Responses to reviewer#1 comments

This is the second review of the manuscript entitled "Long-term (2001-2012) trends of carbonaceous aerosols from remote island in the western North Pacific: an outflow region of Asian pollutants and aging". The revision is ok and can be acceptable for publication in ACP.
However, in this title the phrase "and aging" is little bit absurd. It is suggested to remove it. As a suggestion, the title "Long-term (2001-2012) trends of carbonaceous aerosols over a remote island in the western North Pacific rim: an outflow region of Asian pollutants" will be fine hopefully.
Response: Following the reviewer's suggestion, we modified the title in the revised manuscript as "Long-term (2001-2012) trends of carbonaceous aerosols from a remote island in the western North Pacific: an outflow region of Asian pollutants**".**

And little minor revisions (i.e., addition of couple of suitable references) are still needed as follows before the final and formal acceptance of the manuscript as follows:
Line 403: "EC scatters the short-wave incoming solar radiation less than OC……"
Although it is well known still the authors need to include some suitable references

Ex: Magi, B. I., 2009. Chemical apportionment of southern African aerosol mass and optical depth. Atmos. Chem. Phys., 9, 7643–7655.
Magi, B.I., 2011.Corrigendum to "Chemical apportionment of southern African aerosol mass and optical depth" published in Atmos. Chem. Phys., 9, 7643–7655, 2009. Atmos. Chem. Phys., 11, 4777–4778.
Response: Included. Please see lines 409-410 in the revised manuscript.

Line 405-407: "The single scattering albedo (SSA), defined as the ratio of scattering to the extinction coefficient of aerosols, is an important property for determining the direct RF (Pani et al., 2016)." It is suggested to add here the reference "Pani et al., 2016a" also

Pani, S.K., Wang, S.H., Lin, N.H., Lee, C.T., Tsay, S.C., Holben, B.N., Janjai, S., Hsiao, T.C., Chuang, M.T. and Chantara, S. (2016a). Radiative effect of springtime biomass-burning aerosols over Northern Indochina during 7-SEAS/BASELInE 2013 campaign. Aerosol Air Qual. Res., 16, 2802–2817.
Good Luck.
Response: Added. Please see line 412 in the revised manuscript.

Responses to reviewer#2 comments

-Marine Aerosol
The authors did tone down the language of the marine discussion some to use "suggests" instead of "shows", so it is better. But, it is still flawed, it not a main point of their work, and it should probably just be removed.
Response: We do not agree with the reviewer comment that suggests to remove the discussion on the marine contribution of organic matter in summer.
Summer is a good season to examine the ocean-derived organic matter because most of the air masses are originating from the central Pacific and there are almost negligible/no continental sources. Based on the backward trajectory analysis and WSIM/WSOM ratios, we demonstrated that source of organic matter is limitted from marine emissions. This point is

very important in this study. Thus, we prefer to keep this discussion in the revised manuscript.

The authors state that the larger ratio of WIOM to WSOM is an indicator of fresh organic matter from the ocean (because the cited works associate WIOM with primary marine emissions). But then, WIOM, which is supposedly primary, does not correlate with sea salt (not to mention the lack of wind speeds high enough to actually produce primary marine aerosol). The authors state that the lack of correlation then suggests that the source of organic is still from the ocean but from a source independent of wind speed and sea salt. This would then be the secondary organic which is associated with WSOM (according to the cited papers), making the whole argument circular and contradictory.
The authors should state that this may be from a marine source but that it is far more likely that it is from a non-marine source. There may be some marine particles mixed with those from other non-marine (anthropogenic) sources. It is incredibly difficult to perfectly separate marine air masses and sample only marine emissions. The only evidence that these particles are marine are the back trajectories from over the ocean.
Response: Based on the reviewer comment, we added following statement in the revised manuscript.

"It is also worthy to note that, although marine sources are major contributors to organic matter during summer, there are some minor influence from non-marine sources (for example, transport of biomass burning products from Southeast Asia as suggested by higher ratios of nss-K^+/EC in summer), mixed with marine sources."
Please see lines 326-330.

Additionally, there is no explanation on how Na+ was measured. If it is from a different paper, it should be still discussed briefly here.
Response: Following the reviewer comment, we added an explanation on how Na^+ was measured in section 2.2. Please see line 156 in the revised manuscript.

