**Responses to editor's comments**

We really appreciate the efforts made to address the reviewers questions and comments. Nevertheless I believe there are still some minor points that need the author revision, in order to improve accuracy of the discussion on carbonaceous aerosol sources. Here is a list of editor's comments:

**Response:** We thank the Editor for the careful reading and valuable suggestions on our manuscript. We revised the manuscript according to the editor's comments. Our responses are indicated by the blue color. The changes in the revised manuscript are highlighted with yellow color. Please find the responses followed by the revised manuscript

Line 90: rephrase as: "Using the emission estimated by Model of Emissions of Gases and Aerosols from Nature (MEGAN) and combined with the MOdel of HYdrocarbon Emissions from the CANopy (MOHYCAN) model,"

**Response:** Rephrased. Please see lines 91-92 in the revised manuscript.

Line 233: please rephrase as follows to take into account aqueous phase chemistry: "gas-to-particle conversion and heterogeneous phase processing in the atmosphere

**Response:** Rephrased. Please see lines 232 in the revised MS. Thank you.

Line 239: "The OC/EC ratios > 2.0 have been used to point out the presence of secondary organic aerosols (SOA)". But it can also be due to biomass burning emissions, which are POA.

**Response:** We rephrased this statement in the revised manuscript as given below.

"Atmospheric aerosols emitted from fossil fuel combustion are characterized by lower OC/EC ratios (< 2.0) whereas higher OC/EC ratios (> 2.0) have been used to point out the presence of secondary OA (SOA) (Cao et al., 2003; Chow et al., 1996; Kunwar and Kawamura, 2014; Pani et al., 2017) in the atmosphere with a limited impact of biomass burning."

Please see lines 237-241 in the revised MS.

Line 251: this line seems to contradict line 247, where SOA is recognized as the main source of carboncaeous aerosol "…biomass burning and fossil fuel combustion are important sources for contribute to carbonaceous aerosols over the western North Pacific in winter to spring.

**Response:** Rephrased. Please see lines 250-251 in the revised MS.

Line 253 : Please rephrase as :It is well documented that nss-K+ and EC are the can be used as tracers…"

These are not the unique sources of EC and nss-K+.

**Response:** Rephrased. Please see line 252 in the revised MS.

Line 273 :" (Kanakidou et al., 2005; Kondo et al., 2007) and references therein).

**Response:** Rephrased. Please see lines 272-273 in the revised MS. Thank you.

Line 272-284: this paragraph is confused. It uses WSOC/OC as an indicator of SOA, but it also says that biomass burning (a POA component) emits WSOC. I would suggest to rephrase the sentence as follows: "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), in ambient with limited biomass burning impact 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."

Gilardoni et al., 2016 is not an appropriate reference here since it refers to an environment strongly affected by wood burning emissions.
**Response:** Rephrased as suggested. Please see lines 276-280 in the revised manuscript.

Line 321-326. Please rephrase the sentence. It is not clear as it is written now.
In addition, the WIOM is attributed to marine primary aerosol, although it does not correlate with wind speed and sea salt. This attribution is weak. The link between the WIOC in summer and autumn and marine sources is based on the higher concentration of azelaic acid in these seasons. The increase of azelaic acid in summer and autumn could also be due to the higher contribution of biomass burning, in agreement with higher nss $K^+$/EC. In fact, azeliac acid is also found in biomass burning plumes form oxidation of fatty acids released by fires (Graham et al., 2002 JGR).
**Response:** Rephrased as "This result suggests that an additional source of organic matter (completely independent from sea salt production and wind speed) which is evidenced by the higher $MSA^-$/nss-$SO_4^{2-}$ mass ratios (Boreddy and Kawamura, 2015) and higher concentrations of azelaic acid (Boreddy et al., 2017) during summer and autumn. $MSA^-$/nss-$SO_4^{2-}$ mass ratios have been suggested as an indicator for the relative contribution of oceanic dimethyl sulfide (DMS) vs. anthropogenic sources to sulfate (Gondwe et al., 2004; Savoie and Prospero, 1989). Higher ratios indicate that nss-$SO_4^{2-}$ is derived from the atmospheric oxidation of oceanic DMS, while lower ratios suggest the anthropogenic contribution of $SO_2$. On the other hand, azelaic acid is a specific photochemical oxidation product of unsaturated fatty acids emitted from the ocean surface (Kawamura and Sakaguchi, 1999) and also found in biomass burning plumes (Graham et al., 2002)."
Please see lines 320-330 in the revised MS.

Line 345: Since high OC/EC and OC/TC ratio can indicate both higher SOA mass fraction or higher biomass burning mass fraction, I would suggest to rephrase the sentence as follows:
"However, the annual trends of OC/EC and OC/TC ratios increased significantly (p<0.05; +0.46% yr-1 and +0.06% yr-346 ) 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 primary fossil fuel combustion to carbonaceous aerosols has declined during the sampling period.

**Response:** Rephrased. Please see lines 349-352 in the revised MS.

Line 358-371: Since the site is affected by biomass burning emissions from south Asia, and biomass burning emits WSOC species, the use of WSOC or WSOC/OC as an indicator of SOA increase over years is misleading. Do you have any idea about the sudden decrease of WSOC/OC in 2007-2008?

**Response:** Rephrased as "Previous studies suggested that SOA is largely composed of water-soluble organic matter (Weber et al., 2007; Kondo et al., 2007). In this study, the annual trend of WSOC showed a significant increase ($p<0.05$; +0.18% $yr^{-1}$) from 2001 to 2012 (Figure 5c). 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 increased concentrations of WSOC over the western North Pacific are significantly linked with increased photochemical aging of organic aerosols and oxidation of various VOCs during long-range atmospheric transport (Zhang et al., 2007; Decesari et al., 2010). An increasing trend of WSOC/TC ($p<0.05$; +0.15% $yr^{-1}$; Table 3) again suggests that photochemical formation of WSOC and its contributions to SOA have increased over the western North Pacific during 2001-2012. We observed an abrupt decrease in the WSOC/OC ratios between 2007 and 2008 (Figure 5f), probably due to enhanced OC that may be caused by unknown sources. However, it should be noted that an observed decline in the WSOC/OC ratios does not affect the decadal trend even if those data are excluded from the trend analysis."

Please see lines 360-376 in the revised MS.

