic fractions that are
414 derived from the bulk measurements only; however, the size of the particle also plays a role
415 on RF as well as their morphology, chemical composition and mixing state (Jacobson, 2001;
416 Lohmann and Feichter, 2005; Zhang et al., 2008).

417

418 **4. Conclusion**

419 Based on the long-term (2001-2012) trends of carbonaceous aerosols from Chichijima
420 Island in the western North Pacific, we conclude that the seasonal variations of carbonaceous
421 aerosols strictly followed seasonal trends of wind pattern at Chichijima in the western North

422 Pacific. The annual trends of OC and WSOC with significant increases over the western
423 North Pacific are probably due to the enhanced photochemical oxidation of biomass burning-
424 and biogenic-derived VOCs during long-range atmospheric transport over the western North
425 Pacific. This inference is supported by significant increases in the annual trends of OC/EC,
426 WSOC/OC, OC/TC, WSOC/TC, nss-K⁺/EC mass ratios and MSA⁻ concentrations. On the
427 other hand, a decrease in the concentrations of EC during 2001-2012 suggests that the
428 contribution of Fossil fuel-derived sources to carbonaceous aerosols may be decreased over
429 the western North Pacific. Further, a good correlation (r=0.69) between WSOC and CCN
430 concentrations suggests that not only nss-SO₄²⁻ but also water-soluble organic aerosols play a
431 role in CCN formation. Therefore, the results from this study have important implications
432 toward the **regional radiative balance**, especially over the North Pacific.

433

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842 **Table 1.** Monthly mean (\pm standard deviation) values of EC, OC, WSOC concentrations
 843 and their ratios during 2001-2012 over the western North Pacific.
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Month	EC ($\mu\text{g m}^{-3}$)	OC ($\mu\text{g m}^{-3}$)	WSOC ($\mu\text{g m}^{-3}$)	OC/EC	WSOC/OC	nss-K ⁺ /EC
January	0.18 \pm 0.07	0.80 \pm 0.41	0.54 \pm 0.28	4.85 \pm 2.01	0.69 \pm 0.14	0.29 \pm 0.16
February	0.25 \pm 0.07	0.95 \pm 0.36	0.55 \pm 0.17	3.95 \pm 1.31	0.63 \pm 0.22	0.35 \pm 0.39
March	0.28 \pm 0.05	1.13 \pm 0.37	0.59 \pm 0.22	4.11 \pm 1.19	0.56 \pm 0.19	0.22 \pm 0.09
April	0.22 \pm 0.10	0.77 \pm 0.32	0.48 \pm 0.28	3.89 \pm 1.37	0.62 \pm 0.20	0.26 \pm 0.12
May	0.14 \pm 0.08	0.80 \pm 0.31	0.35 \pm 0.19	7.68 \pm 4.11	0.44 \pm 0.19	0.40 \pm 0.27
June	0.08 \pm 0.07	0.74 \pm 0.35	0.30 \pm 0.18	21.1 \pm 30.4	0.44 \pm 0.17	0.54 \pm 0.36
July	0.06 \pm 0.06	0.58 \pm 0.35	0.22 \pm 0.07	19.0 \pm 16.7	0.44 \pm 0.17	0.97 \pm 0.94
August	0.04 \pm 0.03	0.63 \pm 0.27	0.27 \pm 0.16	33.2 \pm 52.5	0.46 \pm 0.23	0.70 \pm 0.69
September	0.05 \pm 0.04	0.60 \pm 0.26	0.20 \pm 0.10	22.3 \pm 17.3	0.38 \pm 0.19	1.02 \pm 0.82
October	0.08 \pm 0.04	0.62 \pm 0.18	0.27 \pm 0.12	12.2 \pm 9.07	0.45 \pm 0.19	0.50 \pm 0.43
November	0.15 \pm 0.10	0.75 \pm 0.39	0.42 \pm 0.20	6.68 \pm 4.89	0.61 \pm 0.20	0.44 \pm 0.26
December	0.18 \pm 0.09	0.73 \pm 0.29	0.39 \pm 0.08	4.63 \pm 1.65	0.59 \pm 0.18	0.21 \pm 0.12

