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Atmospheric Chemistry and Physics Discussions

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

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Abstract

The present study reports on long-term trends of carbonaceous aerosols in total suspended particulate (TSP) samples collected at Chichijima Island in the western North Pacific during 2001-2012. Seasonal variations of elemental, organic, and water-soluble organic carbon (EC, OC and WSOC) concentrations showed maxima in winter to spring and minima in summer. These seasonal differences in the concentrations of carbonaceous aerosols are associated with the outflows of polluted air masses from East Asia, which are clearly distinguishable from pristine air masses from the central Pacific. The higher concentrations of carbonaceous aerosols during winter to spring are associated with long-range atmospheric transport of East Asian 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, WSOC and WSOC/OC showed significant ($p<0.05$) increases during the period of 2001-2012, suggesting that an enhanced secondary formation of organic aerosols (SOA) via photochemical oxidation of anthropogenic and biogenic volatile organic compounds (VOCs) during long-range atmospheric transport. We found a significant increase in nss-K^+/EC ratios, demonstrating that biomass burning-derived organic aerosols are increased, while combustion-derived anthropogenic sources are decreased over the western North Pacific. Further, secondary biogenic emissions are also important over the western North Pacific as inferred from a significant increase in the concentrations of methanesulfonate (MSA^-, a tracer for biogenic source). We also found significant increases in OC/TC and WSOC/TC ratio, suggesting that contribution of SOA to total carbon (TC) are significantly increased over the western North Pacific followed by long-range atmospheric transport.

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

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1. Introduction

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

The major sources of carbonaceous aerosol are fossil fuel and biomass burning in addition to the atmospheric oxidation of anthropogenic and biogenic volatile organic compounds (VOCs) (Samset, 2016). 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 and hence act as cloud condensation nuclei (CCN) (Novakov and Penner, 1993;Matsumoto et al., 1997;Asa-Awuku et al., 2009). According to the recent report of intergovernmental panel on climate change (IPCC 2013), the radiative forcing of BC and OA associated with fossil fuel and bio fuel combustions is in the range of +0.05 to +0.8 (mean: +0.4) W m^{-2} and -0.4 to -0.1 (-0.12) W m^{-2}, respectively. It is +0.0 (−0.2 to +0.2) W m^{-2} as a result of their change offset when BC and OA are emitted by biomass burning (Boucher et al., 2013). Therefore, carbonaceous aerosols have a net warming effect on the climate as per an IPCC 2013 report. However, there is still a large uncertainty in radiative forcing of carbonaceous aerosols, particularly with regard to OA (Reddy and Boucher, 2004) because of knowledge gap on their specific sources and formation processes.

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

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

2. Instrumentation and data analyses

2.1. Sampling site and aerosol collection

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Chlorophyll-*a* data are superimposed in Figure 1, which were downloaded from the MODIS (Moderate Resolution Imaging Spectroradiometer) satellite during winter 2008, in order to see the intensity of biogenic emissions from the ocean during westerly season. Total suspended particulate (TSP) samples were collected at the Satellite Tracking Center of the Japan Aerospace Exploration Agency (JAXA, elevation: 254 m) in Chichijima Island (27°04′N; 142°13′E) on a weekly basis (Chen et al., 2013;Boreddy and Kawamura, 2015). Aerosol samples are collected on pre-combusted (450° C for 3-5 h) quartz filter (20 × 25 cm, Pallflex 2500QAT-UP) using a high volume air sampler (HVS) with a flow rate of 1 m^3 min^{-1}. The HVS was installed at a height of 5 m above the ground level. The filters were placed in a pre-baked (450°C for 6 h) glass jar (150 mL) with a Teflon-lined screw cap before sample collection. After aerosol collection, the filters were recovered into the glass jar, transported to the laboratory in Hokkaido University, Sapporo, and stored in a freezer room at −20 °C prior to analysis. A total of 545 aerosol samples and about 56 field blank samples were used for the analysis of carbonaceous components during 2001-2012.

2.2. Analyses of carbonaceous aerosols

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

To determine WSOC, a punch of 20 mm in diameter of each filter was extracted with 20 mL organic-free ultra pure water (>18.2 MΩ cm, Sartorius arium 611 UV) and ultrasonicated for 30 min. These extracts were passed through a disk filter (Millex-GV, 0.22 μm pore size, Millipore) to remove the filter debris and insoluble particles and analyzed using a total organic carbon (TOC) analyzer (Shimadzu, TOC-Vcsh) equipped with a catalytic oxidation column and non-dispersive infrared detector (Miyazaki et al., 2011).