1   **Long-term (2001-2012) trends of carbonaceous aerosols from a remote island in the**
2   **western North Pacific: an outflow region of Asian pollutants**
3

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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 that photochemical formation of WSOC and its contributions to secondary organic aerosols (SOAs) have increased over the western North Pacific via 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 primary 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, further suggesting that photochemical formation of WSOC and its contributions to SOAs have increased over the western North Pacific during 2001-2012 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 the 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 the IPCC 2013 report. However, there still exist large uncertainties in quantifying radiative forcing of carbonaceous aerosols, particularly with regard to OA (Reddy and Boucher, 2004).

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

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

118

119    **2. Instrumentation and data analyses**

120    **2.1. Sampling site and aerosol collection**

121        Figure 1 shows the location of the sampling site and its adjacent Asian countries in

122    the western North Pacific. TSP samples were collected at the Satellite Tracking Centre of the

123    Japan Aerospace Exploration Agency (JAXA, elevation: 254 m) in Chichijima Island

124    (27°04′N; 142°13′E) on a weekly basis (Boreddy and Kawamura, 2015). Aerosol samples are

125    collected on pre-combusted (450° C for 3-5 h) quartz filter (20 × 25 cm, Pallflex 2500QAT-

126    UP) using a high volume air sampler (HVS) with a flow rate of 1 m$^3$ min$^{-1}$. The HVS was

127    installed at a height of 5 m above the ground level. The filters were placed in a pre-baked

128    (450°C for 6 h) glass jar (150 mL) with a Teflon-lined screw cap before sample collection.

129    After aerosol collection, the filters were recovered into the glass jar, transported to the

130    laboratory in Hokkaido University, Sapporo, and stored in a freezer room at −20 °C prior to

131    analysis. A total of 545 aerosol samples and about 56 field blank samples were used for the

132    analysis of carbonaceous components during 2001-2012.

133

134    **2.2. Analyses of carbonaceous aerosols**

135        Concentrations of OC and EC were determined using a Sunset Laboratory carbon

136    analyzer following the IMPROVE (Interagency Monitoring of Protected Visual

137    Environments) thermal/optical evolution protocol (Wang et al., 2005), assuming carbonate

138    carbon (CC) in  the aerosol samples to be insignificant (Chow and Watson, 2002). Previous

139    studies have also shown that carbonate, particularly calcium carbonate, levels were low or

140    negligible in most ambient samples, which were analyzed by IMPROVE protocol (Wang et

141    al., 2005; Clarke and Karani, 1992; Chow et al., 2001). A filter cut of 1.54 cm$^2$ of each filter

142    was placed in a quartz tube inside the thermal desorption chamber of the analyzer and then

143    stepwise heating was applied. Helium (He) gas was applied in the first ramp and was

144    switched to mixture of He/O$_2$ in the second ramp. The evolved CO$_2$ during the oxidation at

145    each temperature step was measured by non dispersive infrared (NDIR) detector system. The

146    calculated detection limits of OC and EC were 0.05 and 0.02 μgC m$^{-3}$, respectively. The sum

147    of OC and EC was considered to as total carbon (TC) in this study.

148        To determine WSOC, a punch of 20 mm in diameter of each filter was extracted with

149    20 mL organic-free ultra pure water (>18.2 MΩ cm, Sartorius arium 611 UV) and

150    ultrasonicated for 30 min. These extracts were passed through a disk filter (Millex-GV, 0.22

151    μm pore size, Millipore) to remove the filter debris and insoluble particles and analyzed using

152  a total organic carbon (TOC) analyzer (Shimadzu, TOC-Vcsh) equipped with a catalytic

153  oxidation column and non-dispersive infrared detector (Miyazaki et al., 2011).

154      Concentrations of water-soluble methanesulfonate (MSA$^-$), non sea-salt sulfate (nss-

155  SO$_4^{2-}$), non sea-salt potassium (nss-K$^+$) and sodium (Na$^+$) were taken from the study of

156  Boreddy and Kawamura (2015), in order to support the inferences related to carbonaceous

157  species over the western North Pacific, which were determined using ion chromatography

158  (761 Compact IC, Metrohm, Switzerland).

159      The analytical errors in the replicate analyses were less than 10% for OC, EC and

160  WSOC in this study. The concentrations of carbonaceous aerosols reported in this study were

161  corrected for field blanks. The levels of blanks were less than 5% for all the parameters in

162  real samples.

163

164  **2.3. Statistical analyses**

165      Two statistical approaches were used to better conduct the trend analyses in time

166  series of WSOC, EC, and OC and their ratios during 2001-2012. First, the tendency (linear

167  trend) equation  was  used for each time series (Draper and Smith, 1966). Second, all trends

168  were assessed by using the Mann-Kendall non-parametric test (Mann, 1945; Kendall, 1975),

169  which is completely independent of the first approach. More detailed information about these

170  statistical analyses are described in supporting information (SI).

171

172  **3. Results and discussion**

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

174      To better understand the influence of heterogeneity in air masses to carbonaceous

175  aerosols, we computed daily 7-day isentropic air mass back trajectories at an altitude of 500

176  m for each month using a hybrid single particle Lagrangian-integrated trajectory (HYPLIT)

177  model (Draxler and Rolph, 2013) during 2001-2012 as shown in Figure 2. We also

178  investigated the MODerate resolution Imaging Spectroradiometer (MODIS) derived fire

179  count data along with the back trajectories to understand the intensity of biomass burning

180  over East Asia and South/Southeast Asia. Fire spot data were downloaded from the MODIS

181  website over the region (80° to 150°E; 10°S to 70°N) during the year 2001 as an example for

182  all the years (2001-12) because of overlapping (there is no much difference in the intensity

183  and  area  of  fire  spots).  More  detailed  information  about  the  monthly  air  mass  back

184  trajectories and fire data for each year during 2001-2012 are described elsewhere (Verma et

185  al., 2015). From winter (December-February) to spring (March-May), the air masses carry

186 continental air pollutants and dusts from East Asia to the sampling site in the Pacific by a

187 long-range atmospheric transport (Figure 2). The continental air masses are absent in summer

188 (June to August) with the pristine air masses coming from the central Pacific to the

189 observation site. In autumn (September-November), the air mass pattern shifts from

190 southeasterly to northwesterly with stronger winds towards winter.

191   Figure S1 shows the temporal variations of meteorological parameters such as air

192 temperature (°C), relative humidity (%), wind speed (m s$^{-1}$), and precipitation (mm) at

193 Chichijima Island during the study period of 2001-2012. All the meteorological parameters

194 were downloaded from the Japan Meteorological Agency (JMA). There was a clear seasonal

195 variation in ambient temperature, relative humidity, and precipitation with summer maxima

196 and winter minima. Wind speeds were higher in winter to spring and lower in summer.

