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 followed by the revised manuscript.

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 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; 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 >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 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 (~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 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 know 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

(SO_4^{2-}) 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 SO_4^{2-} 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 back trajectories 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% 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% 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 meglyoxal and pyrivic 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 on 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.

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

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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 are 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 that 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 significant increase (+0.33% yr^{-1}) in nss-K^+/EC ratios, demonstrating that biomass-burning-derived carbonaceous aerosols are increased, while fossil fuel-derived aerosols are 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 source). This point is further supported by a moderate correlation ($r=0.40$) between WSOC and MSA^-. 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 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 invisible 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 hence 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 carbonaceous species, while elemental carbon (EC; alternatively referred as black carbon, BC) encompasses the most refractory and most light absorbing species (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 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). 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 about carbonaceous aerosols and their sources are 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 aerosol 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 exist 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 dominated 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 increased 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, 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 is 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 (Chen et al., 2013; 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 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). 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 is applied in the first ramp and is 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 have been corrected for field blanks. The levels of blanks are 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 is used for each time series (Draper and Smith, 1966). Second, all trends are assessed 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 is 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 South and Southeast Asia. From Figure 2, it is obvious that from winter (December-February) to spring (March-May) the air masses are stronger to transport continental air pollutants and dusts from East Asia to the sampling site in the Pacific by long-range atmospheric transport. The continental air masses are absent in summer (June to August), 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 is a clear seasonal variation in the levels of 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 clearly showed winter-to-spring maxima (highest concentration was in March) and summer minima (lowest in July) and then increase towards autumn. The seasonal pattern is found consistent with the typical seasonal pattern in ambient carbonaceous aerosols over China (Zhang et al., 2008; 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 synoptic wind circulation over the western North Pacific as discussed in section 3.1.

Relatively high 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 are lower in summer or early autumn months (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 are 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 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 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 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). 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 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 tracers for biomass and fossil fuel burning 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; Srinivas and Sarin, 2014; Ram and Sarin, 2011). The higher nss-K^+/EC ratios indicate the dominance of biomass burning emissions, whereas lower ratios suggest the prevalence of fossil fuel burning 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 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). 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; 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 >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 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 (~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 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).

3.3 Annual trends

Figure 4 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. 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.

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 trend of EC showed a decreasing order (-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 trends 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 4d and 4e), 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 decreased 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 4g). 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 sample 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 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). 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 an increase (+0.08% yr^{-1}) in the decadal trend of WSOC/OC ratios (Figure 4f). 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). 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 the ocean surface. However, it should be noted that the observed increase in the WSOC/OC ratios does not change the decadal trend even if those data are deleted. 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^- 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 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, 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, 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 solar 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, 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 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 SO_4^{2-} 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).

4. Conclusion

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 nss-SO_4^{2-} but also water-soluble organic aerosols play a role in CCN formation. Therefore, the results from this 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

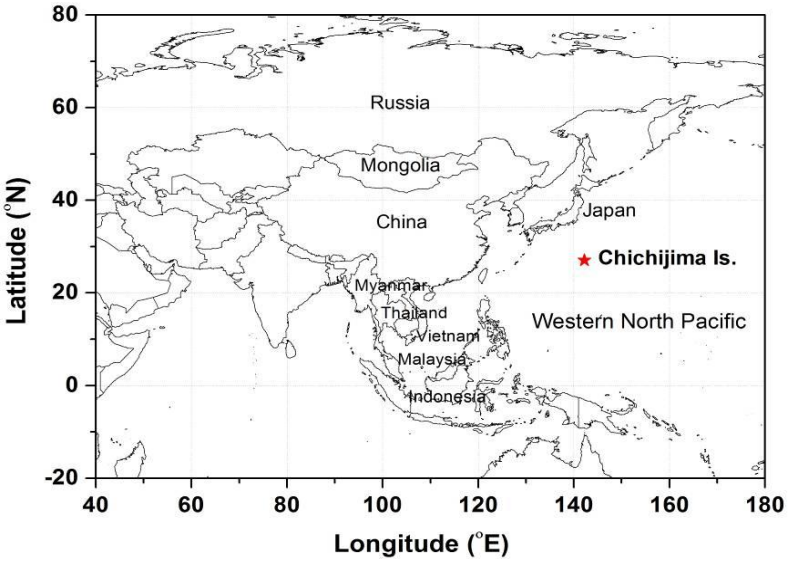

Figure 1. Location of sampling site (indicated by red colored '*') in the western North Pacific and its adjacent Asian countries.

