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 followed by the revised manuscript.

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 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)." 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.

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

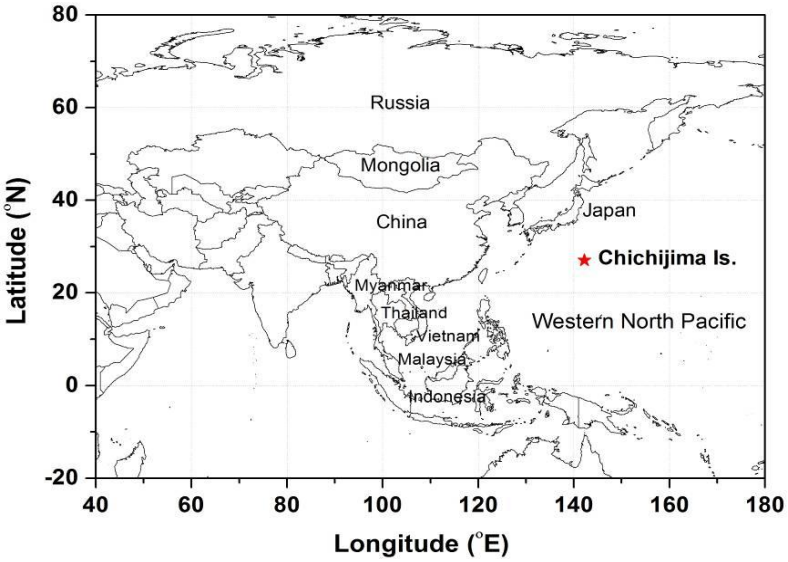

Figure 1. Location of sampling site (indicated by red colored '*') in the western North Pacific and its adjacent Asian countries.

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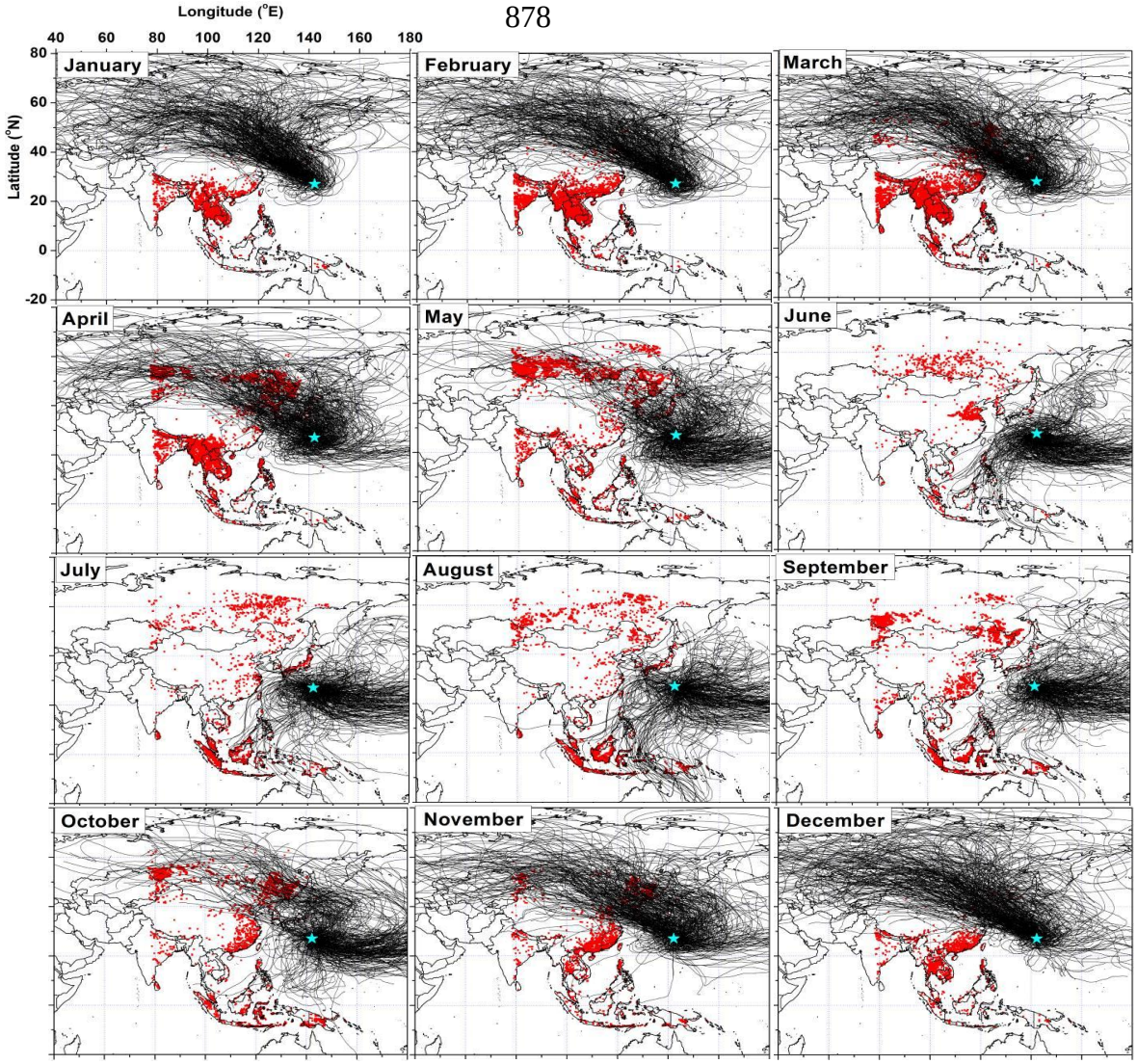