Concentrations of water-soluble methanesulfonate (MSA^-) were taken from the study of Boreddy and Kawamura (2015), in order to support the inferences related to carbonaceous

species over the western North Pacific, which were determined using ion chromatography (761 Compact IC, Metrohm, Switzerland).

The analytical errors in the replicate analyses were less than 10% for OC, EC and WSOC in this study. The concentrations of carbonaceous aerosols reported in this study have been corrected for field blanks. The levels of blanks are less than 5% for all the parameters in the real samples.

2.3. Statistical analyses

Two statistical approaches were used to better conduct the trend analyses in time series of WSOC, EC, and OC and their ratios during 2001-2012. First, the tendency (linear trend) equation for each time series (Draper and Smith, 1966). In the second approach, all trends are assessed using the Mann-Kendall test, which is completely independent of the first approach.

2.3.1. 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 μg m^{-3}, a is the slope, x is the time in years, and b is concentrations at the beginning of the period (intercept).

This approach gives results which are simple to interpret; both analytically and graphically on the basis of the shape and parameters of the trend equation (Gavrilov et al., 2016). 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.

2.3.2 The Mann-Kendall test

This statistical approach is simple, robust and widely used non-parametric tests to detect the significant trends in time series (Mann, 1945;Kendall, 1975). According to this approach, two hypotheses were tested: the null hypothesis, H0, that there is no trend in the time series; and the alternative hypothesis, Ha, that there is a significant trend in the series, for a given α significance level. Probability (p value) was calculated to determine the level of confidence in the hypothesis. If the p value is lower than the chosen significance level α (α=5% or 0.05), the H0 should be rejected, and Ha should be accepted (means there is a trend). In case, the p value is greater than the significance level α, the H0 cannot be rejected (there is no trend). In this study, we used XLSTAT software (http://www.xlstat.com/en/) for

Mann-Kendall test analysis. The absolute value of Kendall *tou* (τ) is compared to the standard normal cumulative distribution to define if there is a trend or not at the chosen α (0.05) of significance. A positive and negative value of τ indicates an increase and decrease in the trends, respectively.

3. Results and discussion

3.1 Synoptic wind circulation and general meteorology

Figure 2 (a-d) presents mean wind circulation patterns at 850 hPa pressure level, which were obtained from the NCEP/NCAR reanalysis (National Center for Environmental Prediction/National Centre for Atmospheric Research) over the western North Pacific and the adjacent East Asian countries from 2001 to 2013 for the months December, March, July, and October, which cover a particular month of each seasons. The arrowhead indicates wind direction and the length of the arrow represents the mean wind speed. It is clearly seen from Figure 2 that from winter (December-February) to spring (March-May) the winds are stronger to transport continental air masses containing pollutants and dusts from East Asia to the sampling site in the Pacific by long-range atmospheric transport. The winds are weaker in summer (June-August). They mostly come from the central Pacific and carry pristine air masses to the observation site, whereas in autumn (September-November) the wind circulation pattern shifts from southeasterly to northwesterly and become stronger towards winter.

Figure S1 shows the temporal variations of meteorological parameters such as air temperature (°C), relative humidity (%), wind speed (m s^{-1}), and precipitation (mm) at Chichijima Island during the study period of 2001-2013. All the meteorological parameters were downloaded from the Japan Meteorological Agency. We found a clear seasonal variation in the levels of temperature, relative humidity, and precipitation with summer maxima and winter minima. Wind speeds were higher in winter to spring and lower in summer.

3.2 Monthly/seasonal variations

Figure 3 (a-f) presents the monthly/seasonal variations in the concentrations of EC, OC, WSOC and their ratios during the years 2001-2012 at Chichijima Island in the western North Pacific. The corresponding statistical data were reported in Table 1. All measured species clearly showed winter-to-spring maxima and summer minima and then increase in autumn. This seasonal pattern is consistent with a typical seasonal pattern in ambient

carbonaceous aerosols over China (Zhang et al., 2008;Cao et al., 2006), indicating a common source for these components, which are long-range transported to the western North Pacific. This, of course, can also be influenced by seasonal meteorology and synoptic wind circulation over the western North Pacific as discussed in the above section.