--CCN Discussion
Where did the concentration of sea salt come from? If this is the same that was mentioned as Calculated from Na+, this should be noted here. It is also unclear that "sea salt is not a major source of WSOC". Should this instead be "sea spray" or "ocean sources" instead? Sea salt is not a source of WSOC in general.
Response: We changed as sea spray instead of sea salt in the revised manuscript. Please see line 459.

The new discussion is better in that it shows the correlation of sea salt to CCN, in addition to WSOC to CCN. The slight increase in the correlation with WSOC+sea salt might actually be the most interesting point here. Together, they represent a larger fraction of the actual particle mass and may influence CCN activation. (The text states r = 0.69, and the figure says r = 0.68.) However, it is clear that the sea salt concentrations control that correlation, even when WSOC is added, since WSOC concentrations are so much smaller.
It is good that the authors noted that particle size is not included here, but more discussion should be added – size plays a really important role in CCN activation.
Response: We already mentioned the role of size in CCN activation in the manuscript. However, we briefly added following statements in the revised manuscript.

"Although fine particles are important for CCN activation, physico-chemical processes (coagulation, condensation and other heterogeneous reactions) can make the particles from fine to coarse mode in aqueous phase, particularly over the marine atmosphere.

Thus, bulk parameters of organic matter and its role in CCN activation are important in the remote marine atmosphere." Please see lines 455-459.

--- Grammar
This paper still needs to be edited for proper grammar. Some additional suggestions are below (but there are many more that need to be addressed).
Response: The whole manuscript was again checked carefully for English grammer and fixed errors.

L. 403: Remove "that" from "less than OC and that EC"
Response: We rephrased this sentence in the revised manuscript. Please see line 407 in the revised manuscript.

L.317: Remove "the" from "source for the both sea salt"
Response: Removed. Please see line 317 in the revised manuscript.

The following sentences are still unclear and need to be rephrased or edited.
L.247-248: "This result suggests that the dominance of SOA in carbonaceous aerosol over the western North Pacific."
Response: Rephrased in the revised manuscript as "This result suggests a dominance of SOA over the western North Pacific." Please see line 247.

L.301-303: "On the other hand, lower ratios of WSOC/OC in summer may suggest that the primary emission of OC from the ocean surface via sea-to-air flux due to the dominance of pristine marine air masses."
Response: Rephrased in the revised manuscript as "On the other hand, we found lower ratios of WSOC/OC in summer. This result may suggest a minor contribution of water-soluble organic matter in summer due to a negligible contribution of aged continental air masses and/or significant contribution of fresh marine air masses from the central Pacific." See lines 300-303 in the revised manuscript.

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

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

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

1. Introduction

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

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

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

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

2. Instrumentation and data analyses

2.1. Sampling site and aerosol collection

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

2.2. Analyses of carbonaceous aerosols

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

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

153 a total organic carbon (TOC) analyzer (Shimadzu, TOC-Vcsh) equipped with a catalytic
154 oxidation column and non-dispersive infrared detector (Miyazaki et al., 2011).
155 Concentrations of water-soluble methanesulfonate (MSA^-), non sea-salt sulfate (nss-
156 SO_4^{2-}), non sea-salt potassium (nss-K^+) and sodium (Na^+) were taken from the study of
157 Boreddy and Kawamura (2015), in order to support the inferences related to carbonaceous
158 species over the western North Pacific, which were determined using ion chromatography
159 (761 Compact IC, Metrohm, Switzerland).
160 The analytical errors in the replicate analyses were less than 10% for OC, EC and
161 WSOC in this study. The concentrations of carbonaceous aerosols reported in this study were
162 corrected for field blanks. The levels of blanks were less than 5% for all the parameters in the
163 real samples.
164
165 **2.3. Statistical analyses**
166 Two statistical approaches were used to better conduct the trend analyses in time
167 series of WSOC, EC, and OC and their ratios during 2001-2012. First, the tendency (linear
168 trend) equation was used for each time series (Draper and Smith, 1966). Second, all trends
169 were assessed by using the Mann-Kendall non-parametric test (Mann, 1945; Kendall, 1975),
170 which is completely independent of the first approach. More detailed information about these
171 statistical analyses are described in supporting information (SI).
172
173 **3. Results and discussion**
174 **3.1 Air mass back trajectories and general meteorology**
175 To better understand the influence of heterogeneity in air masses to carbonaceous
176 aerosols, we computed daily 7-day isentropic air mass back trajectories at an altitude of 500
177 m for each month using the hybrid single particle Lagrangian-integrated trajectory (HYPLIT)
178 model (Draxler and Rolph, 2013) during 2001-2012 as shown in Figure 2. We also
179 investigated the MODerate resolution Imaging Spectroradiometer (MODIS) derived fire
180 count data along with the back trajectories to understand the intensity of biomass burning
181 over East Asia and South/Southeast Asia. Fire spot data were downloaded from the MODIS
182 website over the region (80°-150°E; -10-70°N) during the year 2001 as an example for all the
183 years (2001-12) because of overlapping (there is no much difference in the intensity and area
184 of fire spots). More detailed information about the monthly air mass back trajectories and fire
185 data for each year during 2001-2012 was described elsewhere (Verma et al., 2015). From
186 Figure 2, it is obvious that from winter (December-February) to spring (March-May) the air