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Figure 2. 7-day daily air mass back trajectories at 500 m a.g.l. computed using HYPLIT model for each month during 2001-2012 at Chichijima Island in the western North Pacific. The symbol '*' indicates the sampling site and red dots represent the MODIS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

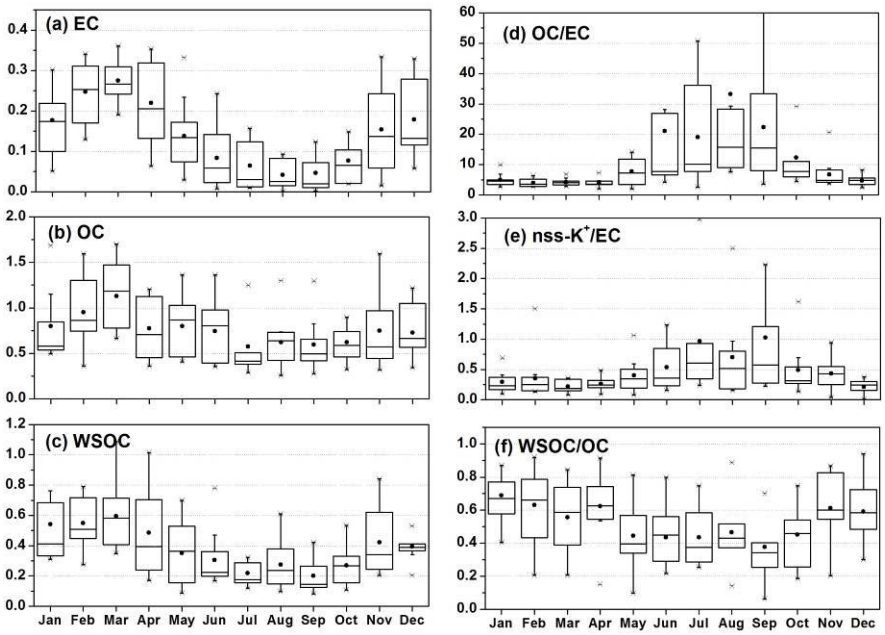

Figure 3. Box-whisker plots of monthly variations of carbonaceous aerosol components (μg m^{-3}) and their ratios at Chichijima Island in the western North Pacific during 2001-2012. The horizontal line and small dot inside the box indicate maiden and mean, respectively. The vertical hinges represent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

