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Author(s)	Boreddy, S. K. R.; Kawamura, K.
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# A 12-year observation of water-soluble ions in TSP aerosols collected at a remote marine location in the western North Pacific: an outflow region of Asian dust

S. K. R. Boreddy and K. Kawamura

Institute of Low Temperature Science, Hokkaido University, N19, W8, Kita-ku, Sapporo 060-0819, Japan

Correspondence to: K. Kawamura (kawamura@lowtem.hokudai.ac.jp)

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**Abstract.** In order to characterize the long-term trend of remote marine aerosols, a 12-year observation was conducted for water-soluble ions in TSP (total suspended particulate) aerosols collected from 2001 to 2012 in the Asian outflow region at Chichijima Island in the western North Pacific. We found a clear difference in chemical composition between the continentally affected and marine background air masses over the observation site. Asian continental air masses are delivered from late autumn to spring, whereas marine air masses were dominated in summer. Concentrations of non-sea salt (nss-)  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , nss- $\text{K}^+$  and nss- $\text{Ca}^{2+}$  are high in winter and spring and low in summer. On the other hand,  $\text{MSA}^-$  (methanesulfonate) exhibits higher concentrations during spring and winter, probably due to springtime dust bloom or due to the direct continental transport of  $\text{MSA}^-$  to the observation site. We could not find any clear decadal trend for  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$  and nss- $\text{Ca}^{2+}$  in all seasons, although there exists a clear seasonal trend. However, concentrations of nss- $\text{SO}_4^{2-}$  continuously decreased from 2007 to 2012, probably due to the decreased  $\text{SO}_2$  emissions in East Asia especially in China. In contrast, nss- $\text{K}^+$  and  $\text{MSA}^-$  concentrations continuously increased from 2001 to 2012 during winter and spring seasons, demonstrating that biomass burning and/or terrestrial biological emissions in East Asia are being increasingly transported from the Asian continent to the western North Pacific. This study also demonstrates that Asian dusts can act as an important source of nutrients for phytoplankton and thus sea-to-air emission of dimethyl sulfide over the western North Pacific.

## 1 Introduction

The atmosphere is mostly composed of gases but also contains suspended liquid and solid particles called aerosols. Knowledge of the physical and chemical properties of aerosols is important, because of their role in atmospheric processes and climate change. Marine aerosols perturb Earth's radiation balance directly by scattering and absorbing the incoming solar radiation or indirectly by acting as cloud condensation nuclei (CCN) and thus altering their water uptake properties (Twomey, 1977; Charlson et al., 1991; Ramanathan et al., 2001). The strength of these direct and indirect effects depends on the concentration, size distribution, and chemical composition of the atmospheric aerosols (Coakley et al., 1983). In addition, marine aerosols play an important role in the atmospheric sulfur cycle of the marine portion (O'Dowd et al., 1997; Faloon, 2009). Thus, meticulous information on the chemical and physical properties of marine aerosol is crucial for the aerosol studies.

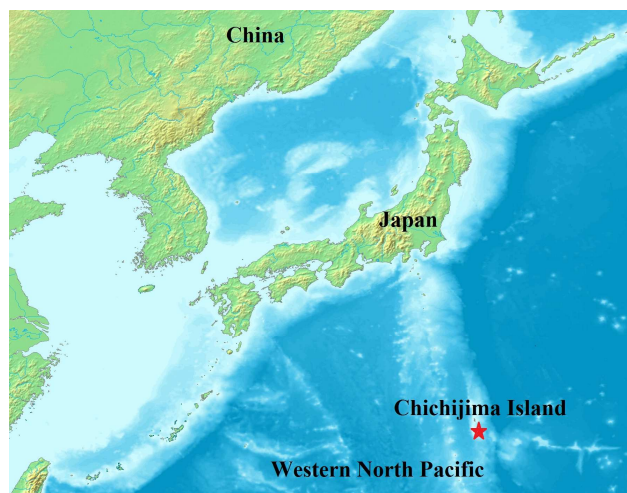
Sea salt, a ubiquitous and major component in the marine total suspended particulate (TSP) mass has been recognized as the dominant contributor to the clear-sky albedo over the oceans (Haywood et al., 1999). Sea salt aerosols are produced at the ocean surface through the bubble bursting mechanism (Woodcock, 1953). They can affect the chemical and microphysical properties of other aerosol components by taking up and releasing chemically reactive compounds including sulfur and halogen compounds. The sea salt concentration primarily depends on wind speed ranging from 2 to  $100 \mu\text{g m}^{-3}$  (Fitzgerald, 1991). Additionally, sea salt aerosol particles are hygroscopic by nature (Tang et al., 1997) and

hence act as CCN (O'Dowd et al., 1999; Quinn et al., 2000; Ayash et al., 2008).