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

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

3.2 Monthly/seasonal variations

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

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

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

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

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

It is well documented that nss-K^+ and EC are the tracers for biomass burning and fossil fuel combustion emissions, respectively. Therefore, nss-K^+/EC ratios were widely used

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

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

In this study, we found that monthly mean WSOC/OC ratios were >4.0 for all months except for September, indicating a significant contribution from SOA over the western North Pacific. The seasonal variation of WSOC/OC showed higher values (monthly mean: 0.44 to 0.62) during winter-spring months (Figure 3f), implying that the SOA formation was

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

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

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

biota, which is further evidenced by the higher concentrations of azelaic acid (a specific photochemical oxidation product of biogenic unsaturated fatty acids emitted from the ocean surface (Kawamura and Sakaguchi, 1999)) during summer and autumn over the western North Pacifc for the same study period (Boreddy et al., 2017). It is also worthy to note that, although marine sources are major contributors to organic matter during summer, there are some minor influence from non-marine sources (for example, transport of biomass burning products from Southeast Asia as suggested by higher ratios of nss-K^+/EC in summer), mixed with marine sources.

3.3 Annual trends

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

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

significantly over the western North Pacific whereas the contributions of fossil fuel combustion have decreased.

The annual trend of WSOC showed a significant increase ($p<0.05$; +0.18% yr^{-1}) from 2001 to 2012 (Figure 5c), implying an important SOA formation over the western North Pacific because SOA largely consists of water-soluble matter (Weber et al., 2007; Kondo et al., 2007). Generally, atmospheric aging makes aerosols more water-soluble during long-range transport (Aggarwal and Kawamura, 2009; Rudich et al., 2007; Robinson et al., 2007; Jimenez et al., 2009; Kawamura et al., 2010), especially in the remote marine atmosphere (Kawamura et al., 2003). This point is further supported by a decadal increase (+0.08% yr^{-1}) in the WSOC/OC ratios (Figure 5f). These results may demonstrate that the formation of WSOC (or OC) over the western North Pacific is significantly linked with photochemical aging of aerosols and oxidation of various VOCs during long-range atmospheric transport (Zhang et al., 2007; Decesari et al., 2010). A significant increasing trend of WSOC/TC ($p<0.05$; +0.15% yr^{-1}; Table 2) again suggests that formation of SOA and its contributions to carbonaceous aerosols have significantly increased over the western North Pacific during 2001-2012.

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

Zhang et al. (2016) have reported an increase (from 132000 to 175000t yr^{-1}) in the emission of isoprene in northern China during 1982-2010 using an emission model. Consistently, Stavrakou et al. (2014) reported that an increased isoprene emission (+0.52% yr^{-1}) over Asia, especially China during 1979-2012. Based on strong correlations ($r>0.90$) between isoprene and above-canopy temperature, they suggested that oxidations of biogenic

BVOCs from the terrestrial higher plants are important in Asia (especially in China). Since Chichijima is an outflow region of East Asia, long-range atmospheric transport of BVOCs may be possible from terrestrial higher plants in Asia/China to the western North Pacific by westerly winds, which may significantly contribute to the enhanced trends of OC and WSOC during 2001-2012. We found significant ($p<0.05$) increases in the annual trends of methylglyoxal and pyruvic acid, which are tracers of aqueous-phase oxidation of biogenic isoprene (Carlton et al., 2009), over the western North Pacific as shown in Figure S3. We also found a moderate correlation ($r=0.40$, $p<0.01$) between of MSA^- and WSOC concentrations (not shown as a figure). These results demonstrate that increase of WSOC is likely due to the increased photochemical oxidation of BVOCs during long-range transport over the western North Pacific in addition to the other emissions such as biomass burning.

