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**
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20   **Abstract**

21   The present study reports on long-term trends of carbonaceous aerosols in total

22   suspended particulate (TSP) samples collected at Chichijima Island in the western North

23   Pacific during 2001-2012. Seasonal variations of elemental carbon (EC), organic carbon

24   (OC), and water-soluble organic carbon (WSOC) concentrations showed maxima in winter-

25   to-spring and minima in summer. These seasonal differences in the concentrations of

26   carbonaceous aerosols were associated with the outflows of polluted air masses from East

27   Asia, which are clearly distinguishable from pristine air masses from the central Pacific. The

28   higher concentrations of carbonaceous aerosols during winter to spring are associated with

29   long-range atmospheric transport of East Asian continental polluted air masses, whereas

30   lower concentrations may be due to pristine air masses from the central Pacific in summer.

31   The annual trends of OC/EC ($+0.46\%$ yr^{-1}), WSOC ($+0.18\%$ yr^{-1}) and WSOC/OC ($+0.08\%$

32   yr^{-1}) showed significant ($p<0.05$) increases during the period of 2001-2012, suggesting that

33   photochemical formation of WSOC and its contributions to secondary organic aerosols

34   (SOAs) have increased over the western North Pacific via long-range atmospheric transport.

35   We found a significant increase ($+0.33\%$ yr^{-1}) in nss-K^+/EC ratios, demonstrating that

36   concentrations of biomass-burning-derived carbonaceous aerosols have increased, while

37   those of primary fossil fuel-derived aerosols have decreased over the western North Pacific.

38   Further, secondary biogenic emissions are also important over the western North Pacific as

39   inferred from a significant increase ($+0.14\%$ yr^{-1}) in the concentrations of methanesulfonate

40   (MSA$^-$, a tracer for biogenic sources). This point was further supported by a moderate

41   correlation ($r=0.40$) between WSOC and MSA$^-$. We also found a significant increase in

42   OC/TC (total carbon) and WSOC/TC ratios, further suggesting that photochemical formation

43   of WSOC and its contributions to SOAs have increased over the western North Pacific during

44   2001-2012 via long-range atmospheric transport from East Asia.

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46

47   **Keywords:** Carbonaceous aerosols, long-term trends, the western North Pacific, East Asia,

48   biomass burning, biogenic emissions, long-range atmospheric transport, photochemical

49   oxidation.

50

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

220 condition of the western North Pacific is often influenced by the continental outflow via long-
221 range atmospheric transport (Duce et al., 1980). Very low concentrations of EC in summer,
222 whose abundances were up to seven times lower than those in the continental outflow,
223 suggest negligible contribution of local anthropogenic emissions as well as long-range
224 influences over the sampling site. These results are consistent with previous studies, which
225 reported that several times lower concentrations of organic compounds in summer compared
226 to winter/spring over the same observation site (Kawamura et al., 2003; Mochida et al.,
227 2003). Therefore, it is reasonable to believe that the sources of carbonaceous aerosols were
228 transported from the adjacent Asian countries to the western North Pacific via long-range
229 atmospheric transport.