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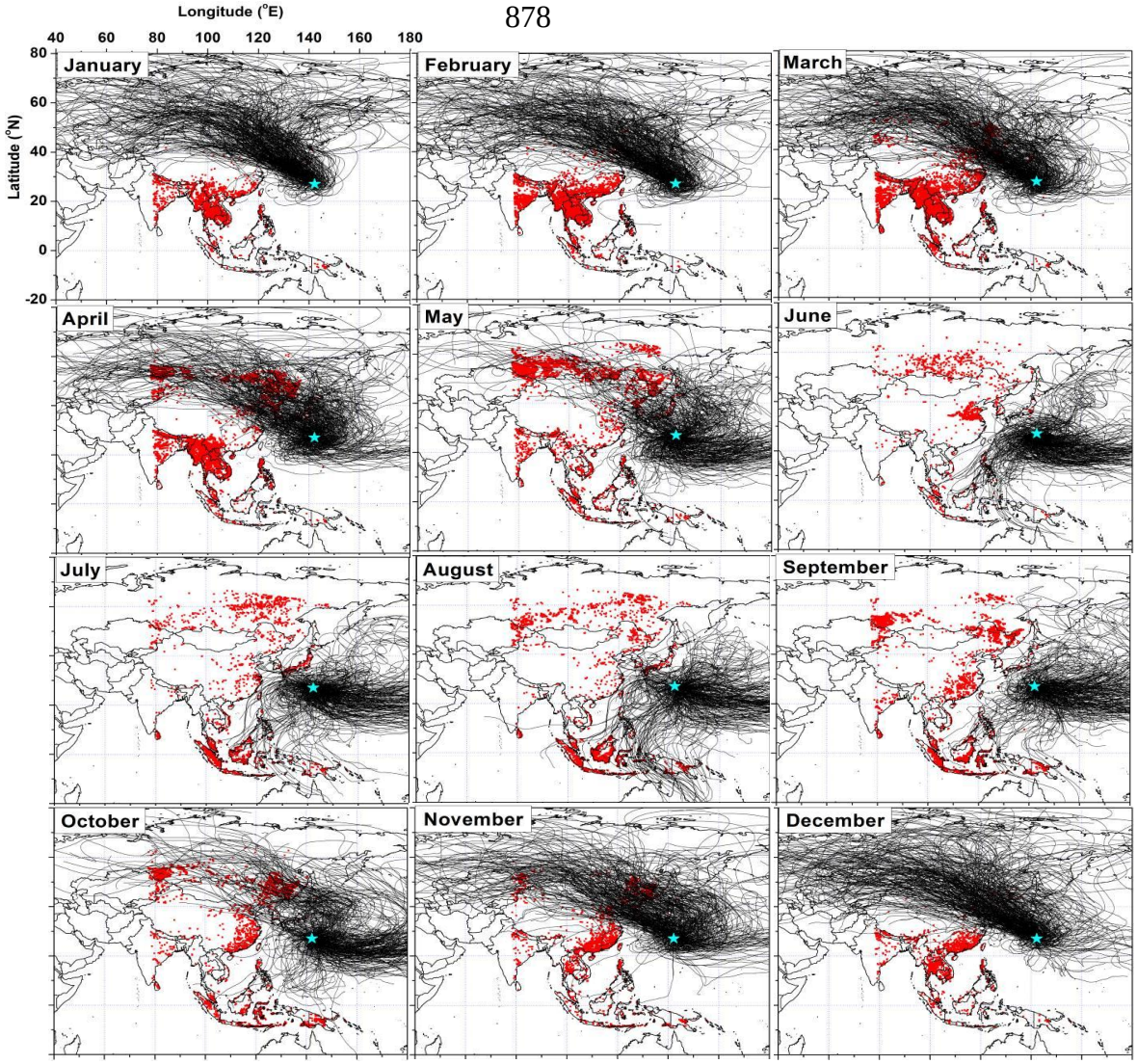