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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, <u>4.1</u> , 1.1	Koch (2001), <u>Cao et al. (2005)</u> , <i>Watson et al. (2001)</i>
Coal combustion	2.7, 12.0	<i>Watson et al. (2001)</i> , Cao et al. (2005)
Biomass burning	9.0, <u>60.3</u> , 5-8	Cachier et al. (1989), <u>Cao et al. (2005)</u> , <i>Andreae and Merlet (2001)</i>
Forest fire	~16.0	Watson et al. (2001)
Diesel truck plume	0.06, <u>0.8</u> , <u>0.3</u>	Dallmann et al. (2014), <i>Na et al. (2004)</i> , <u>Turpin and Huntzicker (1995)</u>
Gasoline vehicle	0.02, 2.2	Dallmann et al. (2014), <i>Na et al. (2004)</i>
Secondary organic carbon	3.3	Saarikoski et al. (2008)
Long-range 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)

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853 **Table 3.** Statistical report on the annual trends in carbonaceous aerosols and their ratios
 854 during 2001-2012 at Chichijima Island in the western North Pacific. ‘*’ indicates that the
 855 trends are significant at $p < 0.05$ level.
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Species	Concentrations ($\mu\text{g m}^{-3}$)				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

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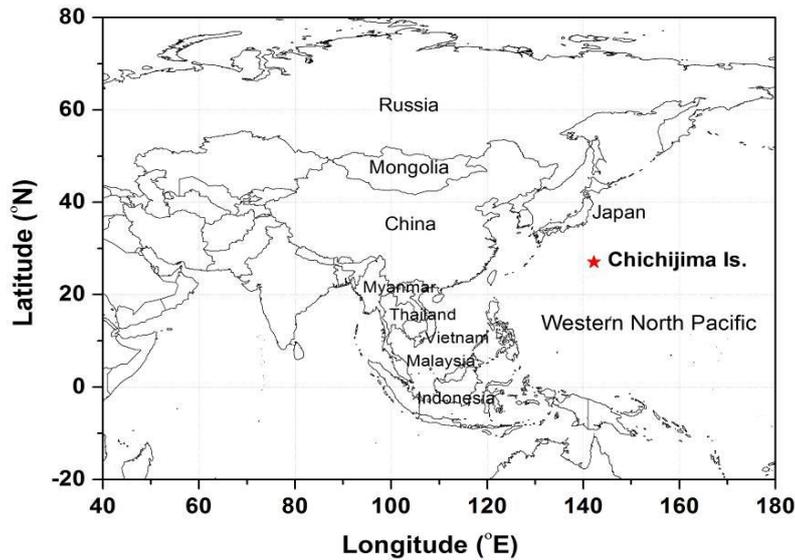
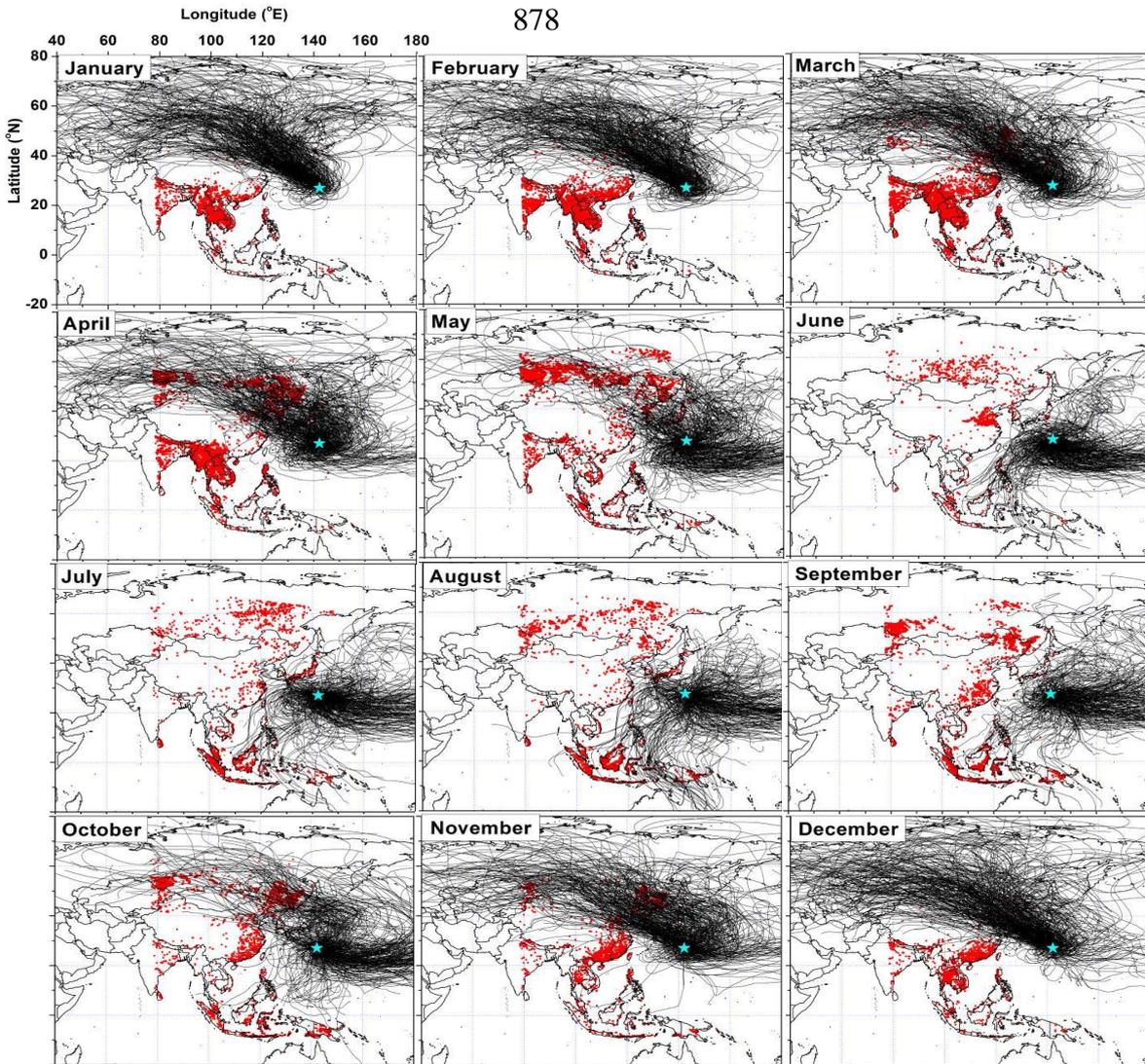


