Long-term (2001-2012) observation of the modeled hygroscopic growth factor of remote marine TSP aerosols over the western North Pacific: impact of long-range transport of pollutants and their mixing states

S.K.R. Boreddy[1], Kimitaka Kawamura[1] and Md. Mozammel Haque[1,2]

[1]Institute of Low Temperature Science, Hokkaido University, N19, W8, Kita-ku, Sapporo 060-0819, Japan.
[2]Graduate School of Environmental Science, Hokkaido University, Sapporo, Japan.

[*]Corresponding author

Kimitaka Kawamura,
Institute of Low Temperature Science,
Hokkaido University,
Sapporo 060-0819, Japan.
E-mail:kawamura@lowtem.hokudai.ac.jp

Abstract

In order to assess the seasonal and annual variability of long-range transported anthropogenic pollutants from East Asia and their effect on the hygroscopicity and precipitation process over the western North Pacific, we conducted a long-term calculation of bulk hygroscopicity, $g(90\%)_{ZSR}$, based on ZSR model using chemical composition data during 2001-2012 at Chichijima Island. We found sea-salts (Na^+ and Cl^-) are the major mass fraction (65%) of total water-soluble matter followed by SO_4^{2-} (20%) and WSOM (6%). Seasonal variation of $g(90\%)_{ZSR}$ showed high in summer to autumn and low in winter to spring months, probably due to the influence of long-range transport of anthropogenic SO_4^{2-}, dust, and organics from East Asia and their interaction with sea-salts by heterogeneous reactions. On the other hand, annual variations of $g(90\%)_{ZSR}$ showed a decrease from 2001 to 2006 and then an increase from 2007 to 2012. Interestingly, the annual variations of SO_4^{2-} mass fractions showed an increase from 2001 to 2006 and then a decrease from 2007 to 2012, demonstrating that SO_4^{2-} seriously suppress the hygroscopic growth of sea-salt particles over the western North Pacific. This is further supported by the strong negative correlation between SO_4^{2-} and $g(90\%)_{ZSR}$. Based on the MODIS satellite data, the present study demonstrates that long-range transported anthropogenic pollutants from East Asia to the North Pacific can act as efficient cloud condensation nuclei but significantly suppress the precipitation by reducing the size of cloud droplet over the western North Pacific.

Keywords: Hygroscopicity, ZSR model, inorganic ions, organics, long-range transport, western North Pacific

1. Introduction

Particulate matter is microscopic solid or liquid suspended in the earth's atmosphere. Although they represent a small portion of atmospheric mass, atmospheric particles largely impact on climate and global biogeochemistry[1]. Sea-salt particle is one of the most widely distributed natural aerosols, which forms via the evaporation of sea-spray droplets produced by the bubble bursting of entrained air during whitecap formation[2]. They are characterized as non-light-absorbing, highly hygroscopic, and coarse particles. Due to its strong hygroscopic nature, a sea salt particle can serve as efficient cloud condensation nuclei (CCN), altering cloud reflectivity, lifetime, and precipitation process[3-5]. Nonetheless, knowledge of hygroscopicity of sea-salt aerosols and their impact on radiative forcing calculations are still unclear[6-7].

Atmospheric aerosols consist of organic and inorganic compounds with their internal or external mixing. Hygroscopicity of aerosol particles is linked to the chemical composition and their mixing states. Cruz and Pandis[8] reported that organic acids such as glutaric and pinonic acids generally increase the water uptake capability of $(NH_4)_2SO_4$ but decrease that of NaCl salts based on a volume fraction relative to that of inorganic salts. Choi and Chan[9] studied the effect of organic species (glycerol, succinic acid, malonic acid, citric acid, and glutaric acid) on the hygroscopic behaviour of pure inorganic salts and found that the presence of all these organics in the mixed particle reduces the water absorption of NaCl but enhance that of $(NH_4)_2SO_4$ relative to that of the pure inorganic salts. Therefore, the interaction between organic and inorganic species (or mixing state) in aerosol particles is complex and this interaction acts either positively or negatively depending on the organic mass fractions and salt types[8, 10].

Zdanovskii-Stokes-Robinson (ZSR) relation[11] is the most common model, used to predict the hygroscopic growth of mixed aerosol particles using chemical composition data. Sjogren et al.[12] reported that the measured hygroscopic growth factors at the high-alpine site, Jungfraujoch, agreed well with predictions made by ZSR model. On the other hand, the hygroscopicity of ambient marine aerosols show a significant underestimation compared to the prediction estimated by numerical thermodynamic models[13].

Anthropogenic emissions from East Asia have significantly increased over recent decades due to the rapid growth of the East Asian economies, which are implausible to decline in the next 20 years[14]. In addition, surface dust in spring is another distinct feature of the air quality over East Asia and the outflow regions[15, 16]. These anthropogenic pollutants and dusts are transported from East Asia to the North Pacific by westerly winds[17, 18] and

perturb the remote marine background conditions and modify the physico-chemical properties of sea-salt particles as well as ocean biogeochemistry by heterogeneous reactions[19]. However, there is still knowledge gap on how long-range transported anthropogenic pollutants affect the precipitation process over the western North Pacific.

Chichijima Island is a remote marine site in the western North Pacific and is geographically located in the outflow region of Asian dusts and anthropogenic pollutants from East Asia during winter and spring, whereas pristine marine air masses dominate over the island in summer and autumn[20]. Therefore, this site is scientifically very important for studying the long-range atmospheric transport of pollutants and mineral dusts and their influence on the precipitation process; however, studies on long-term observations of transported aerosols over the western North Pacific are limited[20, 21]. Moreover, there is no study on the long-term observation of hygroscopic growth factors from the western North Pacific. In this study, we investigate seasonal and annual variation of the bulk hygroscopic growth factor, $g(90\%)_{ZSR}$, derived from ZSR model. We also discuss the impact of long-range atmospheric transport of anthropogenic pollutants and their mixing states on marine bulk hygroscopicity and precipitation process over the western North Pacific during the study period of 2001-2012.

The hygroscopic growth of fine and coarse particles should have different pictures because of different chemical compositions and sizes, thus, their atmospheric importance is dissimilar. Fine size particles are important for CCN formation, while coarse particles are playing a major role on the radiative impacts of aerosol particles. However, physico-chemical processes (coagulation and condensation as well as heterogeneous reactions) could make fine particles to be larger particles in the water mediated atmosphere (under high RH conditions). As a result, background conditions of the atmosphere may perturb, especially over the marine atmosphere. In the present study, the estimated hygroscopic growth factors from TSP aerosols would better elucidate about the mixing state of the above mentioned aerosol particles and their climatic effects.

2. Methods

2.1. Aerosol sampling

Aerosol (TSP) samples were collected on pre-combusted (450 °C, 3 hours) quartz filter (20 x 25 cm, Pallflex 2500QAT-UP) at 5 m above the ground level of Satellite Tracking Centre of Japan Aerospace Exploration Agency (JAXA, elevation 254 m) in Chichijima Island (27˚04' N; 142˚13' E) using a high volume air sampler with a flow rate of 1 m^3 min^{-1} during 2001-2012[20]. Aerosol samples were collected on a weekly basis, because of less local

pollution at Chichijima Island. After sampling, filters were put in a clean glass jar with a Teflon-lined screw cap and stored at -20 °C.