3.4 Atmospheric implications

It is well known that atmospheric aerosols play a key role in the climate system as they can act as cloud condensation nuclei (CCN) and impact cloud formation and thus, radiative forcing (RF) (IPCC, 2013). The RF of aerosol is generally estimated by using the aerosol optical depth (AOD), single scattering albedo (SSA) and asymmetry parameter (Pani et al., 2016a). EC scatters the short-wave incoming solar radiation less than OC, although it strongly absorbs the short-wave solar radiation as well as long-wave outgoing terrestrial radiation in the atmosphere (Charlson et al., 1992; Ramanathan et al., 2001; Magi, 2009; 2011). The single scattering albedo (SSA), defined as the ratio of scattering to the extinction coefficient of aerosols, is an important property for determining the direct RF (Pani et al., 2016a; 2016b). The SSA is highly sensitive to the nature (scattering and/or absorption) of aerosols in the atmosphere. Therefore, although OC has certain uncertainty because of light absorbing brown carbon, the OC/EC ratios can be used to understand the relative contributions of scattering or absorbing aerosols in the atmosphere.

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

implication for radiative forcing because scattering and absorption coefficients are playing crucial role in the radiative forcing calculations as mentioned above.

Novakov and Corrigan (1996) found that pure organic components from biomass smoke emissions can form cloud condensation nuclei (CCN) without the presence of sulfate (SO_4^{2-}) and other inorganic compounds. Roberts et al. (2002) showed that biomass burning derived organic aerosols does serve as CCN. Further, large loadings of CCN in continental air masses were observed over the western North Pacific (Matsumoto et al., 1997; Boreddy et al., 2015). In this study, the enhanced WSOC concentrations and WSOC/OC ratios in continental air masses suggest an important role of WSOC in CCN activity over the western North Pacific in addition to other particles such as SO_4^{2-} and sea-salts. To better understand the impact of WSOC on cloud forming potential, we performed regression analyses between WSOC, sea salt and CCN concentrations as shown in Figure 6. CCN data were downloaded from the MODIS satellite over the region (140°–145° E, 25°–30° N) in the western North Pacific for the period of July 2002 to December 2012. The results show significantly good correlations ($r=0.61$ and 0.64, $p<0.05$) between WSOC versus CCN and sea salt versus CCN concentrations (Figure 6a and 6b), suggesting the importance of WSOC for the formation of CCN over the western North Pacific in addition to sea salt. Further, the correlation coefficient between sea salt and CCN concentrations was slightly increased ($r=0.68$; $p<0.05$) when WSOC was added to the sea salt as shown in Figure 6c. Likely, the slope of the regression line between WSOC+sea salt and CCN concentrations was little higher (2.21E7) than the slope between sea salt and CCN concentrations (2.19E7). These results indicate that WSOC may slightly enhance the cloud forming potential of sea salt, although it has less concentration over the western North Pacific. All these results suggest that significant uncertainty exists in RF due to the contribution of water-soluble organic matter to cloud forming. Therefore, climate modelers should consider WSOC in addition to other factors (sea-salts, sulfate, etc.,), while calculating RF over the western North Pacific. This point is consistent with the previous studies, which explain the contribution of water-soluble organic matter to CCN (Matsumoto et al., 1997; Zhao et al., 2016).

It should be noted that all these ratios are applicable to organic fractions that are derived from the bulk measurements only; however, the size of the particle also plays a role on RF as well as their morphology, chemical composition and mixing state (Jacobson, 2001; Lohmann and Feichter, 2005; Zhang et al., 2008a). Although fine particles are important for CCN activation, physico-chemical processes (coagulation, condensation and other heterogeneous reactions) can make the particles from fine to coarse mode in aqueous phase,

particularly over the marine atmosphere. Thus, bulk parameters of organic matter and its role in CCN activation are important in the remote marine atmosphere. The sea spray is not a major source of WSOC as inferred from Figure 6d, which showed a moderate correlation (r=0.42; p>0.05) between WSOC and sea salt during the study period. In this study, atmospheric processes or chemical aging makes OC more water-soluble during long-range transport over the western North Pacific as discussed in section 3.2.