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Figure 2. 7-day daily air mass back trajectories at 500 m a.g.l. computed using HYPLIT model for each month during 2001-2012 at Chichijima Island in the western North Pacific. The symbol '*' indicates the sampling site and red dots represent the MODIS inferred fire spots.

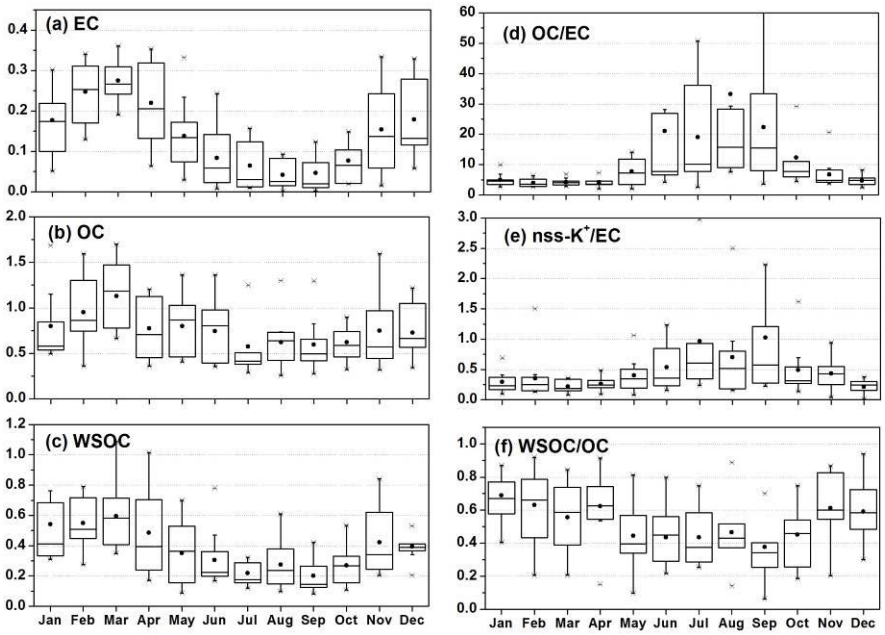

Figure 3. Box-whisker plots of monthly variations of carbonaceous aerosol components (μg m^{-3}) and their ratios at Chichijima Island in the western North Pacific during 2001-2012. The horizontal line and small dot inside the box indicate maiden and mean, respectively. The vertical hinges represent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