197

198 **3.2 Monthly/seasonal variations**

199   Figure 3 (a-f) presents the monthly/seasonal variations in the concentrations of EC,

200 OC, WSOC and some specific mass ratios at Chichijima Island in the western North Pacific

201 during 2001-2012. The corresponding statistical data were reported in Table 1. All measured

202 species (EC, OC, and WSOC) clearly showed winter-to-spring maxima (highest

203 concentration was in March) and summer minima (lowest in July) and then increase towards

204 autumn. The seasonal variation in carbonaceous aerosols observed in this study was found

205 consistent with the typical seasonal pattern in ambient carbonaceous aerosols over China

206 (Zhang et al., 2008b; Cao et al., 2006), indicating a common source for these components,

207 which are long-range transported to the western North Pacific. This, of course, can also be

208 influenced by seasonal meteorology and air mass back trajectories over the western North

209 Pacific as discussed in section 3.1.

210   Relatively higher monthly average concentrations up to 0.28, 1.13 and 0.59 µg m$^{-3}$

211 were observed for EC, OC, and WSOC in March. In contrast, their monthly averages were

212 lower in summer or early autumn (July or September) with the concentrations of 0.04, 0.58,

213 and 0.20 µg m$^{-3}$, respectively (Table 1). It is well documented that in summer, a maritime

214 high-pressure wind dominates over the western North Pacific in which the air masses are

215 pristine and less influenced by the continental outflow from East Asia (Figure 2). This

216 observation is consistent with the fact that concentrations of anthropogenic nss-$SO_4^{2-}$, $NO_3^-$,

217 $NH_4^+$, and nss-$K^+$ showed similar seasonal variations with winter and/or spring maxima and

218 summer minima (Boreddy and Kawamura, 2015). On the other hand, continental air masses

219 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, suggest 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 and heterogeneous phase processing in the atmosphere. The precursors of secondary OC may also come from biogenic sources in addition to fossil fuel combustion 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 (> 2.0) have been used to point out the presence of secondary OA (SOA) (Cao et al., 2003; Chow et al., 1996; Kunwar and Kawamura, 2014; Pani et al., 2017) in the atmosphere with a limited impact of biomass burning. Table 2 summarizes OC/EC ratios reported for various sources of aerosol particles. The split of OC/EC ratios at higher or lower than 2 (fromTable 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 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 contribute to carbonaceous aerosols over the western North Pacific in winter-to-spring.

It is well documented that nss-$K^+$ and EC can be used as 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 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). 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), higher WSOC/OC ratios under ambient conditions with limited biomass burning impact have been used 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). 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 to spring months (Figure 3f), implying that SOA formation was enhanced

due to an 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 from marine biota. 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 = $3.2 \times Na^+$, 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 result suggests that an additional source of organic matter (completely independent from sea salt production and wind speed) which is evidenced by the higher

322   MSA$^-$/nss-SO$_4^{2-}$ mass ratios (Boreddy and Kawamura, 2015) and higher concentrations of

323   azelaic acid (Boreddy et al., 2017) during summer and autumn. MSA$^-$/nss-SO$_4^{2-}$ mass ratios

324   have been suggested as an indicator for the relative contribution of oceanic dimethyl sulfide

325   (DMS) vs. anthropogenic sources to sulfate (Gondwe et al., 2004; Savoie and Prospero,

326   1989). Higher ratios indicate that nss-SO$_4^{2-}$ is derived from the atmospheric oxidation of

327   oceanic DMS, while lower ratios suggest the anthropogenic contribution of SO$_2$. On the other

328   hand, azelaic acid is a specific photochemical oxidation product of unsaturated fatty acids

329   emitted from the ocean surface (Kawamura and Sakaguchi, 1999) and also found in biomass

330   burning plumes (Graham et al., 2002). Therefore, it is worthy to note that, although marine

331   biogenic sources are major contributors to organic matter during summer to autumn, there are

332   some influence from non-marine sources (for example, transport of biomass burning products

333   from Southeast Asia as suggested by higher ratios of nss-K$^+$/EC in summer), mixed with

334   marine sources.

335

336   **3.3 Annual trends**

337        Figure 5 shows the annual trends in the concentrations of EC, OC, TC (EC+OC),

338   WSOC, and WSOC/OC ratios during the period of 2001-2012 over the western North Pacific

339   (see Figure S2 for annual mean variations). Table 3 summarizes the results of the statistical

340   analyses. All the annual trends of chemical species and WSOC/OC ratios seem to present

341   clear seasonal patterns with higher values in winter-spring and lower values in summer. On

342   the other hand, seasonal variations of the OC/EC and nss-K$^+$/EC ratios showed higher values

343   in summer.

344        As seen from Figure 5a-b and Table 3, concentrations of EC, OC, and TC during

345   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

346   μg m$^{-3}$) and 0.28 to 2.01 μg m$^{-3}$ (0.90 μg m$^{-3}$), respectively. The annual variations of EC

347   showed a decreasing trend (-0.007% yr$^{-1}$), while OC and TC trends are continuously

348   increasing (+0.16% yr$^{-1}$ and +0.11% yr$^{-1}$, respectively) from 2001 to 2012 although the rates

349   were not significant (p>0.05). However, the annual trends of OC/EC and OC/TC ratios

350   increased significantly (p<0.05; +0.46% yr$^{-1}$ and +0.06% yr$^{-1}$) from 2001 to 2012 (Figure 5d

351   and 5e), suggesting that the contribution of primary fossil fuel combustion to carbonaceous

352   aerosols has declined during the sampling period. This point is supported by the annual trend

353   of nss-K$^+$/EC mass ratios, which showed a significant increase (p<0.05; +0.33% yr$^{-1}$) during

354   the sampling period (Figure 5g). This observation is consistent with the study of Verma et al.

355   (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.

Previous studies suggested that SOA is largely composed of water-soluble organic matter (Weber et al., 2007; Kondo et al., 2007). In this study, the annual trend of WSOC showed a significant increase (p<0.05; +0.18% $yr^{-1}$) from 2001 to 2012 (Figure 5c). 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 increased concentrations of WSOC over the western North Pacific are significantly linked with increased photochemical aging of organic aerosols and oxidation of various VOCs during long-range atmospheric transport (Zhang et al., 2007; Decesari et al., 2010). An increasing trend of WSOC/TC (p<0.05; +0.15% $yr^{-1}$; Table 3) again suggests that photochemical formation of WSOC and its contributions to SOA have increased over the western North Pacific during 2001-2012. We observed an abrupt decrease in the WSOC/OC ratios between 2007 and 2008 (Figure 5f), probably due to enhanced OC that may be caused by unknown sources. However, it should be noted that an observed decline in the WSOC/OC ratios does not affect the decadal trend even if those data are excluded from the trend analysis.