230   As described earlier, EC particles are primary and predominately come from biomass
231 and fossil fuel combustion sources. On the contrary, OC is of either primary origin or
232 secondary formation via gas-to-particle conversion and heterogeneous phase processing in
233 the atmosphere. The precursors of secondary OC may also come from biogenic sources in
234 addition to fossil fuel combustion and biomass burning emissions. The OC/EC ratios often
235 used to distinguish the relative contribution of primary vs. secondary sources as well as
236 biomass vs. fossil fuel burning sources (Turpin and Huntzicker, 1995; Castro et al., 1999;
237 Rastogi et al., 2016). Atmospheric aerosols emitted from fossil fuel combustion are
238 characterized by lower OC/EC ratios (< 2.0) whereas higher OC/EC ratios (> 2.0) have been
239 used to point out the presence of secondary OA (SOA) (Cao et al., 2003; Chow et al., 1996;
240 Kunwar and Kawamura, 2014; Pani et al., 2017) in the atmosphere with a limited impact of
241 biomass burning. Table 2 summarizes OC/EC ratios reported for various sources of aerosol
242 particles. The split of OC/EC ratios at higher or lower than 2 (fromTable 2) may not be the
243 best indicator of SOA because fossil fuel combustion has OC/EC of 1.1 (Watson et al., 2001),
244 4.0 (Koch et al., 2001), and 4.1 (Cao et al., 2005). Monthly mean OC/EC ratios in this study
245 are much larger in the summer and still greater than the cutoff (~ 4.0) in winter to spring as
246 shown in Table 1. This result suggests a dominance of SOA over the western North Pacific.
247 The seasonal variation of OC/EC mass ratios showed maxima in summer (~21 to 33) and
248 minima in winter to spring (3.9 to 7.7). The extremely high OC/EC ratios in summer indicate
249 the secondary formation of OC via oxidation processes, while low OC/EC ratios in winter to
250 spring suggests that both biomass burning and fossil fuel combustion contribute to
251 carbonaceous aerosols over the western North Pacific in winter-to-spring.

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

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

271 Previous studies have shown that SOA is largely composed of oxygenated compounds
272 that are highly water-soluble (Kanakidou et al., 2005; Kondo et al., 2007 and references
273 therein). Thus, measurements of WSOC have been used to estimate the SOA in ambient
274 aerosols (Weber et al., 2007; Snyder et al., 2009; Sudheer et al., 2015; Decesari et al., 2001;
275 Docherty et al., 2008). Because major fraction of biomass burning products is highly water
276 soluble (Sannigrahi et al., 2006; Saarikoski et al., 2008), higher WSOC/OC ratios under
277 ambient conditions with limited biomass burning impact have been used to better understand
278 the photochemical activity and/or aging of aerosols and to discuss SOA formation mechanism
279 in the atmosphere during long-range transport (Miyazaki et al., 2007; Ram et al., 2010b; Ram
280 and Sarin, 2011; Kondo et al., 2007; Weber et al., 2007). The WSOC/OC ratios exceeding 0.4
281 have been used to indicate the significant contribution of SOA (Ram et al., 2010a) and aged
282 aerosols. The WSOC/OC ratios ranged from 0.06 to 0.19 in diesel particles (Cheung et al.,
283 2009) and 0.27 for vehicular emissions (Saarikoski et al., 2008).

284 In this study, we found that monthly mean WSOC/OC ratios were > 4.0 for all months
285 except for September, indicating a significant contribution from SOA over the western North
286 Pacific. The seasonal variation of WSOC/OC showed higher values (monthly mean: 0.44 to
287 0.62) during winter to spring months (Figure 3f), implying that SOA formation was enhanced

288 due to an increased photochemical activity and/or aging of East Asian polluted aerosols
289 during long-range atmospheric transport. The high WSOC/OC ratios are traditionally
290 attributed to the atmospheric oxidation of various VOCs in the presence of oxidants such as
291 ozone and hydroxyl radicals via gas and/or aqueous phase reactions in the atmosphere
292 (Miyazaki et al., 2007; Ram and Sarin, 2012). However, the atmosphere over the western
293 North Pacific is always characterized by high relative humidity (>80%) and air temperature
294 (~24°C) during the whole year (Figure S1). Therefore, higher WSOC concentrations in
295 winter to spring over the western North Pacific were largely attributed to the aqueous-phase
296 oxidation of anthropogenic and/or biogenic VOCs (Gilardoni et al., 2016; Youn et al., 2013),
297 which are emitted over continental East Asia and long-range transported to the western North
298 Pacific.