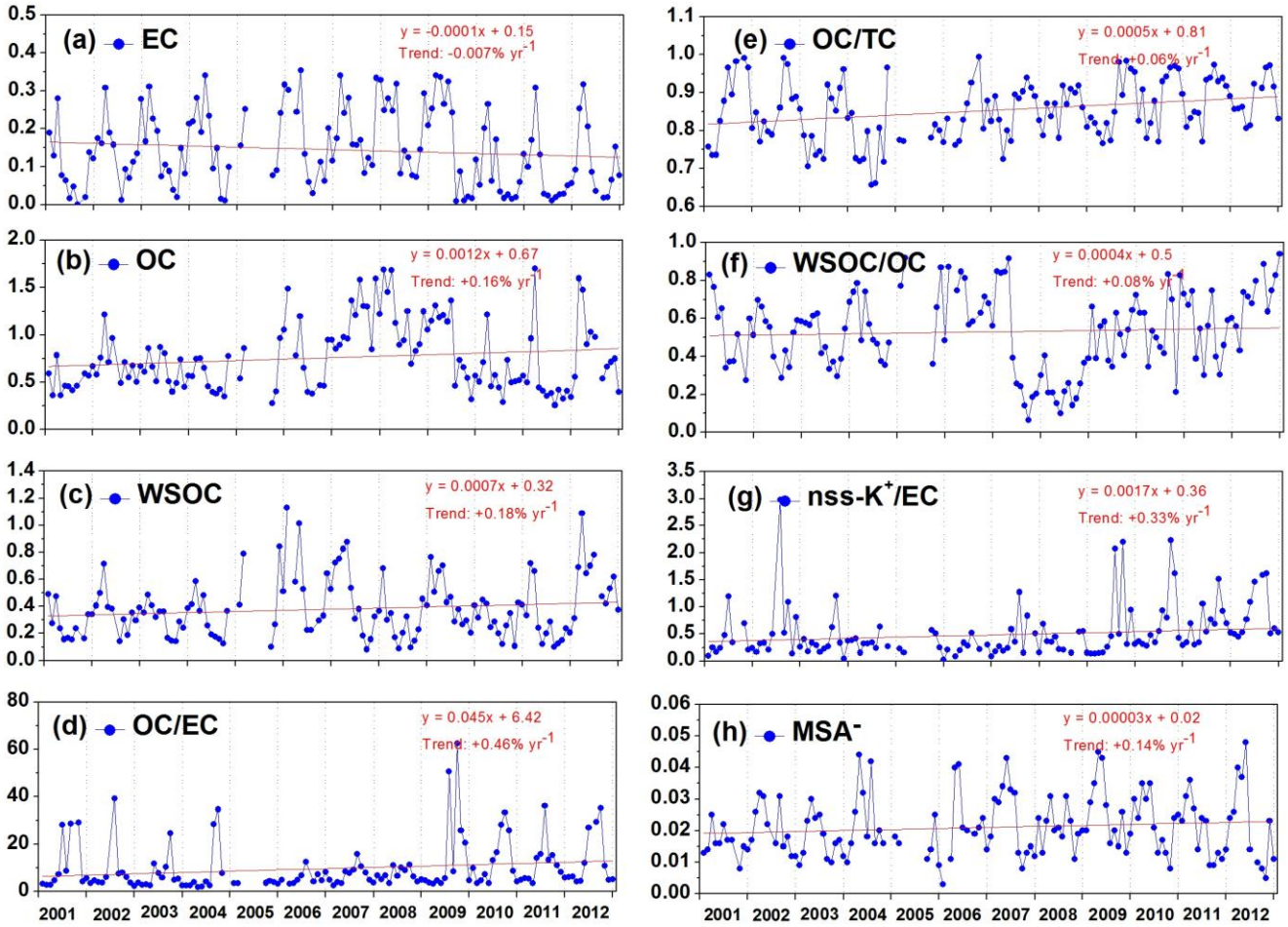

Figure 4. Annual trends (time series) in the concentrations (μg m^{-3}) of carbonaceous aerosol components as well as water-soluble ionic tracer compounds and their mass ratios during 2001-2012 over the western North Pacific. The liner trend equation (y=mx+c) is also shown for the each annual trend.

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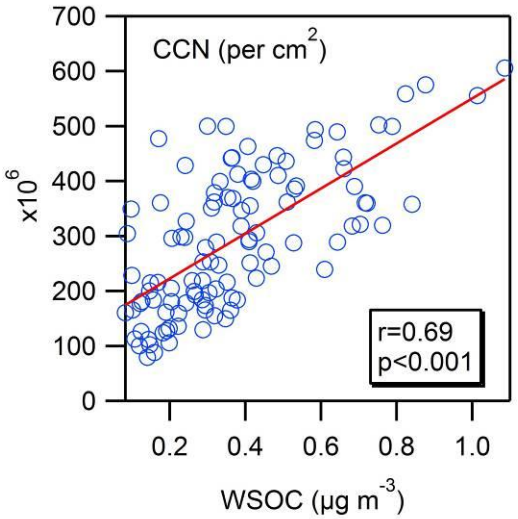

Figure 5. Regression analyses between WSOC and MODIS-derived cloud condensation nuclei (CCN) concentrations over the western North Pacific.