2.2. Analysis of Chemical species

For water-soluble inorganic species, a filter cut of 20 mm in diameter from each filter was extracted with 10 mL of organic-free ultra pure water (>18.2 MΩcm) under ultrasonication and filtrated through disk filters (Millex-GV, 0.22 μm, Millipore). These filtrated extracts were analyzed for inorganic species using an ion chromatography (761 Compact IC, Metrohm) and results were reported in elsewhere (Boreddy and Kawamura, 2015). For water-soluble organic carbon (WSOC), a punch of 20 mm was extracted with 20 mL of organic-free ultra pure water under ultrasonication and filtrated through a disk filters (Millex-GV, 0.22 μm, Millipore). These extracts were analyzed for WSOC using Total Carbon Analyzer (TOC-Vcsh, Shimadzu, Japan)[22].

2.3. The ZSR relation

The Zdanovskii-Stokes-Robinson (ZSR) model[11], which relates the hygroscopicity of mixture to that of the individual components at the same relative humidity (RH). The hygroscopic growth factor of aerosol particle can be predicted from the growth factors of individual components of the aerosol composition and their respective volume fractions (ε) using ZSR relation as,

$$g(RH)_{ZSR} = \left(\sum_i \varepsilon_i g_i (RH)^3\right)^{\frac{1}{3}} \qquad (1)$$

where $g(RH)_{ZSR}$ is the growth factor of the mixed particle, $g_i(RH)$ and ε_i are the growth factor of individual component and their respective volume fraction, respectively. The volume fractions are calculated by assuming that the dry aerosol is composed of sodium chloride, ammonium sulfate, ammonium chloride, sodium nitrate, sodium sulfate and water-soluble organic matter. Rest of the volume fractions is neglected because of its low abundance to WSM.

The ZSR model assumes that the particles are spherical and their mixing behaviour is ideal and also hygroscopic growth of the organic and inorganic components is independent.

3. Results and discussion

3.1 Validation of bulk $g(90\%)_{ZSR}$

In order to validate the retrieved growth factor, $g(90\%)_{ZSR}$, of TSP aerosols obtained from ZSR model, we compared $g(90\%)_{ZSR}$ with measured growth factor, $g(90\%)_{HTDMA}$, using HTDMA during 2001-2003 over the same sampling site[7] as shown in Fig. 1. We found that $g(90\%)_{ZSR}$ are strongly correlated with $g(90\%)_{HTDMA}$ with a correlation coefficient (R^2) of

0.80 and this correlation is statistically significant at the 99% confidence level (probability value less than 0.001). It can be seen from Fig. 1 that the difference in standard deviation (standard error) between the $g(90\%)_{ZSR}$ and $g(90\%)_{HTDMA}$ is 0.04 (0.006). We also found that $g(90\%)_{ZSR}$ are overestimated by on average 15%, probably due to the presence of marine organic compounds and the subsequent formation of less hygroscopic organic salts through aqueous phase reactions[7]. As a result, $g(90\%)_{HTDMA}$ may be decreased due to the internal mixing of chemical species and subsequent formation of less water-soluble salts.

Interestingly, this discrepancy in growth factor showed higher in spring followed by winter and lowest in summer, indicating that interactions of water-soluble organics with dust particles (for example, formation of CaC_2O_4) can suppress the hygroscopic growth of particles in the outflow regions of Asian dust in spring. This point will be discussed more in the following section 3.4. This is further supported by the previous studies[7, 13, 23-26], which reported that ambient marine aerosol particles with less than 30% organic mass show a 15% decrease in the hygroscopic growth factor. This perturbation adds significant uncertainty to the radiative balance calculations. However, in the present study, we found that contribution of WSOM to total water-soluble matter (WSM) is less than 30% (on average 6%). Therefore, it is reasonable to use ZSR model to predict the hygroscopic growth factors over the western North Pacific.

3.2. Temporal and seasonal trends in major mass fractions of WSM and $g(90\%)_{ZSR}$

Fig. 2 presents the temporal variation of major chemical mass fractions (Cl^-, Na^+, SO_4^{2-}, NO_3^- and WSOM) of WSM and the $g(90\%)_{ZSR}$ of TSP aerosols collected at Chichijima Island in the western North Pacific during 2001-2012. Sea-salt components (i.e., Na^+ and Cl^-) are found to compose a major mass fraction (range: 0.00-0.88 and 0.03-0.41, respectively), whose abundances are on average more than three times higher than SO_4^{2-} (0.00-0.77), ten times higher than WSOM (0.00-0.57), and sixteen times higher than NO_3^- (0.00-0.14) mass fractions. The $g(90\%)_{ZSR}$ values ranged from 1.63 to 2.28 with an average of 2.07±0.09 during the study period of 2001-2012. Although there is no clear increasing or decreasing temporal trends in all the species during the study period, a similar variation can be seen between the $g(90\%)_{ZSR}$ and sea-salt components, indicating that the hygroscopicity of Chichijima aerosols is mainly controlled by sea salt particles.

Interestingly, anti-correlations were found between the $g(90\%)_{ZSR}$ and WSOM, SO_4^{2-}, and NO_3^-. These results indicate that anthropogenic pollutants, water-soluble organic matter and their mixing state can alter the hygroscopicity of sea-salt particles through the

heterogeneous reactions, in particular, during the period of continental outflow over the western North Pacific. These points will be discussed in more detail in the following sections.

The seasonal variations in $g(90\%)_{ZSR}$ and major chemical mass fractions of total WSM are shown in Fig. 3a-f during 2001-2012. The vertical hinges represent data points from lower to upper quartile (i.e., 25th and 75th percentiles). The whiskers represent data points from the 5th to 95th percentiles. We found a clear seasonal variation in all the chemical mass fractions, which are clearly reflected in the $g(90\%)_{ZSR}$. These seasonal differences are verified by *t*-test. These results show that these differences are statistically significant with two tailed *p* values of less than 0.001. As illustrated in Fig. 3a, monthly means of $g(90\%)_{ZSR}$ are high in autumn followed by summer and scarce in spring and winter months, probably due to the atmospheric processing associated with dechlorination that may decrease the growth factor over the western North Pacific, especially during the period of continental outflow.

It is noteworthy that the similar seasonal pattern can be seen in the mass fractions of sea-salt particles (see Fig. 3b and c). On the other hand, SO_4^{2-} and NO_3^- mass fractions are maximized in spring followed by winter, probably due to the long-range atmospheric transport of anthropogenic pollutants from East Asia and minimized in summer and autumn months (see Fig. 3d and e). Mass fractions of WSOM are higher in summer followed by spring and lower in autumn (see Fig. 3f). We again found an opposite trend between the mass fractions of Cl^- and SO_4^{2-} and similar trend between the g(90%) and Cl^- mass fraction, demonstrating that SO_4^{2-} seriously suppresses the hygroscopic growth of sea-salt particles along with WSOM via heterogeneous reactions over the western North Pacific. This point will be discussed in more details in the following sections.