Figure 1. Location of sampling site (indicated by red colored ‘*’) in the western North Pacific and its adjacent Asian countries.

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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.

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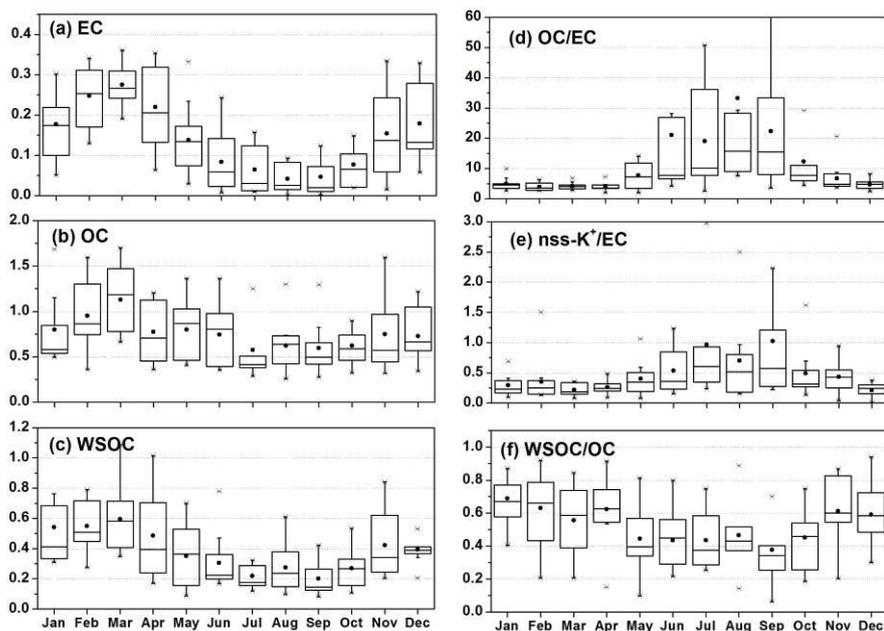


Figure 3. Box-whisker plots of monthly variations of carbonaceous aerosol components ($\mu\text{g m}^{-3}$) and their ratios at Chichijima Island in the western North Pacific during 2001-2012. The horizontal line and small dot inside the box indicate median and mean, respectively. The vertical hinges 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.