4. Conclusions

Based on the long-term (2001-2012) trends of carbonaceous aerosols from Chichijima Island in the western North Pacific, we conclude that the seasonal variations of carbonaceous aerosols strictly followed seasonal trends of wind pattern at Chichijima in the western North Pacific. The annual trends of OC and WSOC with significant increases over the western North Pacific are probably due to the enhanced photochemical oxidation of biomass burning- and biogenic-derived VOCs during long-range atmospheric transport over the western North Pacific. This inference is supported by significant increases in the annual trends of OC/EC, WSOC/OC, OC/TC, WSOC/TC, nss-K^+/EC mass ratios and MSA^- concentrations. On the other hand, a decrease in the concentrations of EC during 2001-2012 suggests that the contribution of fossil fuel-derived sources to carbonaceous aerosols may be decreased over the western North Pacific. Further, a good correlation (r=0.61) between WSOC and CCN concentrations suggests that not only sea salt and nss-SO_4^{2-} but also water-soluble organic aerosols play a role in CCN formation. Therefore, the results from our study have important implications toward the regional radiative balance, especially over the North Pacific.

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

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

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

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

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

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

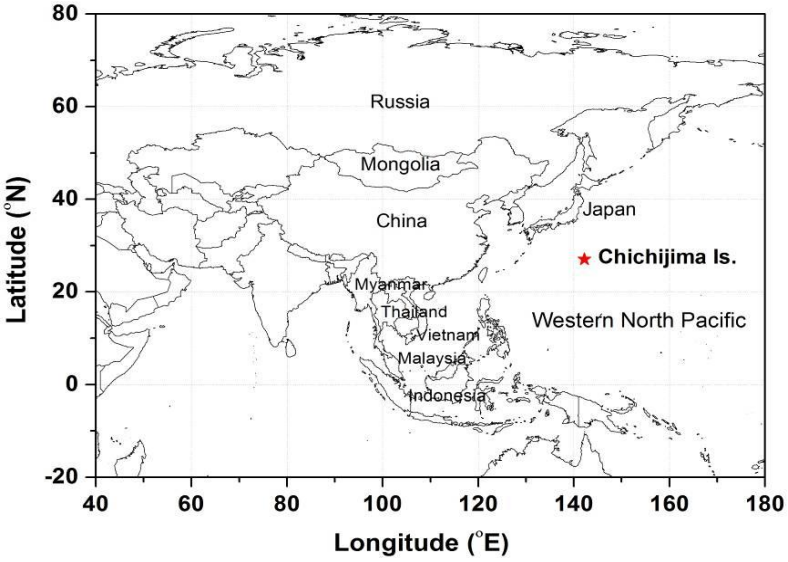

Figure 1. Location of sampling site (indicated by red colored '*') in the western North Pacific and its adjacent Asian countries.