3.3. Annual trends in major mass fractions of WSM and $g(90\%)_{ZSR}$

Fig. 4a-d presents the annual variation of $g(90\%)_{ZSR}$ and mass fractions of selected components for different seasons during the period of 2001-2012. It can be clearly seen from Fig. 4a that $g(90\%)_{ZSR}$ showed a clear annual trend with a decrease from 2001 to 2006 and then an increase from 2007 to 2012 in winter and autumn. In spring, we couldn't find any clear annual trend, probably due to the influence of organo-metallic interaction during long-range transport of Asian dusts[7]. On the other hand, the annual variation of mass fractions of SO_4^{2-} showed an increase from 2001 to 2006 and a decrease from 2007-2012 ($p<0.005$). Lu et al.[27] reported that the emission rate of SO_2 over East Asia slowed down around 2005 and began to decrease after 2006. The reduction in SO_2 emissions in China was mainly due to the wide usage of Flue-Gas Desulfurization (FGD) devices in power plants. Similar annual

pattern can also be seen in the mass fractions of NO_3^-. Mass fractions of WSOM showed a clear annual trend ($p<0.005$) in winter with an increase from 2001 to 2006 and a decrease from 2007-2012 (see Fig. 4d). Based on all these results, we demonstrate that although WSOM often acts to decrease the hygroscopicity over the western North Pacific, anthropogenic SO_4^{2-} and NO_3^- that are long-range transported from East Asia also suppress the hygroscopic growth of sea-salt particles during winter and spring months.

3.4. A relation between $g(90\%)_{ZSR}$ and chemical mass fractions of WSM

Chemical compositions and their mixing states are crucial for modelling studies on the hygroscopic[28] and optical properties[29] of aerosol particles, which provide the information about their chemical aging[30]. Fig. 5 shows the scatter plots between the $g(90\%)_{ZSR}$ and mass fractions of different chemical species and/or components for different seasons during 2001-2012. Their corresponding Pearson correlation coefficient (R) values are reported in Table 1. We found an excellent positive correlation (range: 0.87 to 0.92) between Cl^- mass fractions and $g(90\%)_{ZSR}$ for all seasons, demonstrating that the growth factors at Chichijima Island are mainly controlled by sea-salt particles as shown in Fig. 5a. Mass fractions of Mg^{2+} show good correlations with $g(90\%)_{ZSR}$ in winter (0.56), followed by summer (0.44) and spring (0.34), but weakly correlated in autumn (0.18) (Fig. 5h). These results indicate that Mg^{2+} also can partially contribute to the hygroscopicity because Mg^{2+} largely comes from the ocean rather than continental sources[20]. We also found a strong positive correlation (0.73 to 0.86) between Cl^-/Na^+ mass fraction ratio and $g(90\%)_{ZSR}$ in all seasons (see Fig. 5j). These results demonstrate that the hygroscopicity at Chichijima Island is mainly controlled by the sea-salt particles and atmospheric processing associated with chloride depletion that may suppress the hygroscopic growth of marine aerosol particles.

In contrast, SO_4^{2-} and WSOM showed strong negative correlations (-0.70 to -0.90 and -0.6 to 0.82) with $g(90\%)_{ZSR}$, especially during the period with an influence of continental outflow from East Asia (winter and spring). On the other hand, mass fractions of NH_4^+ and NO_3^- also negatively correlated with $g(90\%)_{ZSR}$. These results demonstrate that mixing of anthropogenic pollutants (such as SO_2 and NO_x) with inorganic or organic species that can convert the high hygroscopic salts (NaCl) into low hygroscopic salts ($(NH_4)_2SO_4$, Na_2SO_4, $NaNO_3$, etc.) by heterogeneous reactions (see reactions R1 to R6) and other physical mechanisms such as coagulation and condensation during long-range atmospheric transport. Moreover, in spring, Asian dusts can interact with organics and leads to the formation of less hygroscopic salts such as calcium oxalate[7] or ammonium oxalate.

This is further supported by the negative correlation (0.25) between $g(90\%)_{ZSR}$ and Ca^{2+} during the spring. We also found good correlation between NH_4^+ and oxalic acid during winter ($R=0.75$; $p<0.0001$) and spring ($R=0.54$; $p<0.001$), suggesting the formation of ammonium oxalate over the western North Pacific. This correlation is more significant in winter than spring, probably due to the long-range atmospheric transport of biomass burning aerosols from East Asia. Reid et al.[31, 32] documented that NH_4^+ was significantly correlated with organic species, such as oxalic acid rather than SO_4^{2-} in the regional haze dominated by biomass burning smoke in Brazil. Our recent study[30] also supported the formation of ammonium oxalate in biomass burning aerosols collected at Tanzania, East Africa. Hence, it is likely that biomass burning may be a significant source of formation of ammonium oxalate. This result is further supported by significant negative correlations between $g(90\%)_{ZSR}$ and oxalic acid during winter (-0.63) and spring (-0.43) (see Table 1).

Ma and He[33] reported that formation of calcium nitrate will also lower the hygroscopicity of particles by mixing with oxalic acid (see reaction R6). The internal mixing of oxalic acid with sea-salt particles also leads to lower the hygroscopicity during the long-range atmospheric transport[34]. This kind of mixing in the dust particles is very important for explaining the mass transfer process in the atmosphere[35] and direct and indirect climate forcing of dust particles[36, 37]. Therefore, it is important to note that the declined $g(90\%)_{ZSR}$ in winter and spring was probably due to the formation of less hygroscopic particles or salts through heterogeneous reactions that play a significant role in aged mineral dust particles and anthropogenic pollutants, resulting in a decrease of the hygroscopic growth of marine aerosol particles. The possible acid displacement reactions, which occur over the western North Pacific, are given below.

$$2\,NaCl + H_2SO_4 \rightarrow Na_2SO_4 + HCl \quad (R1)$$

$$NaCl + HNO_3 \rightarrow NaNO_3 + HCl \quad (R2)$$

$$NaCl + CH_3SO_3H \rightarrow CH_3SO_3Na + HCl \quad (R3)$$

$$2\,NaCl + H_2C_2O_4 \rightarrow Na_2C_2O_4 + 2\,HCl \quad (R4)$$

$$NaCl + CH_3COOH \rightarrow CH_3COONa + HCl \quad (R5)$$

$$Ca(NO_3)_2 + H_2C_2O_4 \rightarrow CaC_2O_4 + 2\,HNO_3 \quad (R6)$$

Previous studies have shown that more hygroscopic group of particles is often observed in remote marine environment[6]. Growth factors of this group ($g(90\%)>1.85$) are larger than those of pure ammonium sulfate ($g(90\%)=1.70$) and pure ammonium bisulphate

(g(90%)=1.79). During the strong influence of continental outflow of air masses, an uptake of H_2SO_4 (or HNO_3) by sea-salt particles followed by the subsequent release of HCl, for example, converts some of NaCl (g(90%)=2.4) into sodium sulfate (g(90%)<1.8) (or sodium nitrate) by the above mentioned reactions (R1 or R2). The formation of sodium sulfate (or sodium nitrate) will result in a significant reduction in the growth factor of sea-salt particles and thus affect the CCN and precipitation process over the western North Pacific.