To better understand the contributions of photochemical oxidation of biogenic VOCs to WSOC during long-range atmospheric transport, we present the annual trend of water-soluble organic ion, i.e., $MSA^-$ (a biogenic tracer; see Figure 5h). 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 summer (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.

390        Zhang et al. (2016) reported an increase (from 132000 to 175000t yr$^{-1}$) in the emission

391    of isoprene in northern China during 1982-2010 using an emission model. Based on strong

392    correlations (r>0.90) between isoprene and above-canopy temperature, they suggested that

393    oxidations of biogenic BVOCs from the terrestrial higher plants are important in Asia

394    (especially in China). Since Chichijima is an outflow region of East Asia, long-range

395    atmospheric transport of BVOCs may be possible from terrestrial higher plants in Asia/China

396    to the western North Pacific by westerly winds, which may significantly contribute to the

397    enhanced trends of OC and WSOC during 2001-2012. We found significant (p<0.05)

398    increases in the annual trends of methylglyoxal and pyruvic acid, which are tracers of

399    aqueous-phase oxidation of biogenic isoprene (Carlton et al., 2009), over the western North

400    Pacific as shown in Figure S3. We also found a moderate correlation (r=0.40, p<0.01)

401    between of MSA$^-$ and WSOC concentrations (not shown as a figure). These results

402    demonstrate that increase of WSOC is likely due to the increased photochemical oxidation of

403    BVOCs during long-range transport over the western North Pacific in addition to the other

404    emissions such as biomass burning.

405

**3.4 Atmospheric implications**

407        It is well known that atmospheric aerosols play a key role in the climate system as

408    they can act as cloud condensation nuclei (CCN) and impact on cloud formation and thus,

409    radiative forcing (RF) (IPCC, 2013). The RF of aerosol is generally estimated by using the

410    aerosol optical depth (AOD), single scattering albedo (SSA) and asymmetry parameter (Pani

411    et al., 2016a). EC scatters the short-wave incoming solar radiation less than OC, although it

412    strongly absorbs the short-wave solar radiation as well as long-wave outgoing terrestrial

413    radiation in the atmosphere (Charlson et al., 1992; Ramanathan et al., 2001; Magi, 2009;

414    2011). The single scattering albedo (SSA), defined as the ratio of scattering to the extinction

415    coefficient of aerosols, is an important property for determining the direct RF (Pani et al.,

416    2016a; 2016b). The SSA is highly sensitive to the nature (scattering and/or absorption) of

417    aerosols in the atmosphere. Therefore, although OC has certain uncertainty because of light

418    absorbing brown carbon, OC/EC ratios can be used to understand the relative contributions of

419    scattering or absorbing aerosols in the atmosphere.

420        Further, a good knowledge of the OC/EC ratios in aerosols (for example, biomass

421    burning) may also help to improve model representation of the absorption caused by organic

422    compounds constituting so-called brown carbon, which contributes to the aerosol RF (Chung

423    et al., 2012; Saleh et al., 2014; Kirchstetter and Thatcher, 2012). In this study, atmospheric

424 aging may make OC more scattering during long-range transport over the western North
425 Pacific. An increasing trend of OC/EC ratios suggests that scattering aerosols are
426 significantly increased over the western North Pacific. In contrast, absorbing aerosols may be
427 decreased during the study period. This result may provide an important implication for
428 radiative forcing because scattering and absorption coefficients are playing crucial role in the
429 radiative forcing calculations as mentioned above.

430 Novakov and Corrigan (1996) found that pure organic components from biomass
431 smoke emissions can form cloud condensation nuclei (CCN) without the presence of sulfate
432 ($SO_4^{2-}$) and other inorganic compounds. Roberts et al. (2002) showed that biomass burning
433 derived organic aerosols do serve as CCN. Further, large loadings of CCN in continental air
434 masses were observed over the western North Pacific (Matsumoto et al., 1997; Boreddy et al.,
435 2015). In this study, the enhanced WSOC concentrations and WSOC/OC ratios in continental
436 air masses suggest an important role of WSOC in CCN activity over the western North
437 Pacific in addition to other aerosol constituents such as $SO_4^{2-}$ and sea-salts. To better
438 understand the impact of WSOC on cloud forming potential, we performed regression
439 analyses between WSOC, sea salt and CCN concentrations as shown in Figure 6. CCN data
440 were downloaded from the MODIS satellite over the region (140°–145° E, 25°–30° N) in the
441 western North Pacific for the period of July 2002 to December 2012.

442 The above results showed significantly good correlations (r=0.61 and 0.64, p<0.05)
443 between WSOC versus CCN and sea salt versus CCN concentrations (Figure 6a and 6b),
444 suggesting the importance of WSOC for the formation of CCN over the western North
445 Pacific in addition to sea salt. Further, the correlation coefficient between sea salt and CCN
446 concentrations was slightly increased (r=0.68; p<0.05) when WSOC was added to the sea salt
447 as shown in Figure 6c. Likely, the slope of the regression line between WSOC+sea salt and
448 CCN was little higher (2.21E7) than the slope between sea salt and CCN (2.19E7). These
449 results indicate that WSOC may slightly enhance the cloud forming potential of sea salt,
450 although it has less concentration over the western North Pacific. All these results suggest
451 that a significant uncertainty exists in RF due to the contribution of water-soluble organic
452 matter to cloud forming. Therefore, climate modelers should consider WSOC in addition to
453 other factors (sea-salts, sulfate, etc.), while calculating RF over the western North Pacific.
454 This point is consistent with the previous studies, which explain the contribution of water-
455 soluble organic matter to CCN (Matsumoto et al., 1997; Zhao et al., 2016).

456 It should be noted that all these ratios are applicable to organic fractions that are
457 derived from the bulk parameters only; however, the size of the particle also plays a role on

458    RF as well as their morphology, chemical composition and mixing state (Jacobson, 2001;

459    Lohmann and Feichter, 2005; Zhang et al., 2008a). Although fine particles are important for

460    CCN activation, physico-chemical processes (coagulation, condensation and other

461    heterogeneous reactions) can make the particles from fine to coarse mode in aqueous phase,

462    particularly over the marine atmosphere. Thus, bulk parameters of organic matter and its role

463    in CCN activation are important in the remote marine atmosphere. Sea spray is not a major

464    source of WSOC as inferred from Figure 6d, which showed a moderate correlation (r=0.42;

465    p>0.05) between WSOC and sea salt during the study period. In this study, atmospheric

466    processes or chemical aging makes OC more water-soluble during long-range transport over

467    the western North Pacific as discussed in section 3.2.