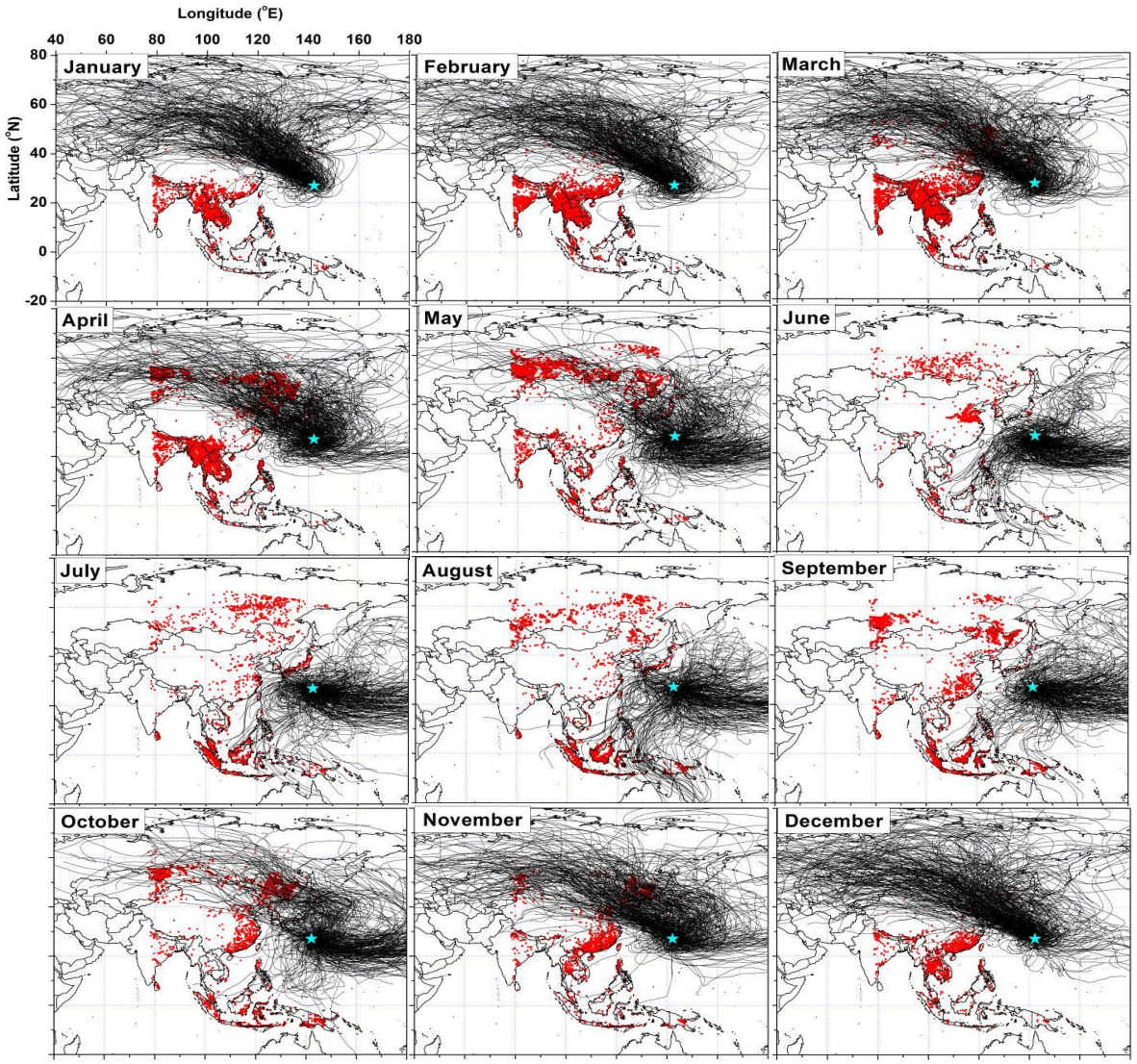

Figure 2. 7-day daily air mass back trajectories at 500 m a.g.l. computed using HYPLIT model for each month during 2001-2012 at Chichijima Island in the western North Pacific. The symbol '*' indicates the sampling site and red dots represent the MODIS inferred fire spots. Fire spots were downloaded for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

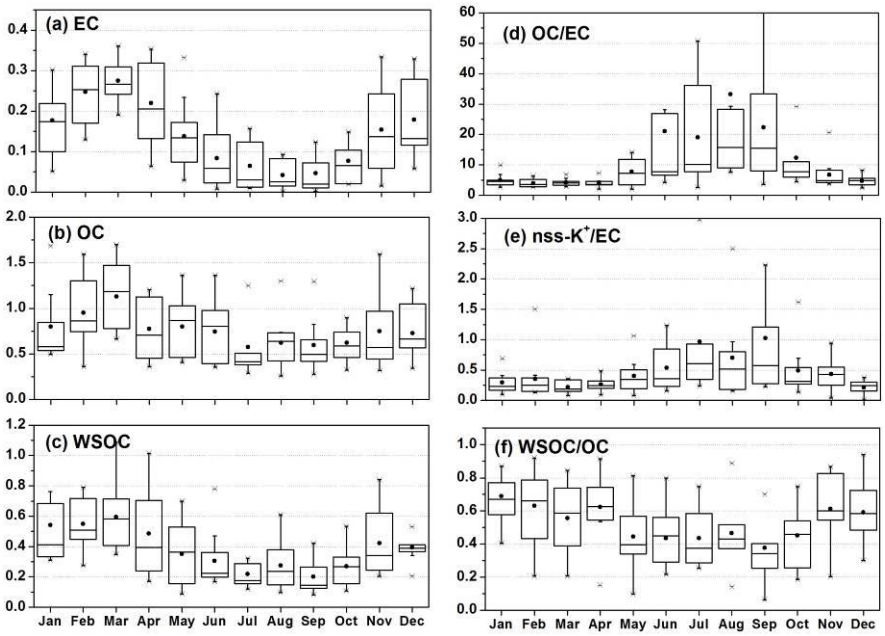

Figure 3. Box-whisker plots of monthly variations of carbonaceous aerosol components (μg m^{-3}) and some specific mass ratios at Chichijima Island in the western North Pacific during 2001-2012. The horizontal line and small dot inside the box indicate maiden and mean, respectively. The vertical hinges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