Relatively high monthly average concentrations up to 0.28, 1.13 and 0.59 μg m^{-3} were observed for EC, OC, and WSOC in winter-spring (Figure 3a-c). In contrast, their monthly averages are lower in summer with the concentrations of 0.04, 0.58, and 0.20 μg m^{-3}, respectively (Table 1). It is well documented that in summer, a maritime high-pressure wind dominated over the western North Pacific in which the air masses are pristine and less influenced by the continental outflow from East Asia (Figure 2). This observation is consistent with the fact that concentrations of anthropogenic nss-SO_4^{2-}, NO_3^-, NH_4^+, and nss-K^+ showed similar seasonal variations with winter and/or spring maxima and summer minima (Boreddy and Kawamura, 2015). On the other hand, continental air masses blow from the Asian continent in winter and spring; therefore, the maritime background condition of western North Pacific is often influenced by the continental outflow via long-range atmospheric transport (Duce et al., 1980).

Very low concentrations of EC in summer, whose abundance are up to seven times lower than those in the continental outflow; suggest a negligible contribution of local anthropogenic emissions over the sampling site. The seasonal variation of OC/EC mass ratio was maximized in summer and minimized in winter-to-spring months (Figure 3d), further suggesting a negligible contribution of local anthropogenic emission at island in summer. 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.

It is well documented that nss-K^+ and EC are tracers for biomass and fossil fuel burning emissions, respectively. Therefore, nss-K^+/EC ratios were widely used to better identify major sources of carbonaceous aerosols over the sampling sites (Wang et al., 2005;Rastogi et al., 2016;Srinivas and Sarin, 2014;Ram and Sarin, 2011). The higher nss-K^+/EC ratios indicate the dominance of biomass burning emissions, whereas lower ratios suggest the prevalence of fossil fuel emissions. In this study, higher nss-K^+/EC mass ratios were observed in midsummer to early autumn (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 synoptic wind circulations during summer (Figure 2c), which clearly show that winds are dominantly coming from Southeast Asia where biomass burning is common phenomena during summer to early autumn, in addition to pristine easterly winds. In this context, Verma et al. (2015) reported significant concentrations of levoglucosan during summer in Chichijima (in the absence of 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.

The WSOC/OC has been suggested to be a unique tracer to better understand the photochemical activity and/or aging of aerosols and secondary organic aerosol (SOA) formation mechanism in the atmosphere during long-range transport (Miyazaki et al., 2007;Ram et al., 2010;Ram and Sarin, 2011). In the present study, the seasonal variation of WSOC/OC showed higher values during winter-spring (Figure 3f), implying that the formation of SOA is enhanced due to increased photochemical activity and/or aging of East Asian polluted aerosols during long-range atmospheric transport. The high WSOC/OC ratios are traditionally attributed to the atmospheric oxidation of various VOCs in the presence of oxidants such as ozone and hydrogen peroxide radicals via gas and/or aqueous phase reactions in the atmosphere. 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, which are emitted over East Asia and long-range transported to the western North Pacific. On the other hand, lower ratios of WSOC/OC in summer suggest that the primary emission of OC from the oceanic surface via sea-to-air flux (Ovadnevaite et al., 2011;Miyazaki et al., 2010) because the low speed easterly winds, which originated from the central Pacific are dominated in summer over the western North Pacific (Figure 2c).

3.3 Annual trends

Figure 4 shows the annual trends in the concentrations of EC, OC, TC (EC+OC), WSOC, and WSOC/OC ratios during the period of 2001-2012 over the western North Pacific. Table 2 summarizes the results of the statistical analyses. It is seen that all the annual

trends of species and their ratios (WSOC/OC) show clear seasonal patterns with higher values in winter-spring and lower values in summer.