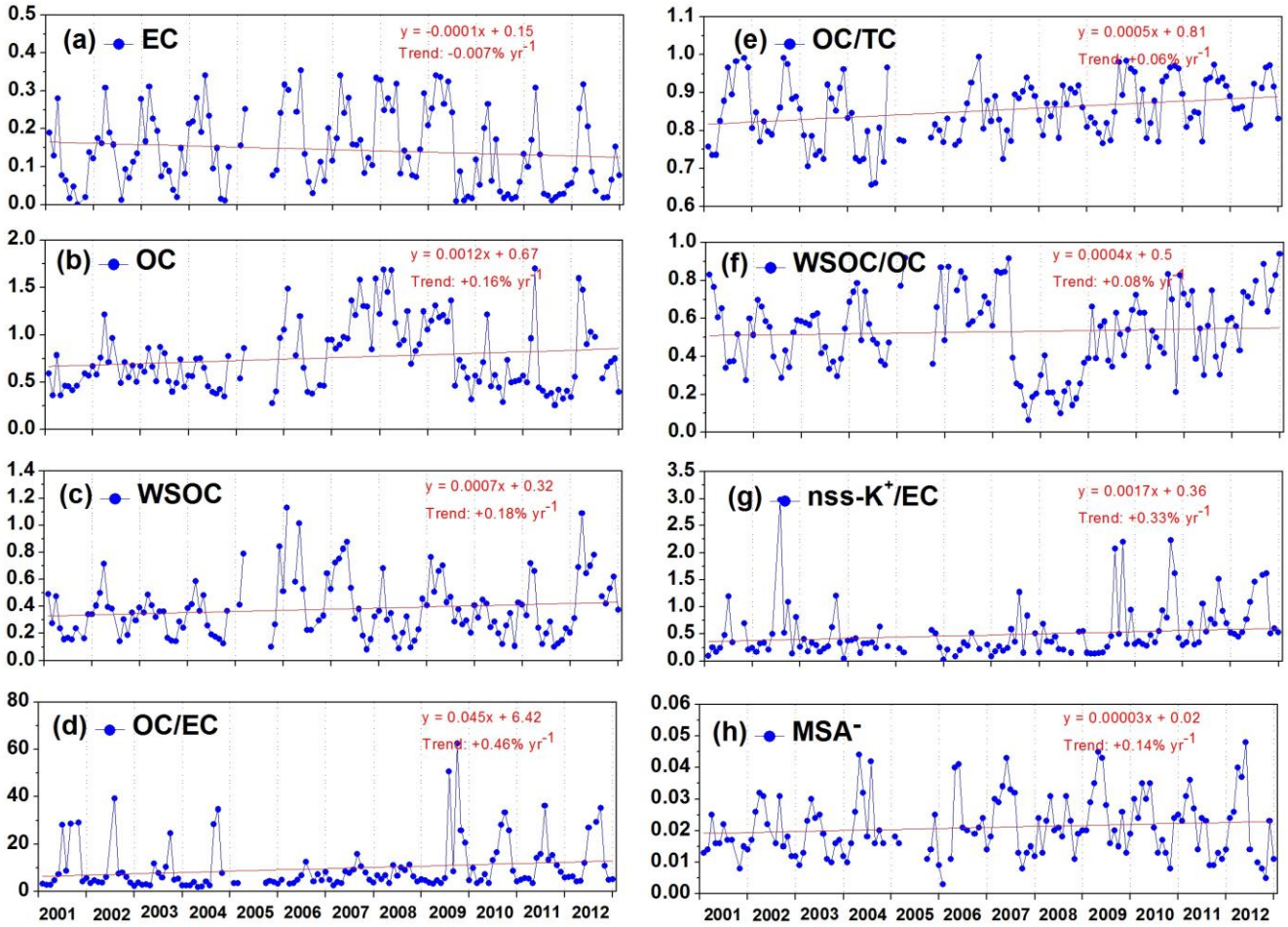

Figure 4. Annual trends (time series) in the concentrations (μg m^{-3}) of carbonaceous aerosol components as well as water-soluble ionic tracer compounds and their mass ratios during 2001-2012 over the western North Pacific. The liner trend equation (y=mx+c) is also shown for the each annual trend.