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

314   Further, laboratory studies have revealed a high abundance of primary organic matter
315 dominated by WIOM in marine aerosols (Facchini et al., 2008; Keene et al., 2007). However,
316 it should be noted that although bubble-bursting process is a common source for both sea salt
317 (sea salt = $3.2 \times Na^+$, where 3.2 is the conservative mass ratio of salinity to Na in seawater,
318 data obtained from Boreddy and Kawamura (2015)) and WIOM in marine aerosols, we found
319 a negative/no correlation (r= -0.22) between sea salt and WIOC concentrations in summer
320 (Figure 4b). This result suggests that an additional source of organic matter (completely
321 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

356   tracer, e.g., Simoneit, 2002) during 2006-2013 over the sampling site. Therefore, all these

357   results demonstrate that the contributions of biomass burning emissions to carbonaceous

358   aerosols have increased significantly over the western North Pacific whereas the

359   contributions of fossil fuel combustion have decreased.

360   Previous studies suggested that SOA is largely composed of water-soluble organic

361   matter (Weber et al., 2007; Kondo et al., 2007). In this study, the annual trend of WSOC

362   showed a significant increase ($p < 0.05$; +0.18% yr^{-1}) from 2001 to 2012 (Figure 5c).

363   Generally, atmospheric aging makes aerosols more water-soluble during long-range transport

364   (Aggarwal and Kawamura, 2009; Rudich et al., 2007; Robinson et al., 2007; Jimenez et al.,

365   2009; Kawamura et al., 2010), especially in the remote marine atmosphere (Kawamura et al.,

366   2003). This point is further supported by a decadal increase (+0.08% yr^{-1}) in the WSOC/OC

367   ratios (Figure 5f). These results may demonstrate that the increased concentrations of WSOC

368   over the western North Pacific are significantly linked with increased photochemical aging of

369   organic aerosols and oxidation of various VOCs during long-range atmospheric transport

370   (Zhang et al., 2007; Decesari et al., 2010). An increasing trend of WSOC/TC ($p < 0.05$;

371   +0.15% yr^{-1}; Table 3) again suggests that photochemical formation of WSOC and its

372   contributions to SOA have increased over the western North Pacific during 2001-2012. We

373   observed an abrupt decrease in the WSOC/OC ratios between 2007 and 2008 (Figure 5f),

374   probably due to enhanced OC that may be caused by unknown sources. However, it should

375   be noted that an observed decline in the WSOC/OC ratios does not affect the decadal trend

376   even if those data are excluded from the trend analysis.

377   To better understand the contributions of photochemical oxidation of biogenic VOCs

378   to WSOC during long-range atmospheric transport, we present the annual trend of water-

379   soluble organic ion, i.e., MSA$^-$ (a biogenic tracer; see Figure 5h). In our previous study

380   (Boreddy and Kawamura, 2015), we reported that MSA$^-$ significantly correlates with

381   continental pollutants such as NH_4^+ (r=0.56), nss-K^+ (0.52) and nss-SO_4^{2-} (0.50) and no

382   correlation with Na^+, suggesting that continentally derived MSA$^-$ may be associated with the

383   terrestrial higher plants and other biogenic sources along with Asian pollutants during the

384   long-range transport. However, we should not ignore the oceanic biogenic emissions,

385   especially in summer (Bikkina et al., 2014), although it has less abundance compared to

386   continental biogenic emissions over the western North Pacific. In this study, the annual trend

387   of MSA$^-$ showed a significant increase ($p < 0.05$; +0.14% yr^{-1}) during 2001-2012, implying

388   that continental transport of biogenic VOCs (BVOCs) over the western North Pacific have

389   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

406   **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.
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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