468

469    **4. Conclusions**

470        Based on the long-term (2001-2012) trends of carbonaceous aerosols from Chichijima

471    Island in the western North Pacific, we conclude that seasonal variations of carbonaceous

472    aerosols strictly followed seasonal trends of wind pattern at Chichijima in the western North

473    Pacific. The annual trends of OC and WSOC with significant increases over the western

474    North Pacific are probably due to the enhanced photochemical oxidation of biomass burning-

475    and biogenic-derived VOCs during long-range atmospheric transport over the western North

476    Pacific. This inference is supported by significant increases in the annual trends of OC/EC,

477    WSOC/OC, OC/TC, WSOC/TC, nss-$K^+$/EC mass ratios and $MSA^-$ concentrations. On the

478    other hand, a decrease in the concentrations of EC during 2001-2012 suggests that the

479    contribution of fossil fuel-derived sources to carbonaceous aerosols may be decreased over

480    the western North Pacific. Further, a good correlation (r=0.61) between WSOC and CCN

481    concentrations suggests that not only sea salt and nss-$SO_4^{2-}$ but also water-soluble organic

482    aerosols play a role in CCN formation. Therefore, the results from our study have important

483    implications toward the regional radiative balance, especially over the North Pacific.

484

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906 **Table 1.** Monthly mean (± standard deviation) values of EC, OC, WSOC concentrations and
907 their ratios during 2001-2012 over the western North Pacific.
908

| Month | EC (µg m$^{-3}$) | OC (µg m$^{-3}$) | WSOC (µg 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 |

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914 **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) |

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917 **Table 3.** Statistical report on the annual trends in carbonaceous aerosols and their ratios
918 during 2001-2012 at Chichijima Island in the western North Pacific. '*' indicates that the
919 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 |