As seen from Figure 4a-c, concentrations of EC, OC, and TC during 2001-2012 ranged from 0.001 to 0.36 μg m^{-3} (mean: 0.142 μg m^{-3}), 0.25 to 1.7 μg m^{-3} (0.76 μg m^{-3}) and 0.28 to 2.01 μg m^{-3} (0.90 μg m^{-3}), respectively. The annual trend of EC showed a decrease, while OC and TC trends are continuously increased from 2001 to 2012, but the trends were not significant ($p>0.05$). However, the annual trends of OC/EC and OC/TC mass ratios increased significantly ($p<0.05$) from 2001 to 2012 (Table 2), suggesting that the enhanced formation of SOA and its contribution to TC continuously increased over the western North Pacific. These results further demonstrate that the contribution of combustion-derived sources to enhanced SOA seems to be decreased significantly during the sampling period. This point is supported by the annual trend of nss-K^+/EC mass ratios, which showed a significant increase during the sampling period (see Table 2 and Figure 4f). This observation is consistent with the study of Verma et al. (2015), who observed a significant enhancement of levoglucosan concentrations during 2006-2013 over the sample sampling site. Therefore, all these results demonstrate that the contributions of biomass burning-derived SOA to TC have increased significantly over the western North Pacific whereas contributions of combustion-derived SOA have decreased.

The annual trend of WSOC showed a significant ($p<0.05$) increase during 2001 to 2012 (Figure 4d), implying that atmospheric processing or aging of organic compounds and its contribution to WSOC is significantly increased over the western North Pacific. Generally, atmospheric process/aging makes aerosol more water-soluble during long-range transport (Aggarwal and Kawamura, 2009), especially in the remote marine atmosphere. This point is further supported by a significant increase in the annual trend of WSOC/OC ratios during the sampling period (Figure 4e). These results demonstrate that the formation of WSOC (or OC) over the western North Pacific may significantly linked with a photochemical oxidation and/or aging of anthropogenic and biogenic VOCs followed by long-range atmospheric transport. A significant ($p<0.05$) increasing trend of WSOC/TC (Table 2) further reveals that photochemical formation of SOA and its contributions to TC are significantly increased over the western North Pacific during 2001-2012.

In order to better understand the contributions of photochemical oxidation of biogenic VOCs to WSOC during long-range atmospheric transport, we showed the annual trend of water-soluble organic ion such as MSA^- (a biogenic tracer; see Figure 4g). The annual trend of MSA^- showed a significant ($p<0.05$) increase in their concentrations during 2001-2012,

implying that biogenic emissions over the western North Pacific have increased significantly during the period of 2001-2012. In this context, Zhang et al. (2016) have recently reported an increasing trend in the emission of isoprene in northern China during 1982-2010 using emission modelling studies. Consistently, Stavrakou et al. (2014) reported that an increased isoprene emissions over Asia, especially China during 1979-2012. Based on strong correlations ($r>0.90$) between isoprene and above-canopy temperature, they suggested that oxidations of biogenic VOCs from the terrestrial higher plants are important in Asia (China). Long-range atmospheric transport of biogenic VOCs may be possible from terrestrial higher plants in Asia/China to the western North Pacific by westerlies, which may significantly contribute to the enhanced trends of OC and WSOC during 2001-2012. We found significant ($p<0.05$) increases in the annual trends of methylglyoxal and pyruvic acid, which are tracers of aqueous-phase oxidation of biogenic isoprene (Carlton et al., 2009), over the western North Pacific (Boreddy and Kawamura, 2016, *unpublished data*). We also found a significant correlation ($r=0.40$, $p<0.01$) between of MSA^- and WSOC concentrations (not shown as a figure). These results demonstrate that increase of WSOC (or SOA) is likely due to the increases of photochemical oxidation of biogenic VOCs during long-range transport over the western North Pacific.

3.4 Atmospheric implications

It is well known that OC and EC aerosols scatter and absorb solar radiation, respectively, in the atmosphere and highly control the single scattering albedo (defined as the ratio of scattering to the extension coefficient of aerosols), which is an important property for determining the direct radiative forcing (Gopal et al., 2017;He et al., 2009). Therefore, OC/EC ratios can be used to understand the relative contributions of scattering or absorbing aerosols in the atmosphere (Ram and Sarin, 2015). In this study, a significant increasing trend of OC/EC ratios suggests that dominance of scattering aerosols that are increased significantly over the western North Pacific. In contrast, absorbing aerosols decreased during the study period. This result may be an important implication for radiative forcing because scattering and absorption coefficients are playing crucial role in the radiative forcing calculations. Further, we also found a significant increase in WSOC/OC, WSOC/TC ratios, suggesting important implications related to cloud forming potential.