Fig. 6 presents the schematic diagram, which shows the changes in microphysical and chemical properties of sea-salt particles under the influence of two distinct air masses that aged over the western North Pacific. The observation site, Chichijima, is a remote Island in the western North Pacific located in the outflow region of Asian dust and anthropogenic pollutants from East Asia, especially from China. This sampling site exists in the boundary of the westerly (in winter and spring) and easterly (in summer and autumn) wind regimes.

During the long-range atmospheric transport of air masses by westerly winds, sea-salt particles are seriously modified by internal mixing of anthropogenic pollutants and dust particles through heterogeneous reactions as mentioned above (R1-R6). This mixing state, together with long-range transport of pollutants from East Asia, can depress the water uptake properties of sea-salts due to the formation of less hygroscopic particles and can increase the number of smaller size CCN particles, leading to the formation of smaller size of cloud droplets, an enhanced reflection of solar radiation (less transmission), and an increase in cloud lifetime. Moreover, smaller size particles absorb more radiation and suppress the precipitation process by cloud evaporation or simply cloud burning.

On the other hand, easterly (trade) winds with low wind speed carry pristine air masses to the sampling site especially in summer and autumn (see Fig. 6). In this process, sea-salt particles uptake more water acting as giant CCNs, which could be nucleated into larger cloud particles. By coagulation and condensation, less absorptive and more transmitant cloud particles grow into rain droplets hence enhancing precipitation process. Although the present study focus on the hygroscopic growth factor of bulk aerosols, the implications of these results (such as a reduction in water uptake of sea-salt particles due to internal mixing of sulfate/nitrate particles and organics) directly affect the CCN number concentrations by decreasing the size of particles and hence increases the number of smaller sized particles due to the continental influence (see Fig.6). However, measurements of particle number size distributions are required to further confirm these results.

These results are further supported by the MODIS aqua satellite (http://gdata1.sci.gsfc.nasa.gov) products and precipitation (downloaded from

http://www.jma.go.jp) at Chichijima Island in the western North Pacific during 2001-2012. Figs. 7a-b illustrate the seasonal variations of $g(90\%)_{ZSR}$ and precipitation at Chichijima Island during 2001-2012. The precipitations at Chichijima clearly increased from winter to autumn with lower precipitation values during westerly and higher values in trade wind regimes. Fascinatingly, we found similar seasonal trend in $g(90\%)_{ZSR}$, although we found a significant reduction in the growth factors during spring, which may be due to the influence of Asian dusts. These results demonstrate that westerly winds transported anthropogenic pollutants that suppress the hygroscopicity as well as precipitation over the western North Pacific by enhancing the CCN, COD (Cloud Optical Depth, a proxy for cloud cover) and other aerosol products, such as AOD (Aerosol Optical Depth at 550 nm, a proxy for fine mode aerosols), and particulate organic carbon concentrations, as shown in Figs. 7c-f, respectively. All the satellite-derived products are abundant during winter and spring (westerly) whereas scarce in summer and autumn (trade wind).

We also found a good opposite seasonal trend between the modeled $g(90\%)_{ZSR}$ and particulate organic carbon concentrations, indicating that organics in aerosols suppress the hygroscopic growth over the western North Pacific. Further, a robust opposite seasonal variation was found between precipitation and particulate organic carbon concentrations, demonstrating that particulate organics repress the precipitation by boosting up the CCN concentrations. Based on the above-mentioned results, it is reasonable to conclude that the long-range atmospheric transport of pollutants from East Asia are significantly enhancing the fine size CCN concentration, but seriously suppress the hygroscopic growth of aerosols affecting the precipitation over the western North Pacific.

Previous studies suggested that polluted aerosols suppress deep convective precipitation by decreasing cloud droplet size and delaying the onset of freezing[38-40]. In the modeling study by Cui et al.[41], the less precipitation is caused by drops evaporating more rapidly in the high aerosol case[42], which eventually reduces ice mass and hence precipitation. In contrast, Koren et al.[43] found, based on satellite data analyses, that increases in aerosol abundance correlated with a higher rate of rainfall in the tropics, subtropics and mid-latitudes. They also mentioned that the similar trends were seen across different locations and environmental conditions, suggesting a link between increased aerosol levels and more intense rainfall. However, their observation period is limited to specific season (June-August 2007) and they didn't discuss the effect of long-range transport of pollutants and their relation to precipitation. The present study should contribute to clarifying the above uncertainty, that

is, anthropogenic chemical species in the midlatitudes can depress the rainfall intensity in the open ocean.

Therefore, the above results highlight the complexity of the aerosol-cloud-precipitation system and demonstrate the sign for the global change in precipitation due to changes in the concentrations and composition of aerosols. It is important to note that microphysical processes can only change the temporal and spatial distribution of precipitation while the total amount of precipitation can only change if evaporation from the surface changes.

3.5 Atmospheric implication and conclusions

The purpose of this study has been to observe the long-term (2001-2012) variations in hygroscopic properties of TSP aerosols and their relation to the precipitation over the western North Pacific. We found the bulk hygroscopicity of remote marine aerosols is mainly controlled by sea-salt particles (NaCl) because of its high abundances in total WSM. However, anthropogenic pollutants that are transported from East Asia are internally mixed with sea-salt particles by heterogeneous reactions, leading to a suppression of the hygroscopic growth thus affecting the CCN properties especially during winter and spring. On the other hand, WSOM may often suppress the hygroscopic growth of remote marine aerosols over the western North Pacific. We also found that there is a serious impact of Asian dust and their interactions with organic/inorganic salts on hygroscopic growth.

Although there is no clear decadal trend in $g(90\%)_{ZSR}$, we found a systematic seasonal variation with high values in autumn and summer and low values in spring and winter. In winter and autumn, the annual variation of $g(90\%)_{ZSR}$ decreased from 2001 to 2007 and then increased continuously toward 2012. At the same time, SO_4^{2-} mass fractions increased from 2001 to 2006 and then decreased to 2012 probably due to the decrease in SO_2 emissions in China after 2006. These results demonstrate that anthropogenic sulfate seriously suppress the hygroscopic growth of marine aerosol particles through heterogeneous reactions over the western North Pacific, especially during long-range atmospheric transport. This is further supported by the regression analyses between $g(90\%)_{ZSR}$ and mass fractions of WSM during the study period. The present study also demonstrates that long-range atmospheric transport of pollutants from East Asia can enhance the CCN activity but suppress the precipitation by reducing the droplet size over the western North Pacific. However, size-segregated measurements may provide a different picture of hygroscopic properties, depending on the particle size, for variable chemical compositions.

390 In this study, we found that these modified sea salts have profound consequences on
391 their evolving physicochemical properties especially on hygroscopic behaviour by increasing
392 cloud droplet number concentration and reducing the cloud droplet size and thus reducing
393 precipitation process. Therefore, in the marine atmosphere, the above consequences should
394 add significant uncertainty to the climatic and radiative models.