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

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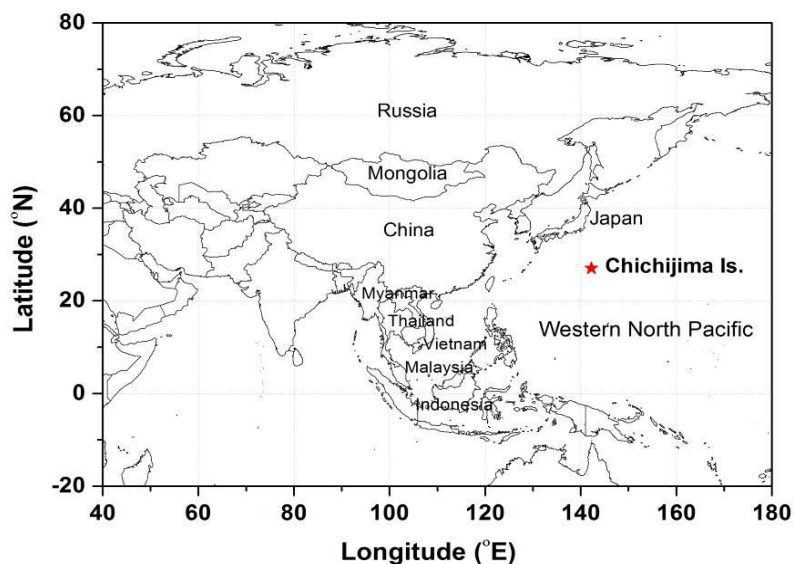
Figure 1. Location of sampling site (indicated by red colored '*') in the western North Pacific and its adjacent Asian countries.
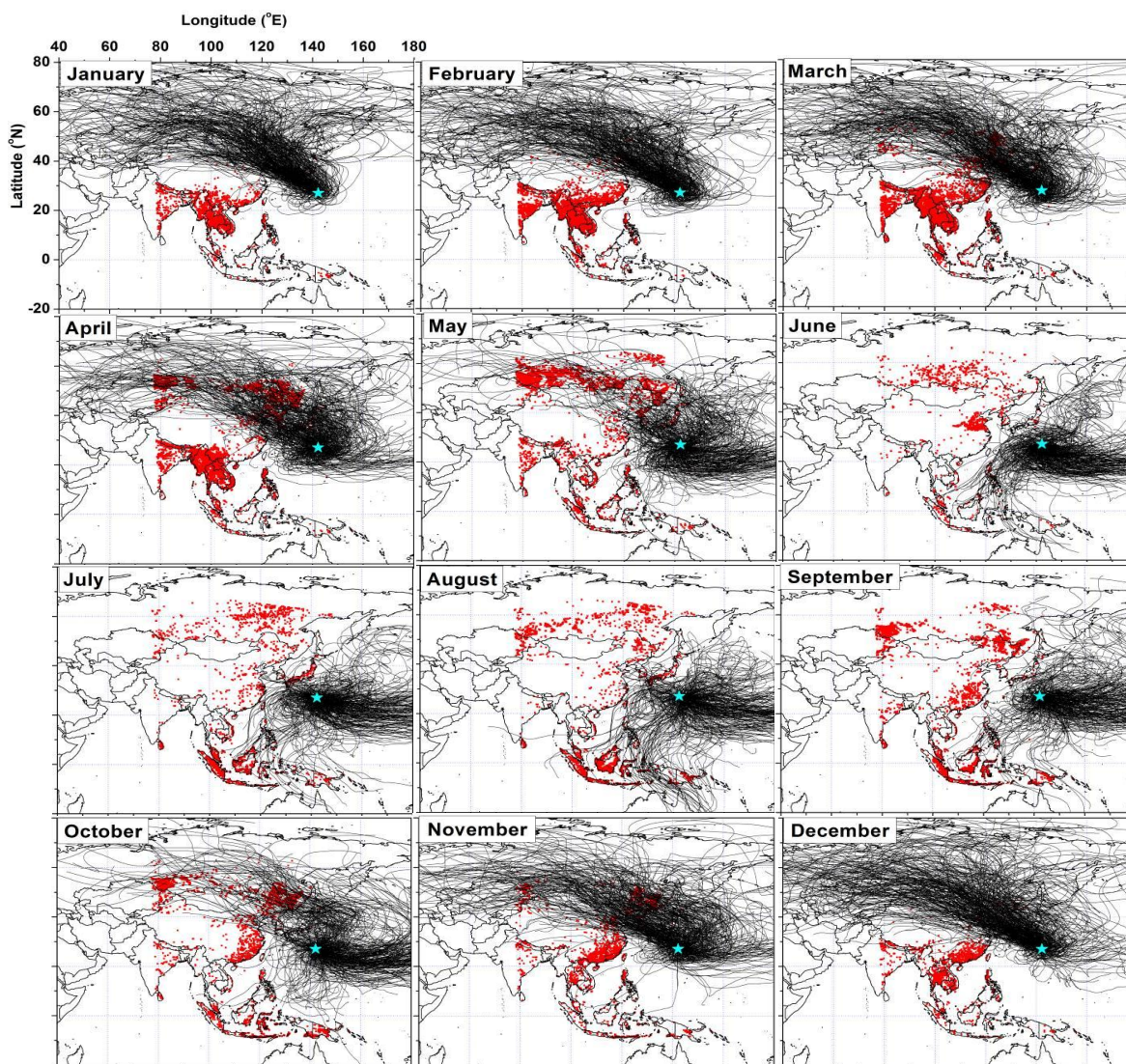
Figure 2. 7-day daily air mass back trajectories at 500 m a.g.l. computed using HYPLIT model for each month during 2001-2012 at Chichijima Island in the western North Pacific. The symbol '*' indicates the sampling site and red dots represent the MODIS inferred fire