Non-sea salt (nss-)  $\text{SO}_4^{2-}$  acts effectively as a reflector of solar radiation and as CCN and, therefore, controls the cloud microphysical properties and cloud albedo (Charlson et al., 1987). The principal source of nss- $\text{SO}_4^{2-}$  in the marine atmosphere is the oxidation of gaseous dimethyl sulfide (DMS) emitted by marine phytoplankton (Charlson et al., 1987). Graf et al. (1997) reported that the global burden of nss- $\text{SO}_4^{2-}$  (0.78 Tg sulfur) is composed 37 % from fossil fuel burning, 36 % from volcanoes, 25 % from marine DMS, and 1.6 % from biomass burning. On the other hand, continental anthropogenic nss- $\text{SO}_4^{2-}$  and nitrate ( $\text{NO}_3^-$ ) are transported over the remote marine locations and perturb the marine background conditions (Duce and Tindale, 1991; Uematsu et al., 1992; Matsumoto et al., 1998). Methanesulfonate (MSA) is also derived by the oxidation of DMS that originates from the biological activity in the ocean/land (Uematsu et al., 1992; Pavuluri et al., 2011; Miyazaki et al., 2012; Kunwar and Kawamura, 2014).

Anthropogenic and mineral aerosols have significant impact on global climate and also influence the atmospheric chemistry as well as marine ecosystems in remote oceanic regions (Matsumoto et al., 2004). Bridgman (1990) reported that on average about  $185\text{--}483 \times 10^6$  ton global aerosols per year are caused by anthropogenic sources including transportation, stationary combustion, industrial process, solid waste disposal and other miscellaneous sources. East Asia is one of the most swiftly developing regions in the world and consumes a significant amount of fossil fuels leading to an apparent increase in anthropogenic emission of gaseous pollutants and particulate matter. In addition, high dust loading in springtime is another discernible feature of air quality over the East Asian region (Sun et al., 2001). The long-range atmospheric transport of anthropogenic and mineral aerosols from the Asian continent to the North Pacific (Kawamura et al., 2003; Matsumoto et al., 2004) and sometimes even North America (Jaffe et al., 2003) by the westerlies may have significant impacts on global radiation balance, atmospheric chemistry, and ocean biogeochemistry (Satheesh and Moorthy, 2005; Rudich et al., 2002; Jickells et al., 2005; Houghton et al., 2001).

Chichijima Island, a remote marine site in the western North Pacific, is located on the lee side of a large industrial area; therefore, this site is well suitable for the study of long-range transport of air pollutants in East Asia and also the perturbation of anthropogenic activity in the remote marine atmosphere. However, the observational data on aerosol chemistry over the western North Pacific are very sparse (Kawamura et al., 2003; Mochida et al., 2003, 2010; Matsumoto et al., 2004; Chen et al., 2013; Boreddy et al., 2014). There is no study on the long-term observations of ionic chemical species from the western North Pacific. In order to investigate the annual and seasonal behavior of water-soluble inorganic ions and to clarify the decadal trend of the long-range



**Figure 1.** The geographical location of Chichijima Island (indicated by red colored star) in the western North Pacific.