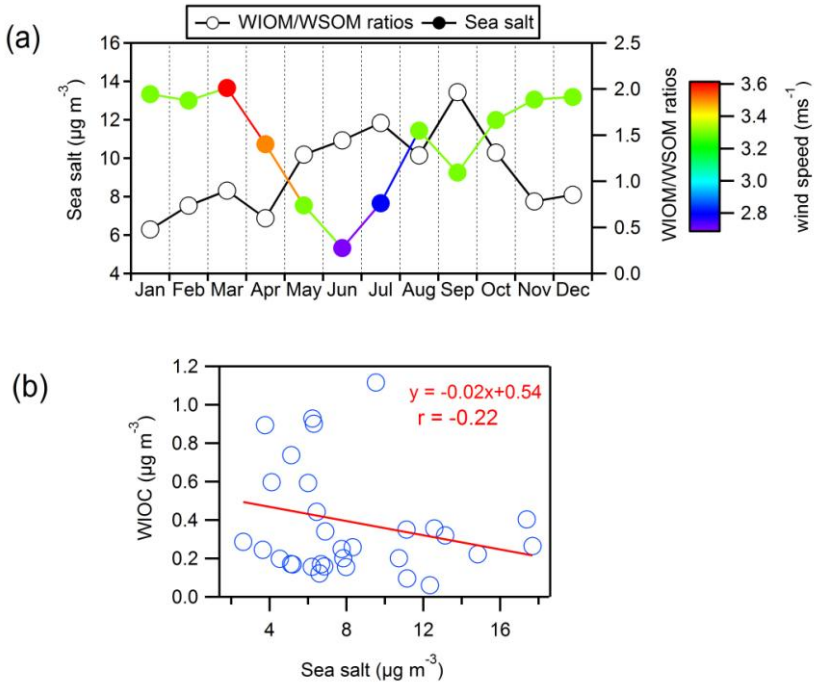

Figure 4. Monthly variations (a) WSIM/WSOM mass ratios and sea salt concentrations and (b) regression analysis between WIOC and sea salt concentrations. The color scale in the Figure 4(a) indicates the wind speed over the western North Pacific.