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 dust

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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

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

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.

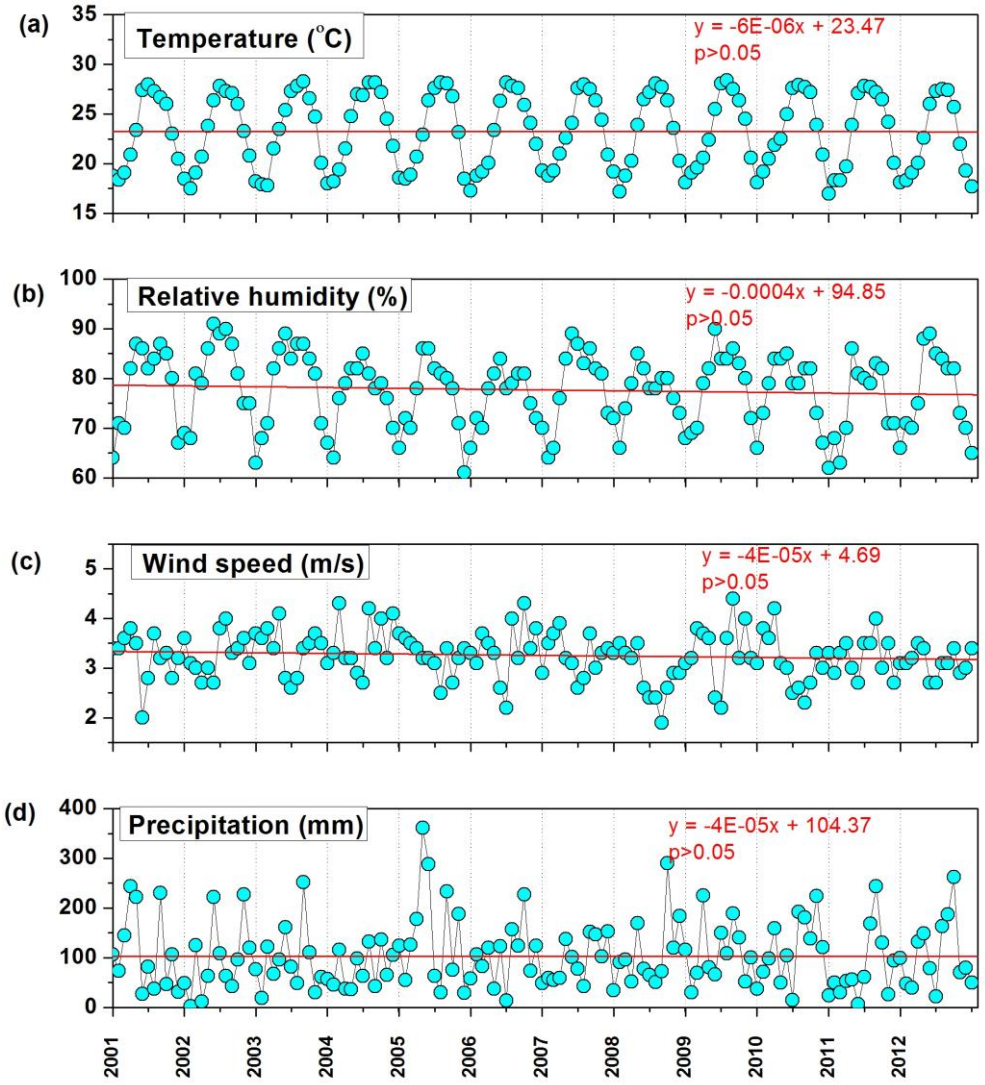

Figure S1. Temporal variations of meteorological parameters such as (a) air temperature (°C), (b) relative humidity (%), (c) wind speed (ms^{-1}), and (d) precipitation (mm) at Chichijima Island during the study period from 2001 to 2012.