395 **Acknowledgements**

396 This study was in part supported by the Japan Society for the Promotion of Science (JSPS)
397 through grant-in-aid 1920405 and 24221001. We appreciate the financial support of a JSPS
398 fellowship to S. K. R. Boreddy. The MODIS data used in this study were acquired as part of
399 NASA's Earth Science Enterprise. The authors wish to thank the data distribution centres for
400 their support.

401

References

1. N. Mahowald et al., *Annu Rev Env Resour.,* 2011, 36, 45-74.
2. D. C. Blanchard, *J. Geophys. Res.: Oceans*, 1985, 90, 961-963.
3. T. Ayash, S. Gong, and C. Q. Jia, *J.* Climat., 2008, 21, 3207-3220.
4. D. Rosenfeld, U. Lohmann , C. D. O'Dowd, M. Kulmala, S. Fuzzi, A. Reissell, and M. O. Andreae, *Sci.,* 2008, 321 (5894), 1309-1313.
5. C. D. O'Dowd, J. A. Lowe, and M. H. Smith, *Atmos. Environ.,* 1999, 33, 3053-3062.
6. M. Mochida et al., *J. Geophys. Res.-Atmos.,* 2011, 116, doi:10.1029/2010jd014759.
7. S. K. R. Boreddy, K. Kawamura, and J. S. Jung, *J. Geophys. Res.-Atmos.,* 2014, 119, 167-178.
8. C. N. Cruz and S. N. Pandis, *Environ. Sci. Technol*., 34, 2000, 4313–4319.
9. M. Y. Choi and C. K. Chan, *Environ. Sci. Technol.*, 2002, 36 (11), 2422–2428.
10. Z. J. Wu, A. Nowak, L. Poulain, H. Herrmann, and A. Wiedensohler, *Atmos. Chem. Phys*., 2011, 11, 12617–12626.
11. R. H. Stokes, and R. A. Robinson, *J. Phys. Chem.* 1966, 70, 2126-2131.
12. S. Sjogren et al., *Atmos. Chem. Phys.,* 2008, 8, 5715-5729.
13. Y. Ming, and L. M. Russell, *J. Geophys. Res.: Atmos.,* 2001, 106, 28259-28274.
14. Y. Zhao, J. Zhang, and C. P. Nielsen, *Atmos. Chem. Phys.,* 2014, 14, 8849-8868.
15. J. Sun, M. Zhang and T. Liu, *J. Geophys. Res.: Atmos.* 2001, 106, 10325-10333.
16. G. Wang, C. Cheng, J. Meng, Y. Huang, J. Li, and Y. Ren, *Atmos. Environ.,* 2015, 113, 169-176.
17. K. Kawamura, Y. Ishimura, and K. Yamazaki, *Global Biogeochem. Cycles* 2003, 17, 1003, doi:10.1029/2001GB001810.
18. K. Matsumoto, Y. Uyama, T. Hayano, and M. Uematsu, *J. Geophys. Res.: Atmos.* 2004, 109, D21206..
19. Y. Rudich, O. Khersonsky, and D. Rosenfeld, *Geophys. Res. Lett.* 2002, 29, 2064.
20. S. K. R. Boreddy, and K. Kawamura, *Atmos. Chem. Phys.* 2015, 15, 6437-6453.
21. S. K. Verma, K. Kawamura, J. Chen, P. Fu, and C. Zhu, *J. Geophys. Res.: Atmos.* 2015, 120, 4155-4168.
22. Y. Miyazaki, K. Kawamura, J. Jung, H. Furutani, and M. Uematsu, *Atmos. Chem. Phys.* 2011, 11, 3037-3049.
23. O.H. Berg, K. Hämeri, E. Swietlicki, J. Zhou, M. Väkevä, and J. M. Mäkelä, *J. Aero. Sci.,* 1998, 29, Supplement 2, S1101-S1102.
24. K. C. Kaku et al., *Atmos. Chem. Phys.* 2006, 6, 4101-4115.
25. E. Swietlicki et al., *Tellus B* 52, 2000, 201-227.
26. J. Zhou, et al., *J. Geophys. Res.- Atmos.,* 2001, 106, 32111-32123.
27. Z. Lu et al., *Atmos. Chem. Phys.* 2010, 10, 6311-6331.
28. K. Okada et al., *Atmos. Environ.,* 2005, 39, 5079-5089.
29. M. Pósfai, J. R. Anderson, P. R. Buseck, and H. Sievering, *J. Geophys. Res.: Atmos.,* 1999, 104, 21685-21693.
30. S. K. R. Boreddy, K. Kawamura, S. Mkoma, and P. Fu, *J. Geophys. Res.: Atmos.,* 2014, 199, 12233-12245.
31 J. S. Reid, P. V. Hobbs, R. J. Ferek, D. R. Black, J. V. Martines, M. R. Dunlap, and C. Liousse, J. Geophys. Res., 1998, 103(D24), 32,059-32,080.
32. J. S. Reid, R. Koppmann, T. F. Eck, and D. P.Eleuterio, Atmos. Chem. Phys., 2005, 5, 799-825.
33. Q. Ma, and H. He, *Atmos. Environ.* 2012, 50, 97-102.
34. Q. Ma, H. He, and C. Liu, *Atmos. Environ.* 2013, 69, 281-288.

35. V. A. Karydis, A. P. Tsimpidi, W. Lei, L. T. Molina, and S. N. Pandis, *Atmos. Chem. Phys*. 2011, 11, 13305-13323.
36. R. C. Sullivan, S. A. Guazzotti, D. A. Sodeman, Y. Tang, G. R. Carmichael, and K. A. Prather, *Atmos. Environ.* 2007, 41, 7166-7179.
37. R. C. Sullivan, M. J. K. Moore, M. D. Petters, S. M. Kreidenweis, G. C. Roberts, and K. A. Prather, *Phys. Chem. Chem. Phys.* 2009, 11, 7826-7837.
38. D. Rosenfeld, *Geophys. Res. Lett.,* 1999, 26, 3105–3108.
39. D. Rosenfeld, and W. L. Woodley, *Nature*, 2000, 405, 440–442.
40. A. P. Khain, D. Rosenfeld, and A. Pokrovsky, *Geophys. Res. Lett.,* 2001, 28, 3887-3890.
41. Z. Q. Cui, K. S. Carslaw, Y. Yin, and S. Davies, *J. Geophys. Res.,* 2006, 111, doi:10.1029/2005JD005981, d05201.
42. H. L. Jiang, H. W. Xue, A. Teller, G. Feingold, and Z. Levin, *Geophys. Res. Lett.*, 2006, 33, doi:10.1029/2006GL026024,114806.
43. I. Koren, O. Altaratz, L. A. Remer, G. Feingold, J. V. Martins, and R. H. Heiblum, *Nature Geosci.,* 2012, 5, 118-122.

Table 1. Pearson correlation coefficient (R) values between $g(90\%)_{ZSR}$ and chemical mass fractions for different seasons during 2001-2012 at Chichijima Island over the western North Pacific.