spots. Fire spots were downloaded for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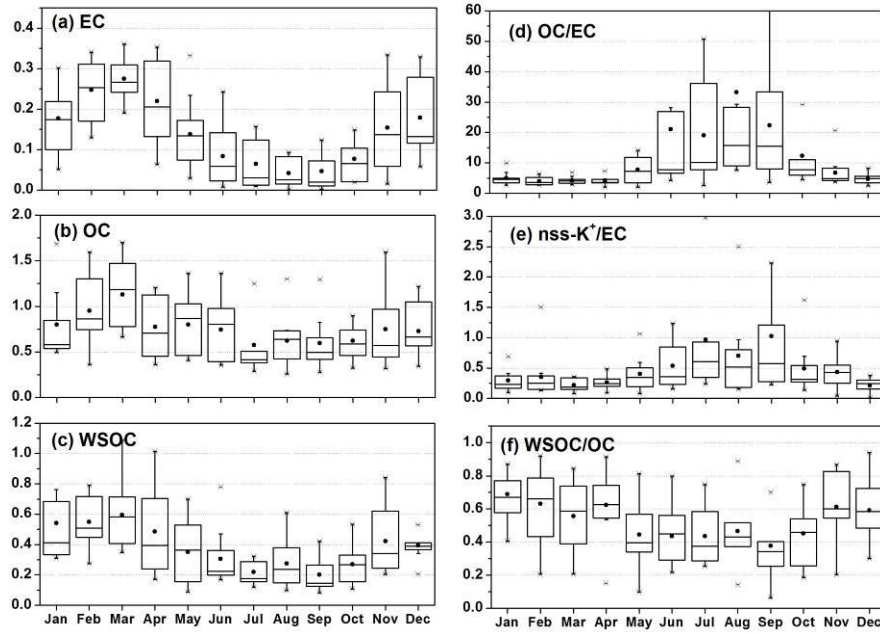
Figure 3. Box-whisker plots of monthly variations of carbonaceous aerosol components (µg m^{-3}) and some specific mass ratios at Chichijima Island in the western North Pacific during 2001-2012. The horizontal line and small dot inside the box indicate maiden and mean, respectively. The vertical hinges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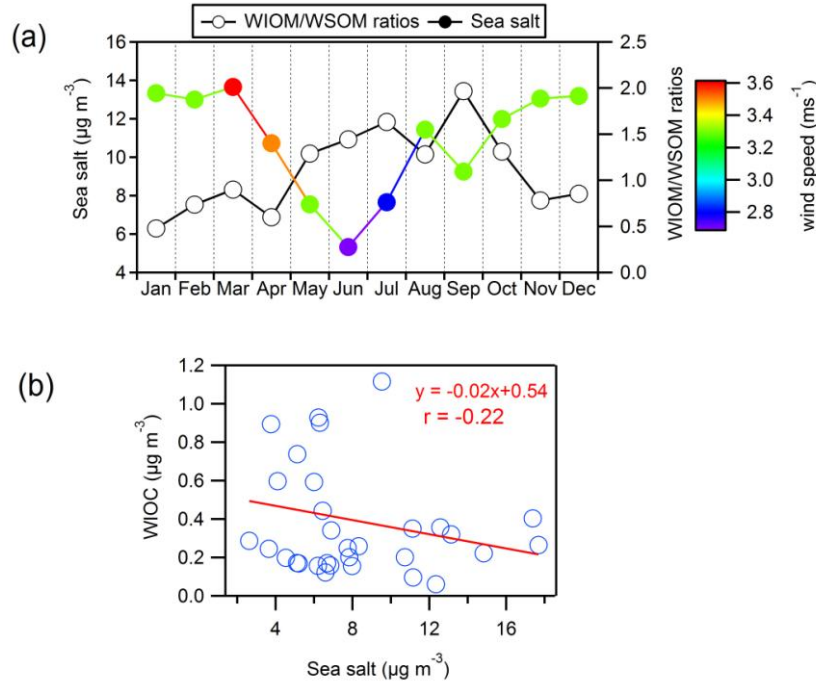