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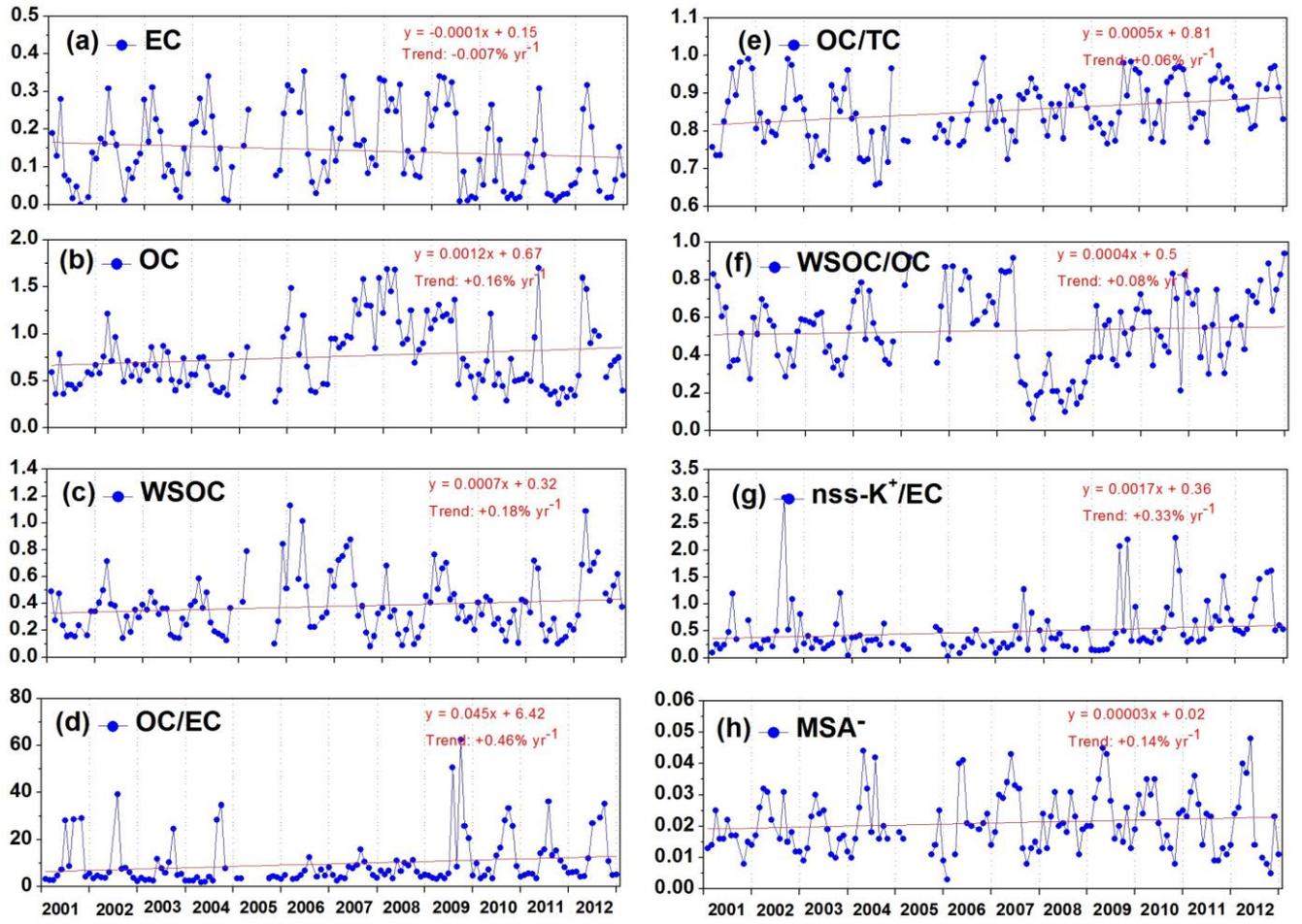


Figure 4. Annual trends (time series) in the concentrations ($\mu\text{g m}^{-3}$) of carbonaceous aerosol components as well as water-soluble ionic tracer compounds and their mass ratios during 2001-2012 over the western North Pacific. The liner trend equation ($y=mx+c$) is also shown for the each annual trend.

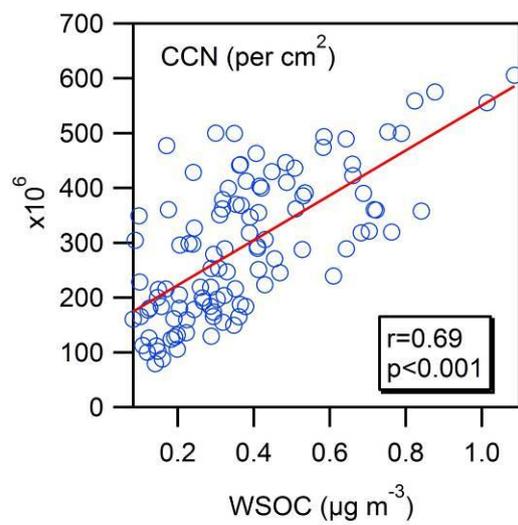


Figure 5. Regression analyses between WSOC and MODIS-derived cloud condensation nuclei (CCN) concentrations over the western North Pacific.