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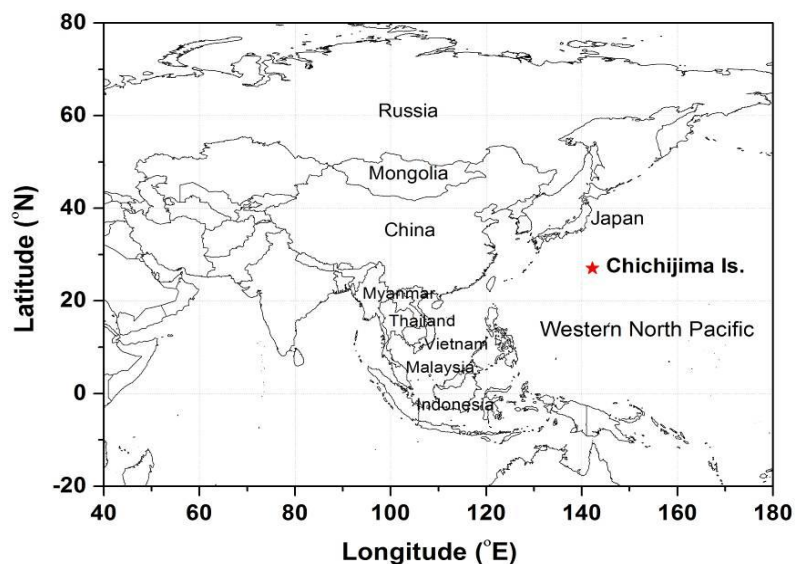
**Figure 1.** Location of sampling site (indicated by red colored '*') in the western North Pacific and its adjacent Asian countries.
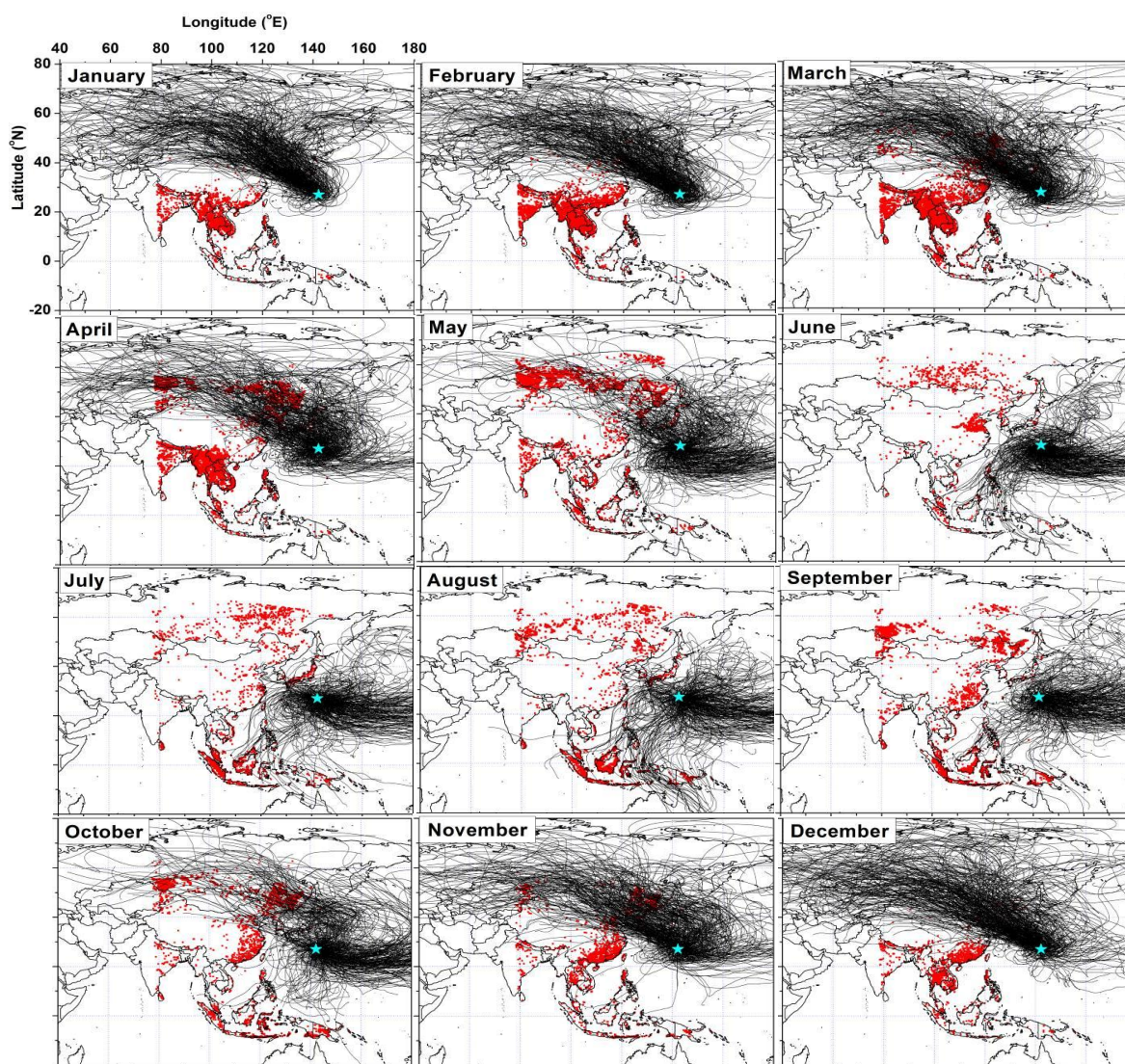
**Figure 2.** 7-day daily air mass back trajectories at 500 m a.g.l. computed using HYPLIT model for each month during 2001-2012 at Chichijima Island in the western North Pacific. The symbol '*' indicates the sampling site and red dots represent the MODIS inferred fire spots. Fire spots were downloaded for region (80°-150°E; -10-70°N) during the year 2001.
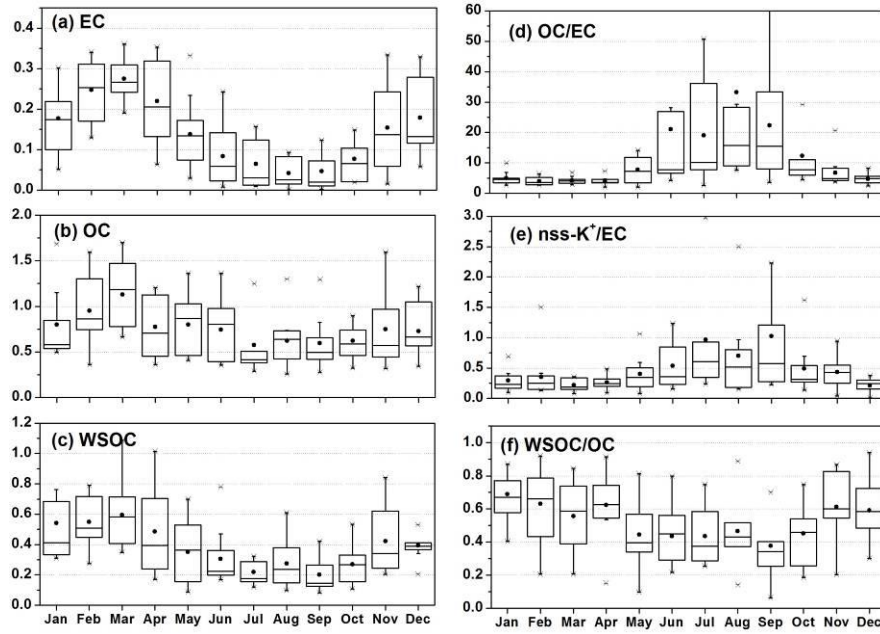
**Figure 3.** Box-whisker plots of monthly variations of carbonaceous aerosol components (μg m$^{-3}$) and some specific mass ratios at Chichijima Island in the western North Pacific during 2001-2012. The horizontal line and small dot inside the box indicate maiden and mean, respectively. The vertical hinges represent data points from the lower to the upper quartile (i.e., 25th and 75th percentiles). The whiskers represent data points from the 1$^{st}$ to 99$^{th}$ percentiles.