Figure 4. Monthly variations (a) WSIM/WSOM mass ratios and sea salt concentrations and (b) regression analysis between WIOC and sea salt concentrations. The color scale in the Figure 4(a) indicates the wind speed over the western North Pacific.
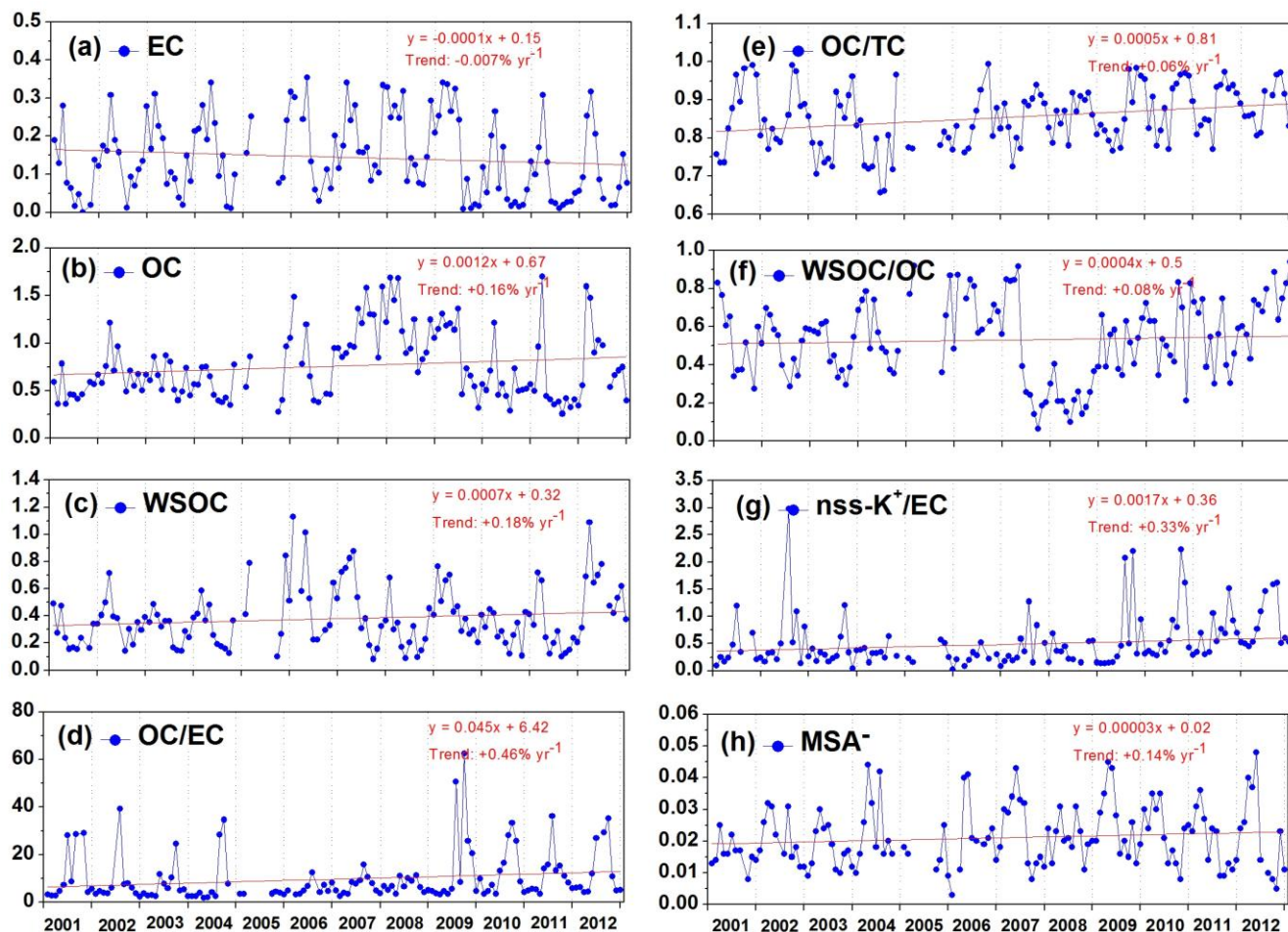
Figure 5. Annual trends (time series) in the concentrations (μg m^{-3}) of carbonaceous aerosol components, water-soluble ionic tracer compound (MSA$^-$) and some specific mass ratios during 2001-2012 over the western North Pacific. The liner trend equation (y=mx+c) is also shown for the each annual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