In order to see the impact of WSOC on cloud forming potential, we performed regression analysis between WSOC and MODIS-derived cloud condensation nuclei (CCN) concentrations. The results show a significantly good correlation ($r=0.69$, $p<0.001$) between

them and as shown in Figure 4. This result suggests that although nss-sulfate is a major contributor to the CCN, water-soluble organic matter also play an important role in CCN formation over the western North Pacific. This point is consistent with previous studies, which explain the contribution of water-soluble organic matter to CCN (Matsumoto et al., 1997;Zhao et al., 2016).

4. Conclusion

Based on the long-term (2001-2012) trends of carbonaceous aerosols from Chichijima Island in the western North Pacific, we conclude that the seasonal variations of carbonaceous aerosols strictly followed seasonal trends of wind pattern at Chichijima in the western North Pacific. The annual trends of OC and WSOC with significant increases over the western North Pacific are probably due to the enhanced photochemical oxidation of biomass burning- and biogenic-derived VOCs during long-range atmospheric transport over the western North Pacific. This inference is supported by significant increases in the annual trends of OC/EC, WSOC/OC, OC/TC, WSOC/TC, nss-K^+/EC mass ratios and MSA^- concentrations. On the other hand, a significant decrease in the concentrations of EC during 2001-2012 suggests that the contribution of combustion-derived anthropogenic VOCs to WSOC may be decreased over the western North Pacific. Further, a good correlation (r=0.69) between WSOC and CCN concentrations suggests that not only nss-SO_4^{2-} but also water-soluble organic aerosols play a key role in CCN formation. Therefore, the results from this study have important implications toward the Earth's radiative forcing, especially over the North Pacific.

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574 **Table 1.** Monthly mean (± standard deviation) values of EC, OC, WSOC concentrations and
575 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	95.9±96.5	0.46±0.23	0.70±0.69
September	0.05±0.04	0.60±0.26	0.20±0.10	47.3±60.3	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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585 **Table 2.** Statistical report on the annual trends in carbonaceous aerosols and their ratios
586 during 2001-2012 at Chichijima Island in the western North Pacific. '*' indicates that the
587 trends are significant at $p<0.05$ level.
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Species	Concentrations ($\mu g\ m^{-3}$)				Mann-Kendall trend test		
	Min	Max	Mean	SD	Kendall's tau (τ)	*p*-value	Sen's slope
OC	0.26	1.70	0.76	0.36	0.07	>0.05	0.0008
EC	0.00	0.36	0.14	0.10	-0.06	>0.05	-0.0002
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	688	19.34	67.9	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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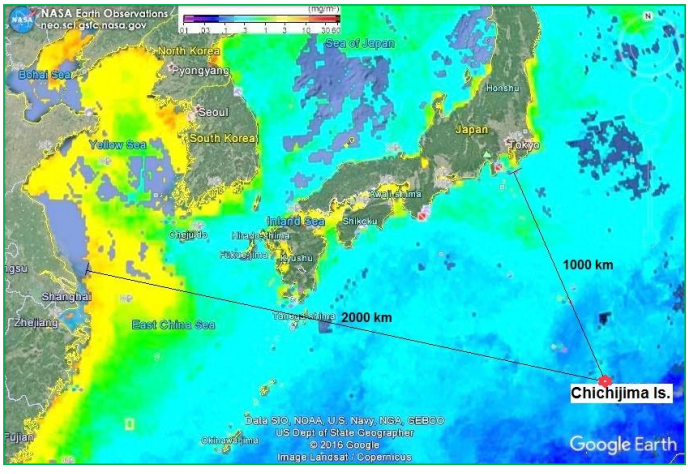

Figure 1. Location of sampling, Chichijima Island, in the western North Pacific. We also showed MODIS-derived Chlorophyll-*a* concentrations during winter 2008.