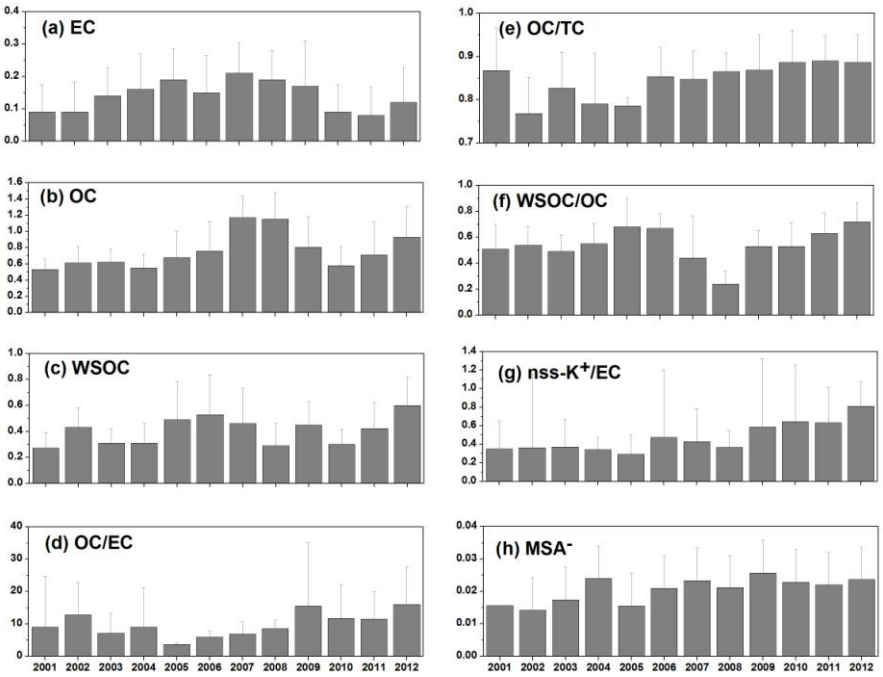

Figure S2. Annual mean variations (μg m^{-3}) of carbonaceous species as well as water-soluble ions and their mass ratios during 2001-2012 over the western North Pacific.

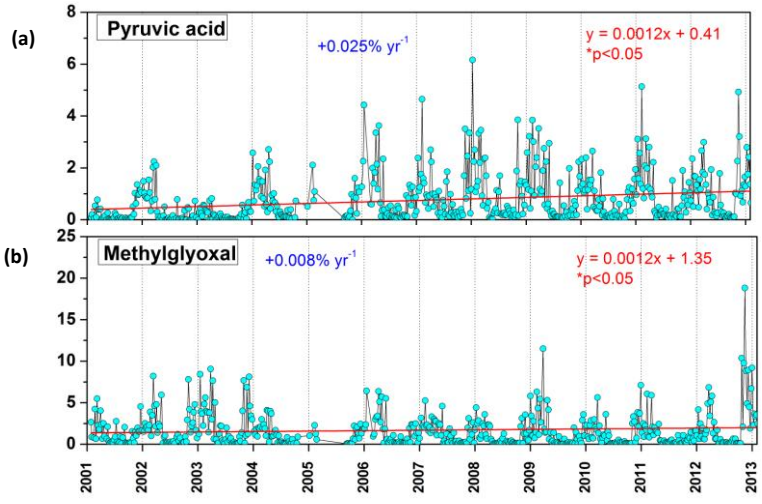

Figure S3. Annual trends in the concentrations (ng m^{-3}) of aqueous-phase photooxidations of biogenic isoprene tracer compounds (a) puruvic acid and (b) methylglyoxal during 2001-2012 over the western North Pacific.