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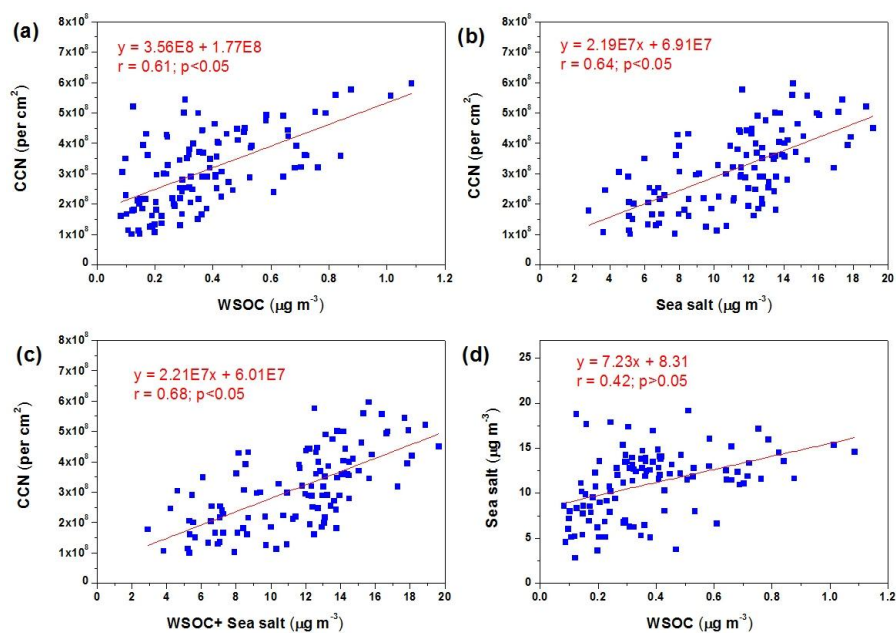
Figure 6. Regression analyses between (a) WSOC and MODIS-derived cloud condensation nuclei (CCN), (b) sea salt and CCN, (c) WSOC+seasalt and CCN, and (d) WSOC and sea salt concentrations over the western North Pacific.