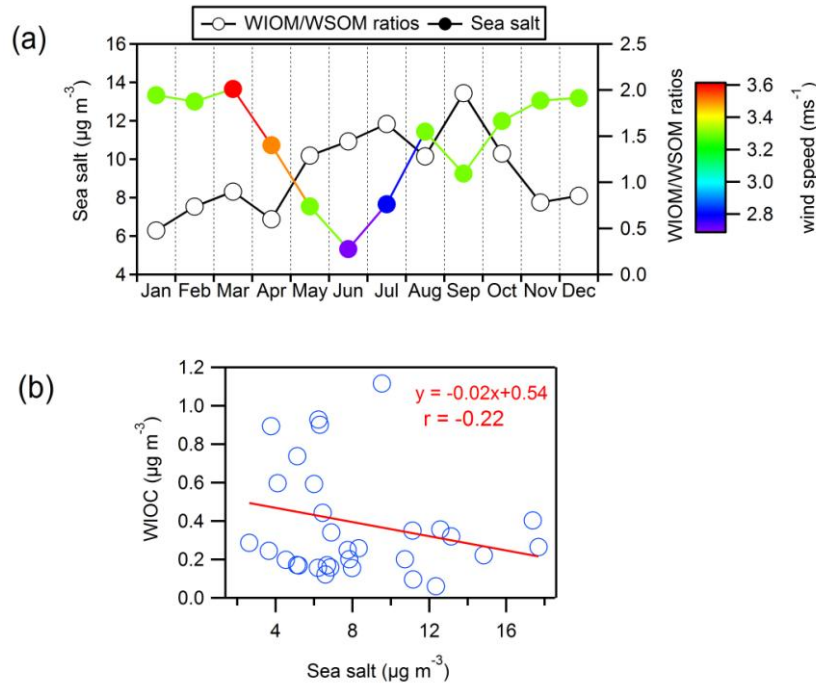
**Figure 4.** Monthly variations (a) WSIM/WSOM mass ratios and sea salt concentrations and (b) regression analysis between WIOC and sea salt concentrations. The color scale in the Figure 4(a) indicates the wind speed over the western North Pacific.
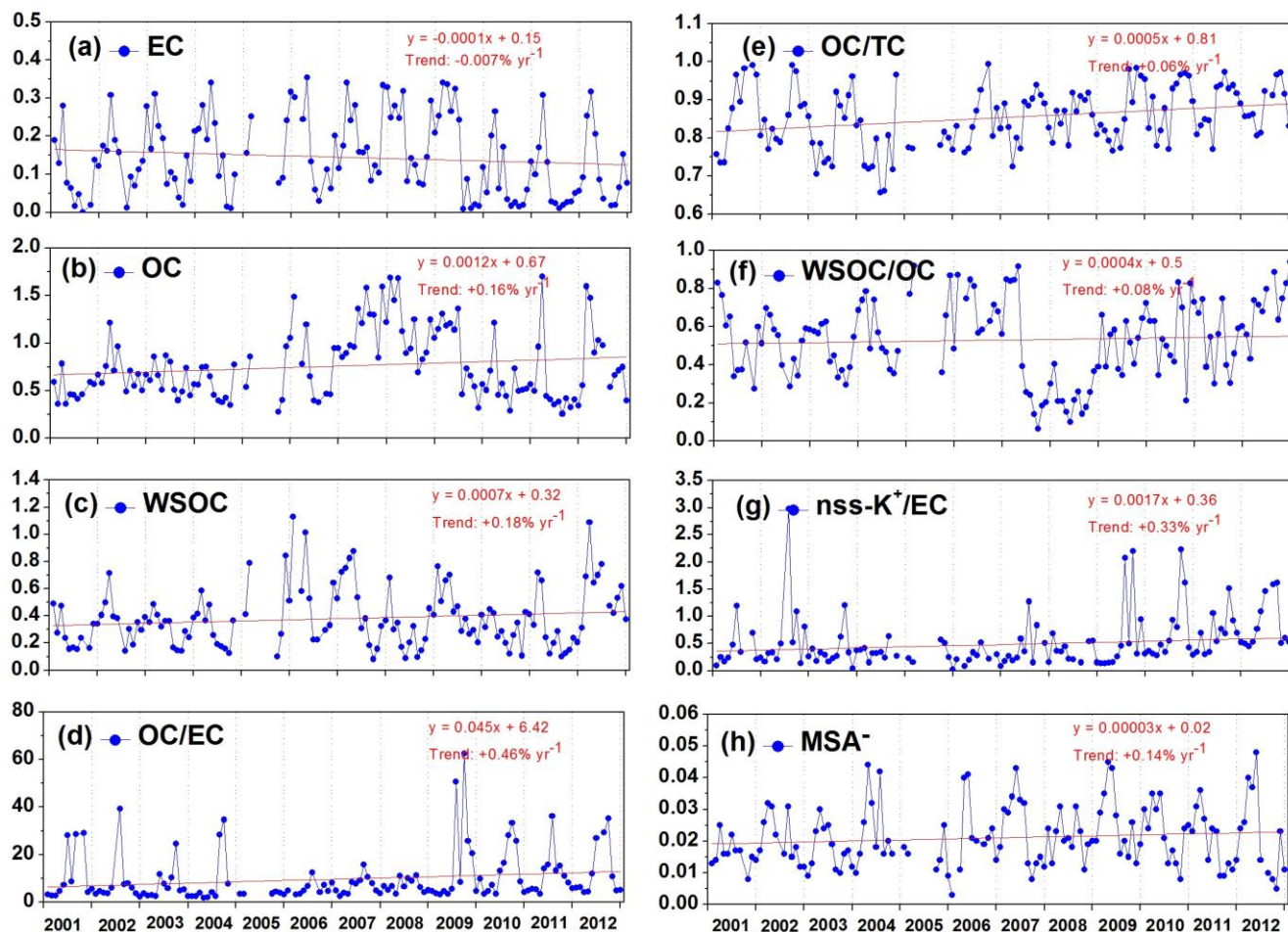
**Figure 5.** Annual trends (time series) in the concentrations (μg m$^{-3}$) of carbonaceous aerosol components, water-soluble ionic tracer compound (MSA$^{-}$) and some specific mass ratios during 2001-2012 over the western North Pacific. The liner trend equation (y=mx+c) is also shown for the each annual trend.
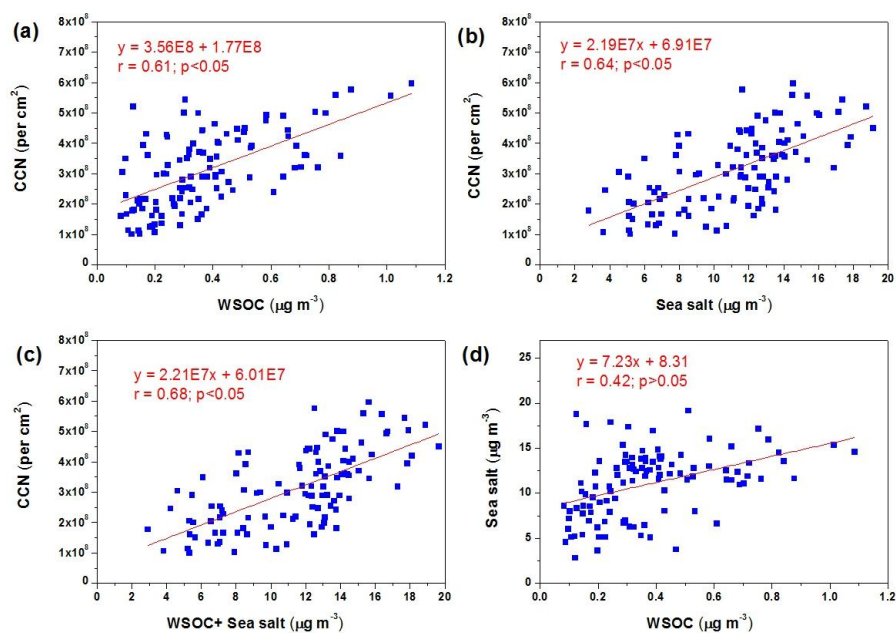
**Figure 6.** Regression analyses between (a) WSOC and MODIS-derived cloud condensation nuclei (CCN), (b) sea salt and CCN, (c) WSOC+seasalt and CCN, and (d) WSOC and sea salt concentrations over the western North Pacific.