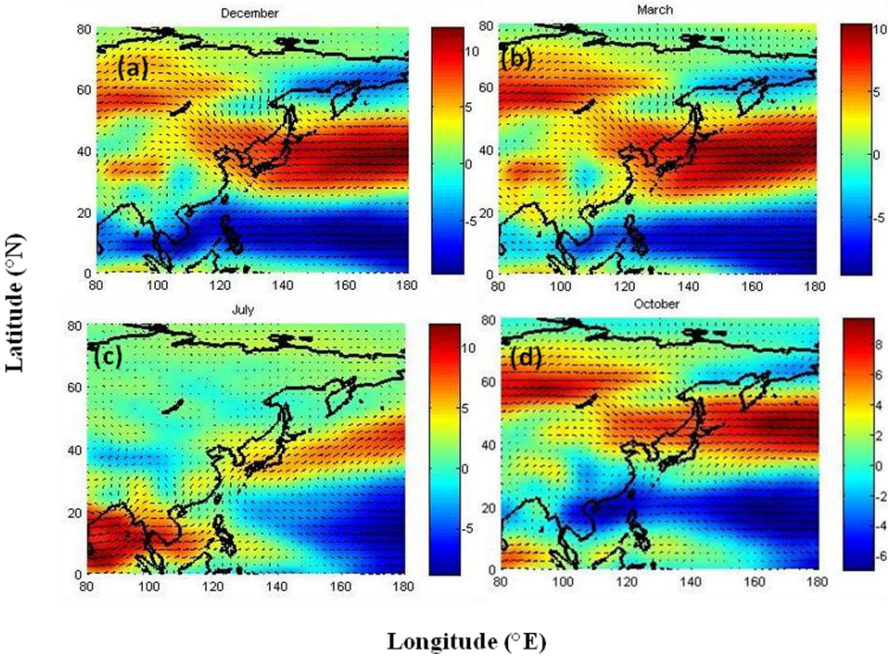

Figure 2. NCEP/NCAR reanalysis of the mean synoptic wind vector (m s^{-1}) at 850 mb pressure level over the western North Pacific during 2001-2012. The length of the arrow (→) indicates wind speed and head denotes the direction of wind.

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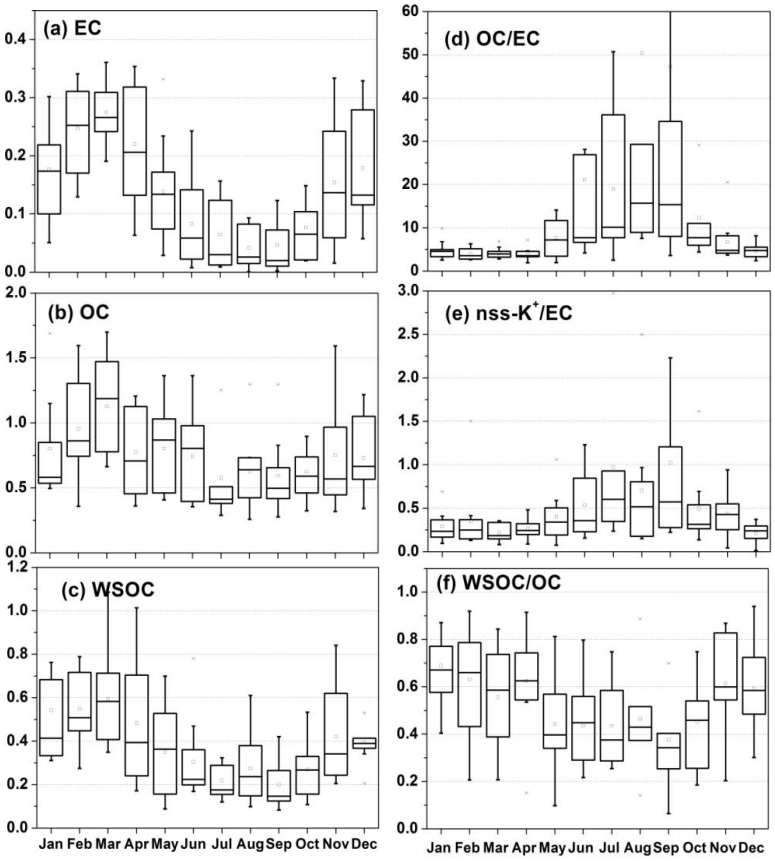

Figure 3. Box-whisker plots of monthly variations of carbonaceous aerosol components (μg m^{-3}) and their ratios at Chichijima Island in the western North Pacific during 2001-2012.