Species	$g(90\%)_{ZSR}$			
	Winter (n=132)	Spring (n=138)	Summer (n=132)	Autumn (n=143)
Cl^-	0.92*	0.90*	0.87*	0.88*
NO_3^-	-0.58*	-0.41*	-0.34*	-0.51*
SO_4^{2-}	-0.88*	-0.82*	-0.70*	-0.90*
Na^+	0.77*	0.74*	0.70*	0.66*
NH_4^+	-0.7*	-0.71*	-0.58*	-0.57*
K^+	-0.49*	-0.33*	-0.39*	-0.44*
Ca^{2+}	-0.15#	-0.25#	-0.19#	-0.23#
Mg^{2+}	0.56*	0.34*	0.44*	0.18#
WSOM	-0.82*	-0.60*	-0.67*	-0.53*
Oxalic acid	-0.64*	-0.43*	-0.39*	-0.57*
Cl^-/Na^+	0.86*	0.73*	0.77*	0.78*

*Correlation is significant at less than 0.001 levels (2-tailed)

#Correlation is significant at 0.05 levels (2-tailed)

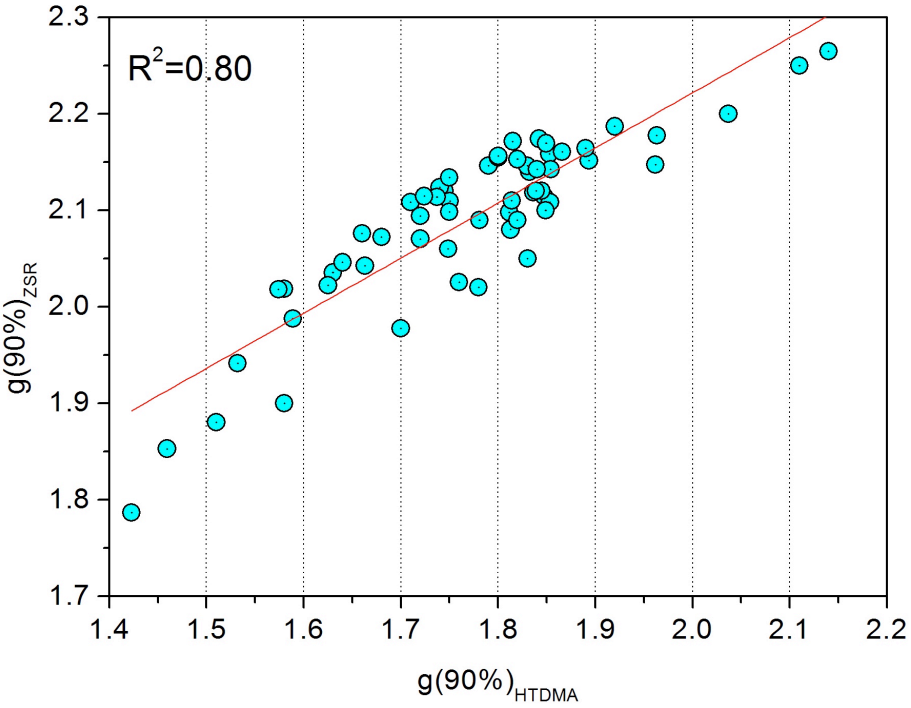

Fig. 1. Validation of modeled $g(90\%)_{ZSR}$ with measured $g(90\%)_{HTDMA}$ at Chichijima Island in the western North Pacific during 2001-2003.

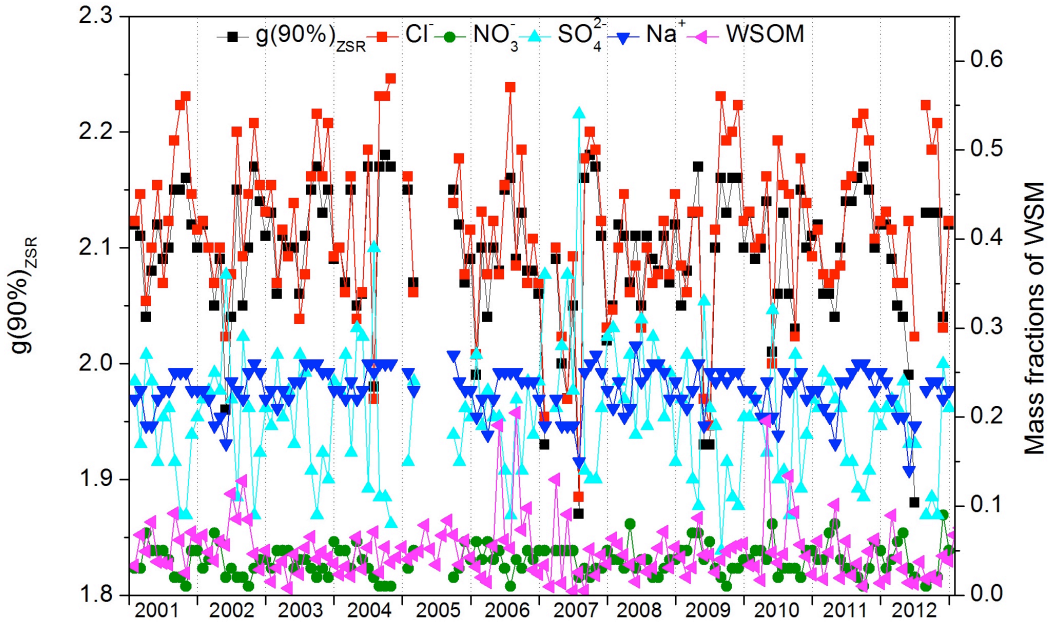

Fig. 2. Temporal variations in the $g(90\%)_{ZSR}$ and mass fractions of water-soluble matter at Chichijima Island in the western North Pacific during 2001-2012. Mass fractions are calculated using the data of ions and WSOC are taken from Boreddy and Kawamura (2015).

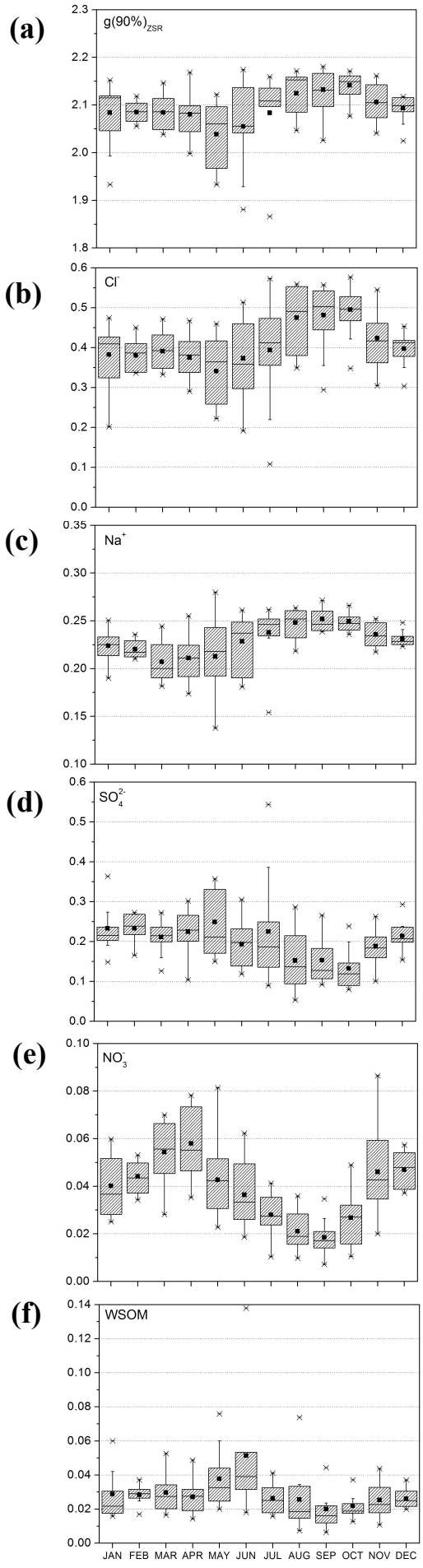

Fig. 3. Box and whisker plot, showing monthly variations in the $g(90\%)_{ZSR}$ and mass fractions of water-soluble matter at Chichijima Island in the western North Pacific during 2001-2012. Mass fractions are calculated using the data of ions and WSOC are taken from Boreddy and Kawamura (2015).