Supporting information for

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

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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

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

where $y$ is the concentrations in $\mu g\ m^{-3}$, $a$ 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 $\alpha$ 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 $\alpha$ ($\alpha=5\%$ 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 $\alpha$, 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* ($\tau$) is compared to the standard normal cumulative distribution to define if there is a trend or not at the chosen $\alpha$ (0.05) of significance. A positive and negative value of $\tau$ indicates an increase and decrease in the trends, respectively.
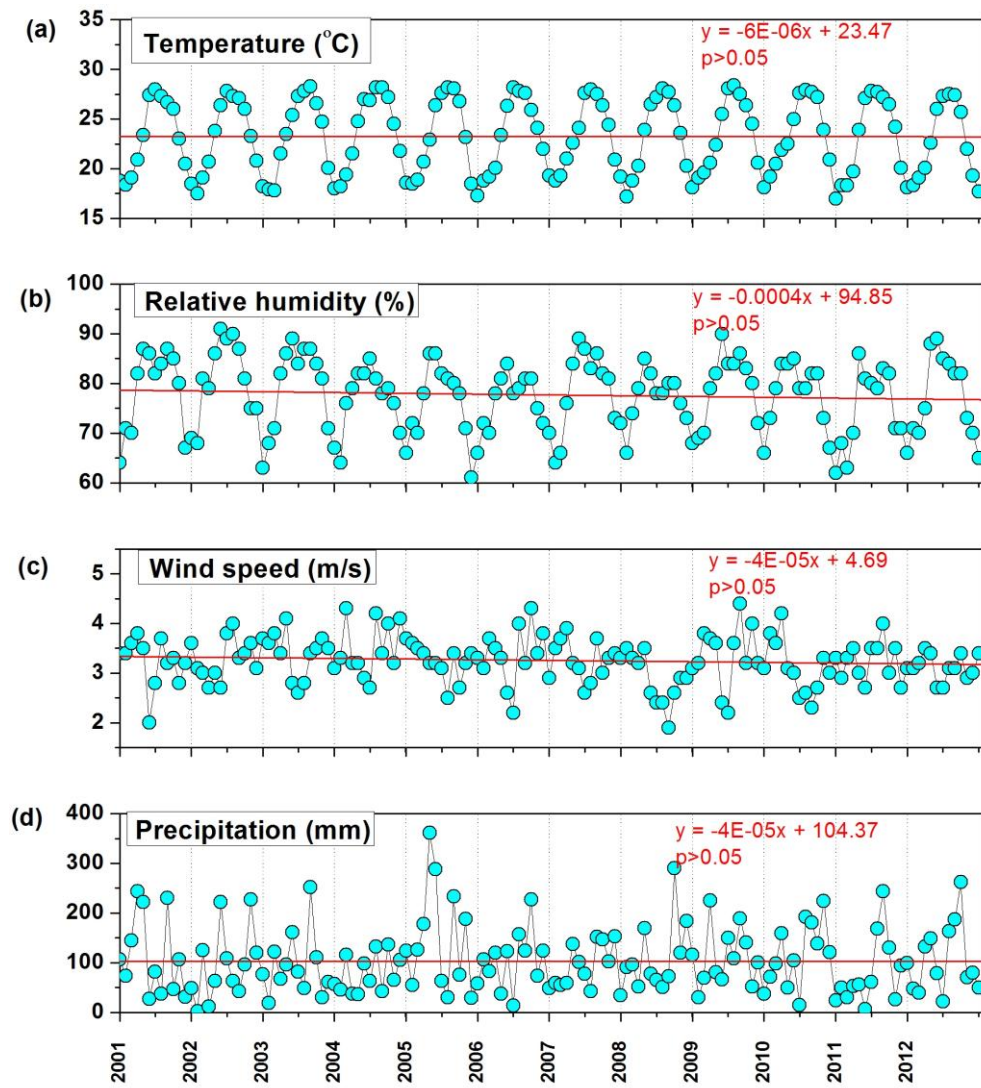
**Figure S1.** Temporal variations of meteorological parameters such as (a) air temperature (°C), (b) relative humidity (%), (c) wind speed (ms$^{-1}$), and (d) precipitation (mm) at Chichijima Island during the study period from 2001 to 2012.
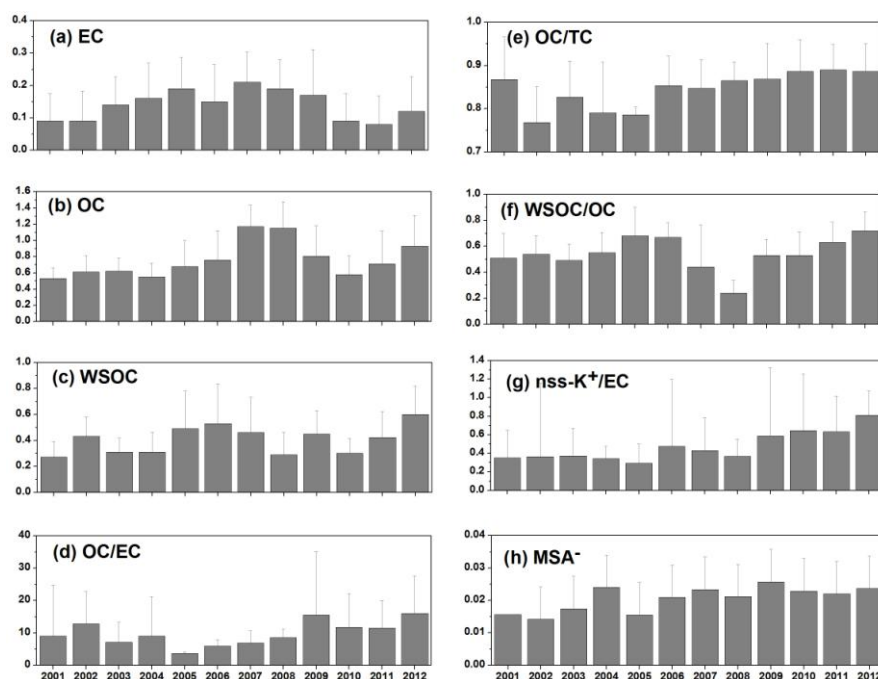
**Figure S2.** Annual mean variations (μg m$^{-3}$) of carbonaceous species as well as water-soluble ions and their mass ratios during 2001-2012 over the western North Pacific.
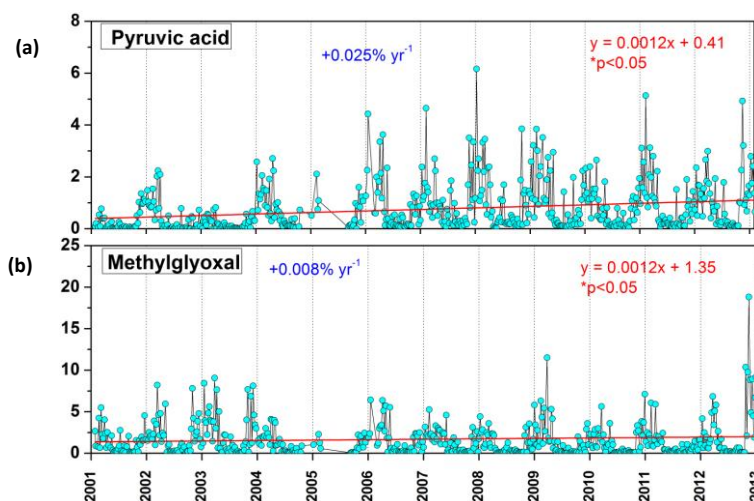
**Figure S3.** Annual trends in the concentrations (ng m$^{-3}$) of aqueous-phase photooxidations of biogenic isoprene tracer compounds (a) puruvic acid and (b) methylglyoxal during 2001-2012 over the western North Pacific.