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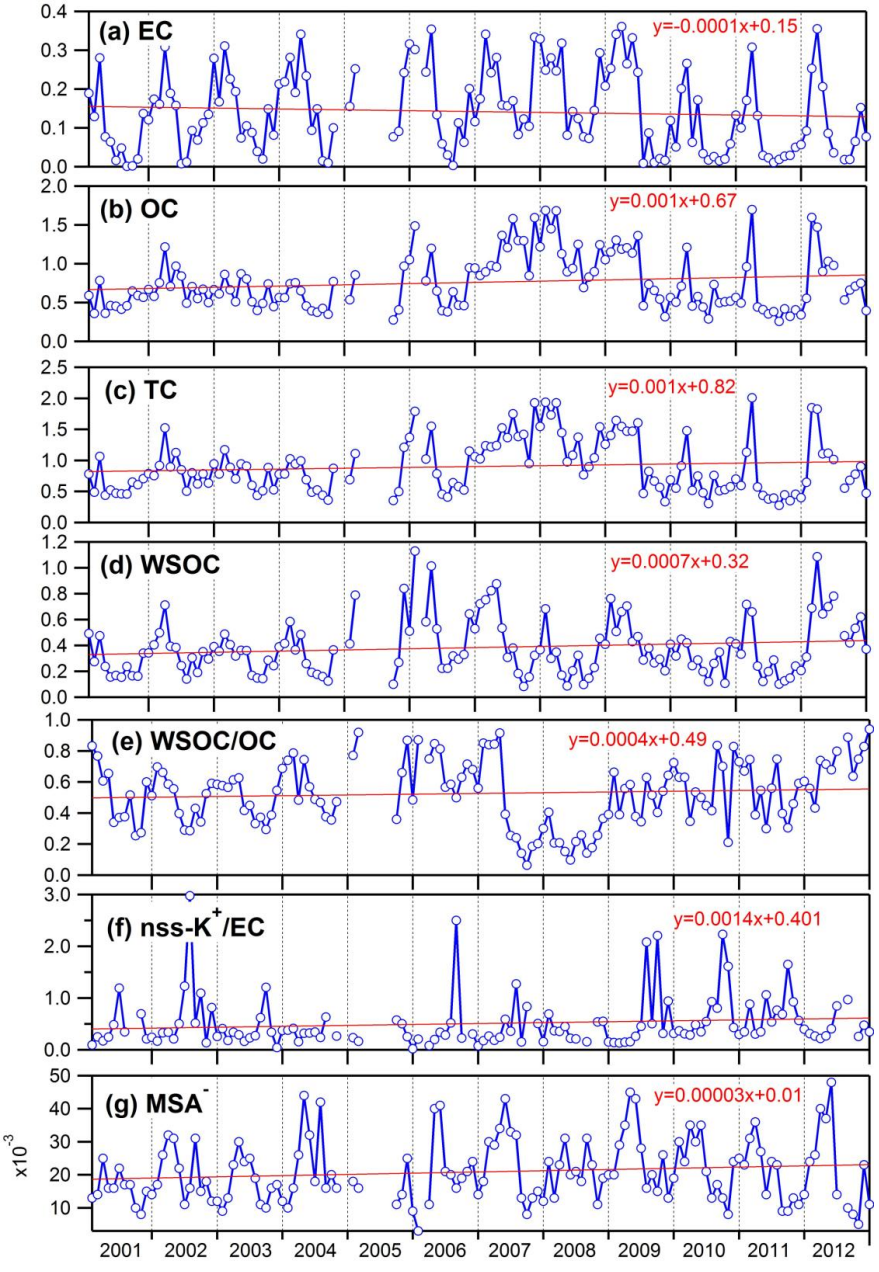

Figure 4. Annual trends in the concentrations (μg m^{-3}) of (a-f) carbonaceous aerosol components and their ratios, (g) methanesulfonate (MSA^-) during 2001-2012 over the western North Pacific. The liner trend equation (y=mx+c) is also shown for the each annual trend.

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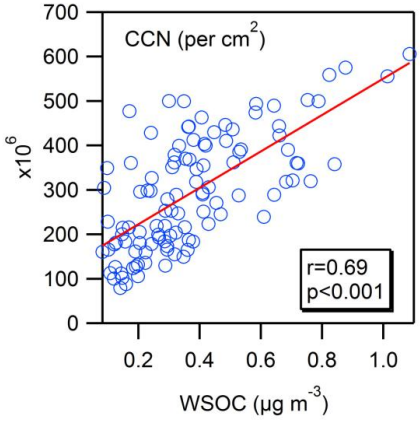

Figure 5. Regression analyses between WSOC and cloud condensation nuclei (CCN) concentrations over the western North Pacific.