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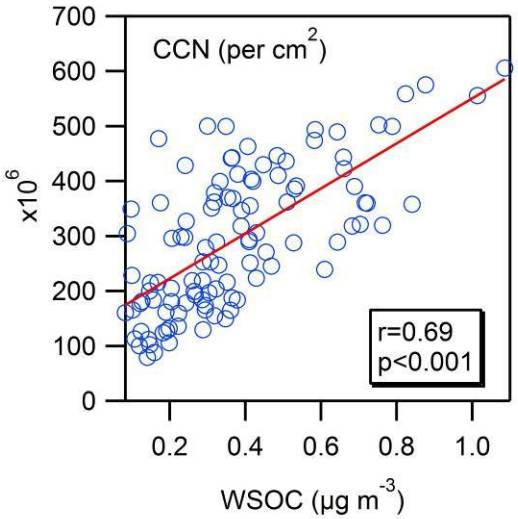

Figure 5. Regression analyses between WSOC and MODIS-derived cloud condensation nuclei (CCN) concentrations over the western North Pacific.

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.

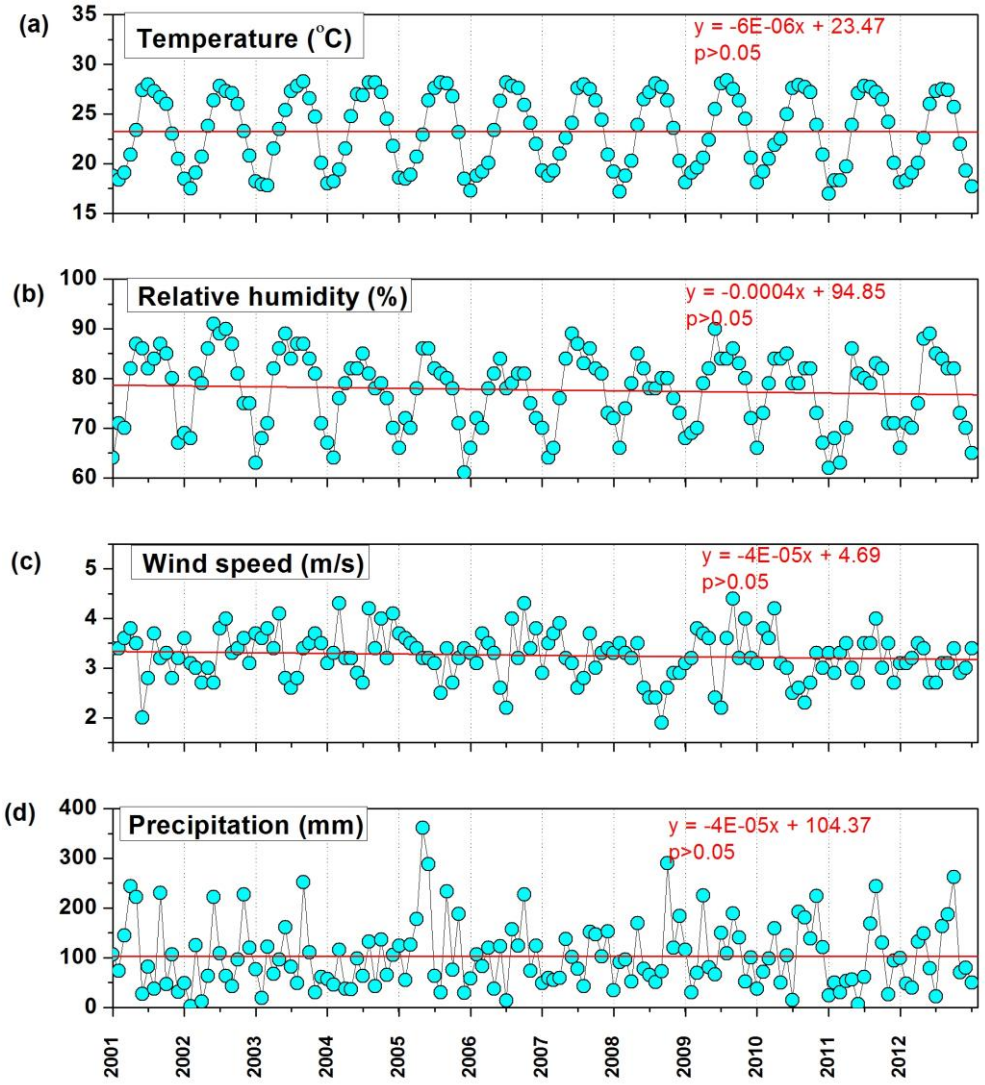

Figure S1. Temporal variations of meteorological parameters such as (a) air temperature (°C), (b) relative humidity (%), (c) wind speed (ms^{-1}), and (d) precipitation (mm) at Chichijima Island during the study period from 2001 to 2012.