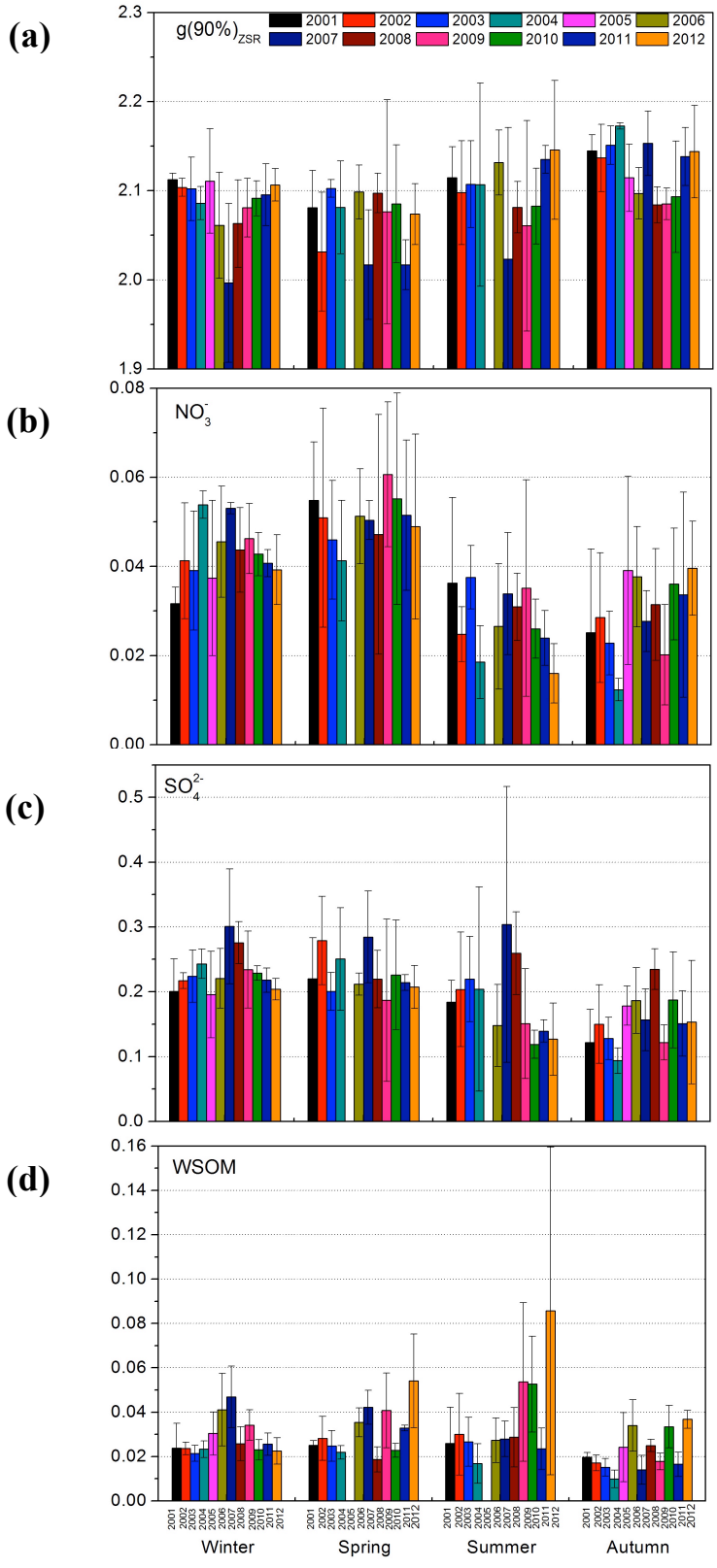

Fig. 4. Annual variations in the $g(90\%)_{ZSR}$ and mass fractions of WSM for different seasons. The data of ions and WSOC are from Boreddy and Kawamura (2015). Mass fractions are calculated using the data of ions and WSOC are taken from Boreddy and Kawamura (2015).