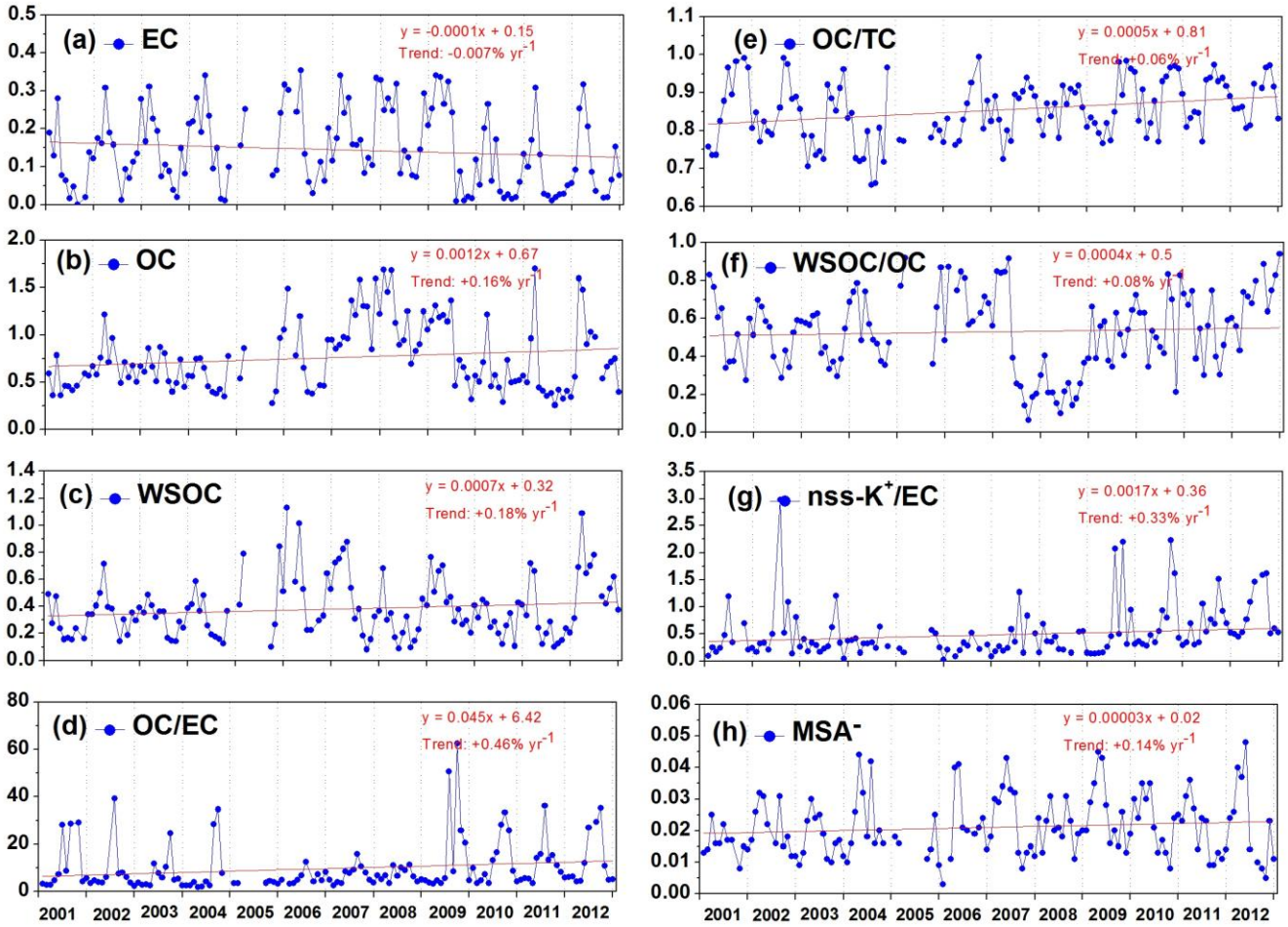

Figure 5. Annual trends (time series) in the concentrations (μg m^{-3}) of carbonaceous aerosol components, water-soluble ionic tracer compound (MSA^-) and some specific mass ratios during 2001-2012 over the western North Pacific. The liner trend equation (y=mx+c) is also shown for the each annual trend.

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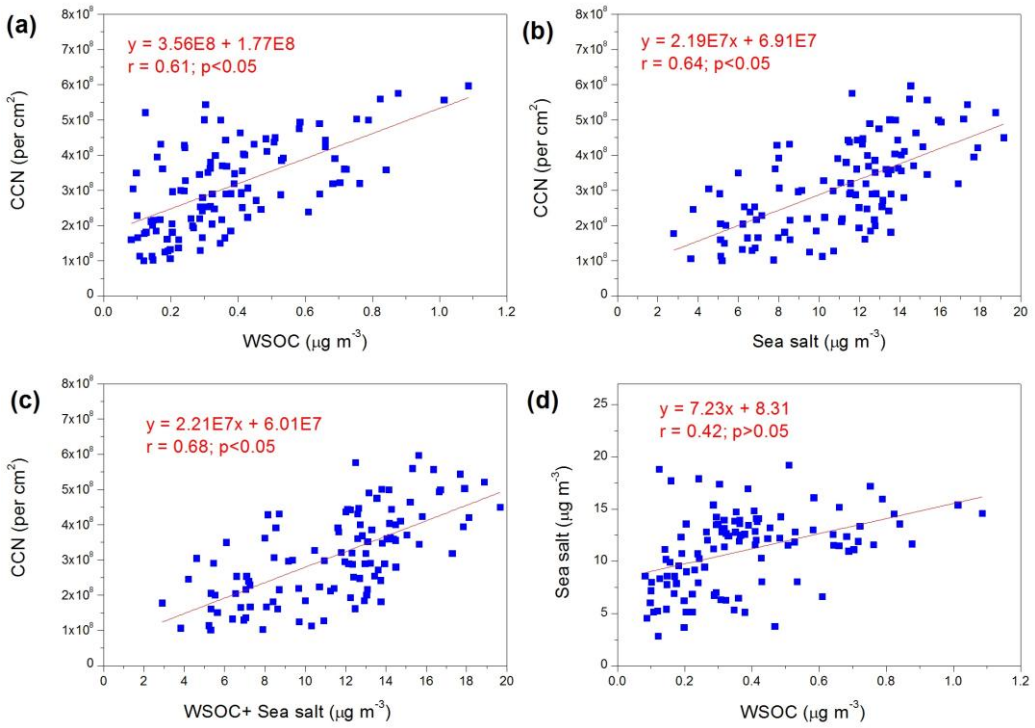

Figure 6. Regression analyses between (a) WSOC and MODIS-derived cloud condensation nuclei (CCN), (b) sea salt and CCN, (c) WSOC+seasalt and CCN, and (d) WSOC and sea salt concentrations over the western North Pacific.