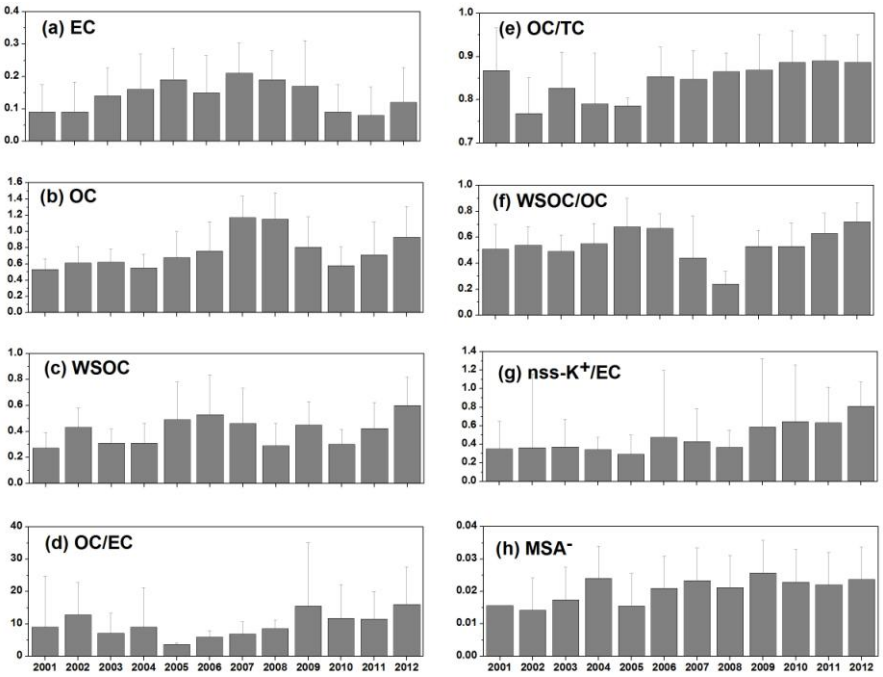

Figure S2. Annual mean variations (μg m^{-3}) of carbonaceous species as well as water-soluble ions and their mass ratios during 2001-2012 over the western North Pacific.

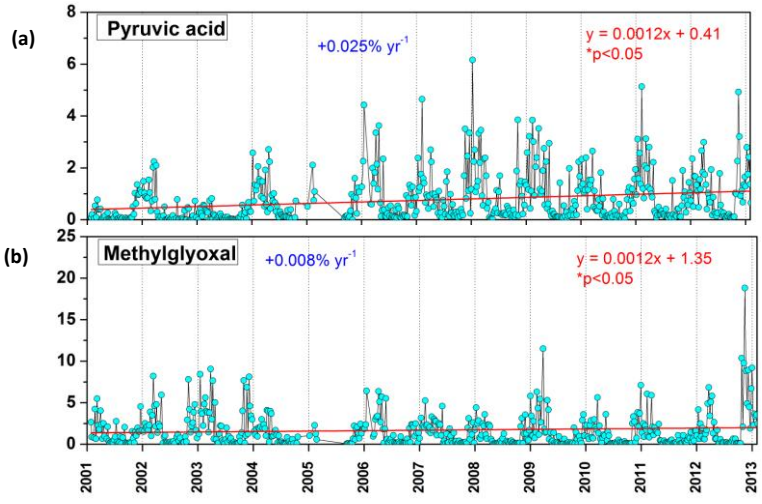

Figure S3. Annual trends in the concentrations (ng m^{-3}) of aqueous-phase photooxidations of biogenic isoprene tracer compounds (a) puruvic acid and (b) methylglyoxal during 2001-2012 over the western North Pacific.