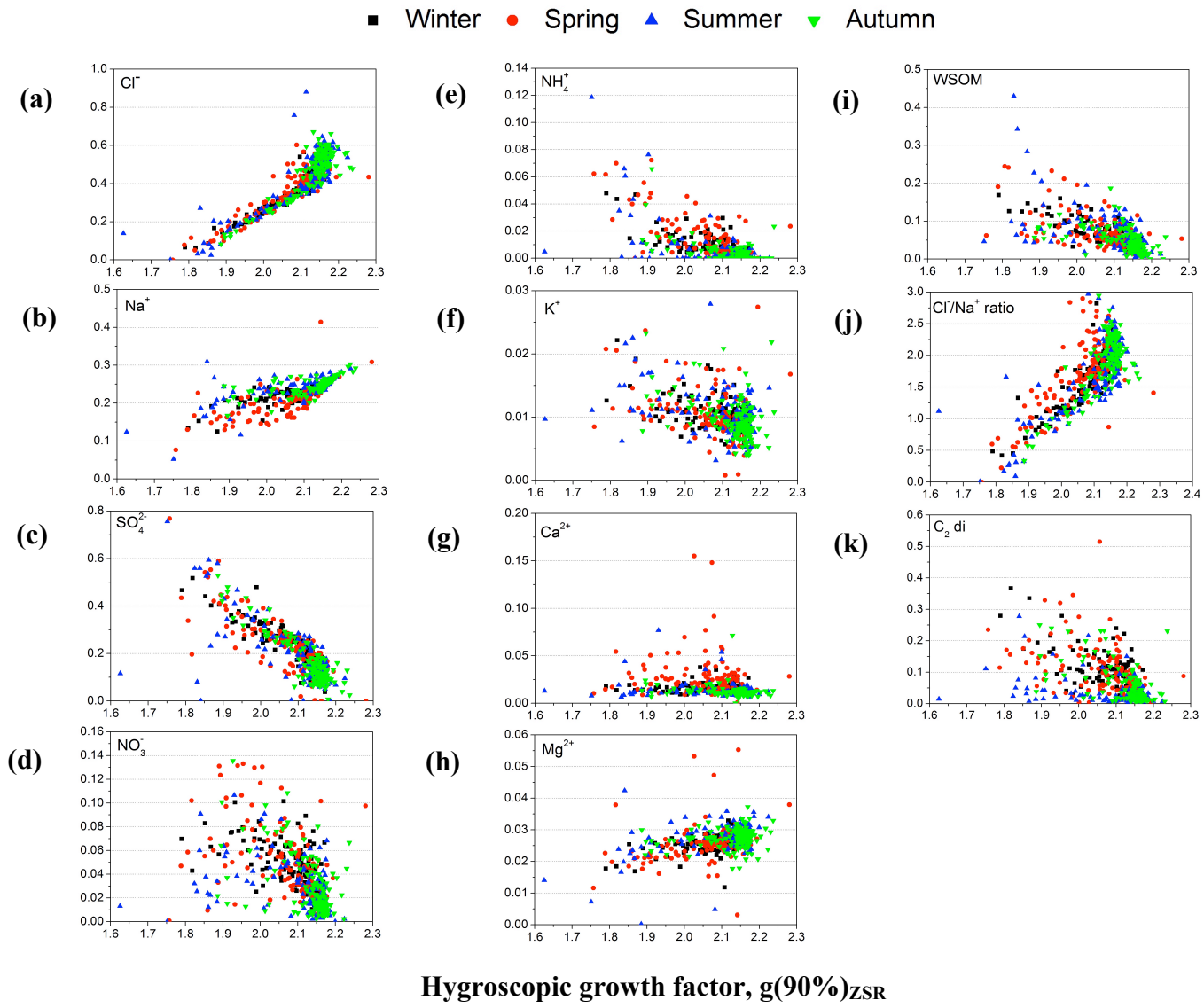

Fig. 5. Scatter plot, showing relation of the $g(90\%)_{ZSR}$ with (a-i) mass fractions of WSM, (j) Cl^-/Na^+ mass fraction ratio, and (k) C_2 di (μgm^{-3}) over the western North Pacific during 2001-2012. Mass fractions are calculated using the data of ions and WSOC are taken from Boreddy and Kawamura (2015).

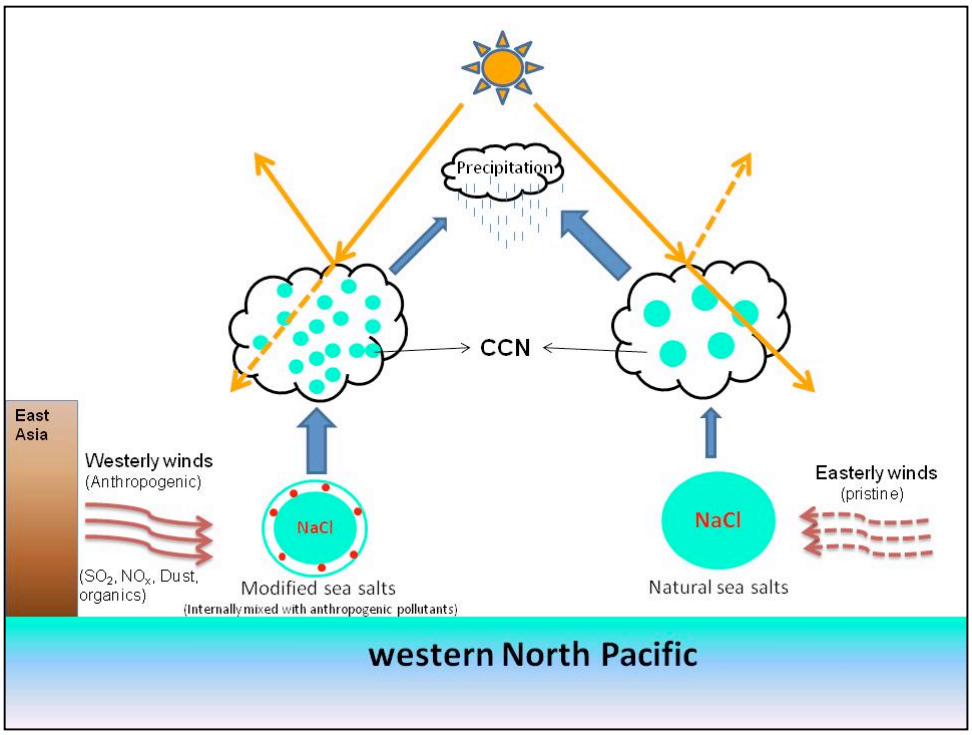

Fig. 6. Schematic diagram, showing changes in physico-chemical properties of sea-salt particles under the influence of two distinct aged air masses over the western North Pacific.

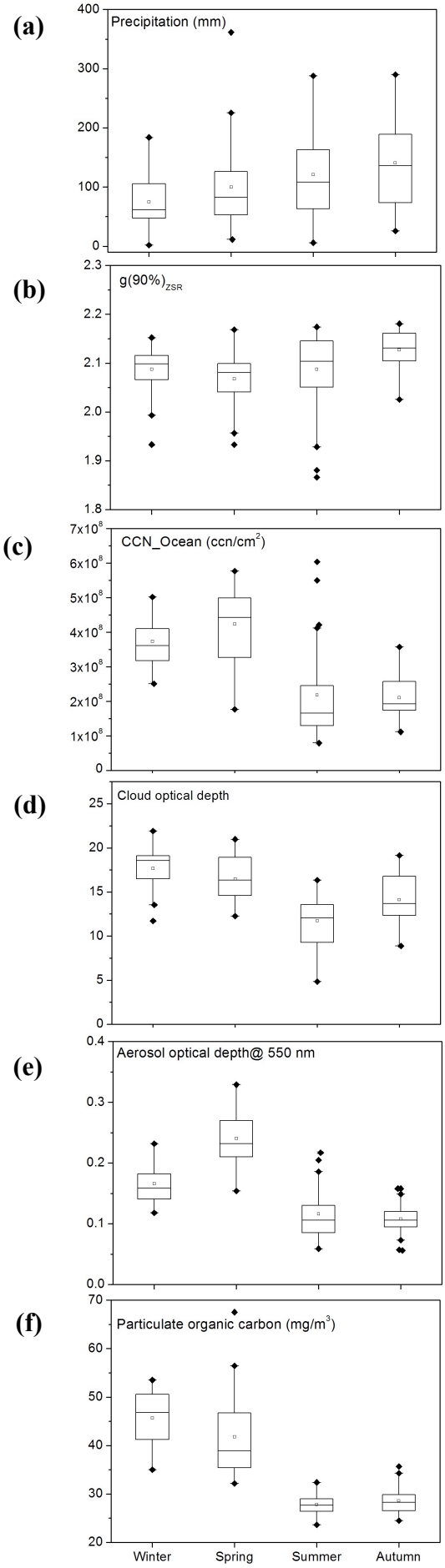

Fig. 7. Box and whisker plots, showing seasonal variations in (a) precipitation, (b) $g(90\%)_{ZSR}$, (c-f) MODIS Aqua satellite products of CCN number concentrations, cloud optical depth, aerosol optical depth, and particulate organic carbon, respectively for the region [140-145˚E; 25-30˚ N] over the western North Pacific during the period of 2001-2012.