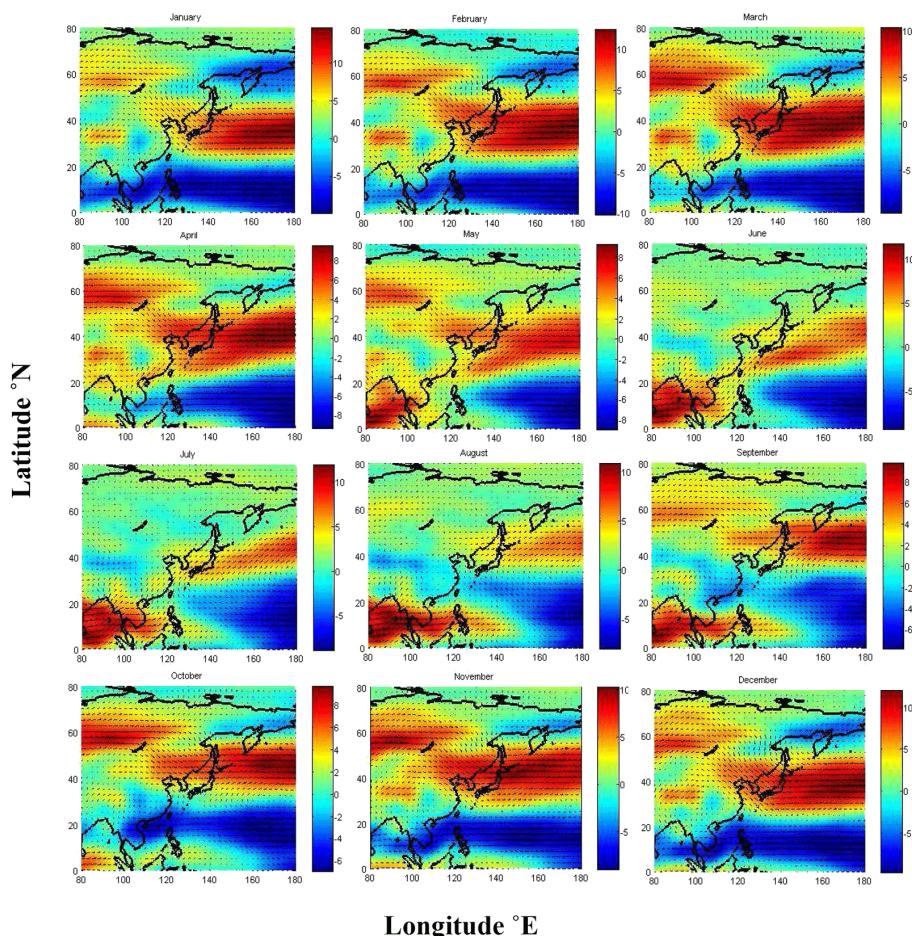
transport of continental aerosols to the remote ocean area, we carried out measurements of atmospheric aerosols at Chichijima Island in the western North Pacific.

## 2 Experimental

### 2.1 Sampling site and aerosol sampling

Figure 1 shows the sampling location of Chichijima Island in the western North Pacific and its surrounding East Asian regions. This island is about 1000 km from the main Japanese island, Honshu, and 2000 km away from the Asian continent. The area within 40 km of this station is covered by oceans and seas. The population of Chichijima is about 2300 and the island's area about 24 km<sup>2</sup> according to the report of the Tokyo metropolitan government bureau of general affairs (<http://www.soumu.metro.tokyo.jp/07ogasawara/28.html>, accessed in November 2011). The observatory is not affected by local pollution but by the long-range transport of polluted air from the Asian continent during winter and spring. Therefore, the observations at Chichijima Island are useful in discussing the long-range transport of polluted air on a regional scale.

TSPs were collected on a weekly basis at the Satellite Tracking Center of Japan Aerospace Exploration Agency (JAXA, elevation: 254 m) in Chichijima Island (27°04' N, 142°13' E) at a height of 5 m above ground level during 2001–2012. Aerosol particles were collected on pre-combusted (450 °C, 3 h) quartz filters (20 × 25 cm, Pallflex 2500QAT-UP) using a high volume air sampler with a flow rate of 1 m<sup>3</sup> min<sup>-1</sup> (Kawamura et al., 2003). Filters were placed in a clean glass jar with a Teflon-lined screw cap during the transport and storage. After the sampling, the filters



**Figure 2.** NCEP/NCAR reanalysis of the mean synoptic wind vector ( $\text{m s}^{-1}$ ) at 850 mb pressure level for each month over the study area during 2001–2012.

were recovered into the glass jar and stored in a freezer room at  $-20^{\circ}\text{C}$  prior to analysis.

## 2.2 Analysis of chemical species

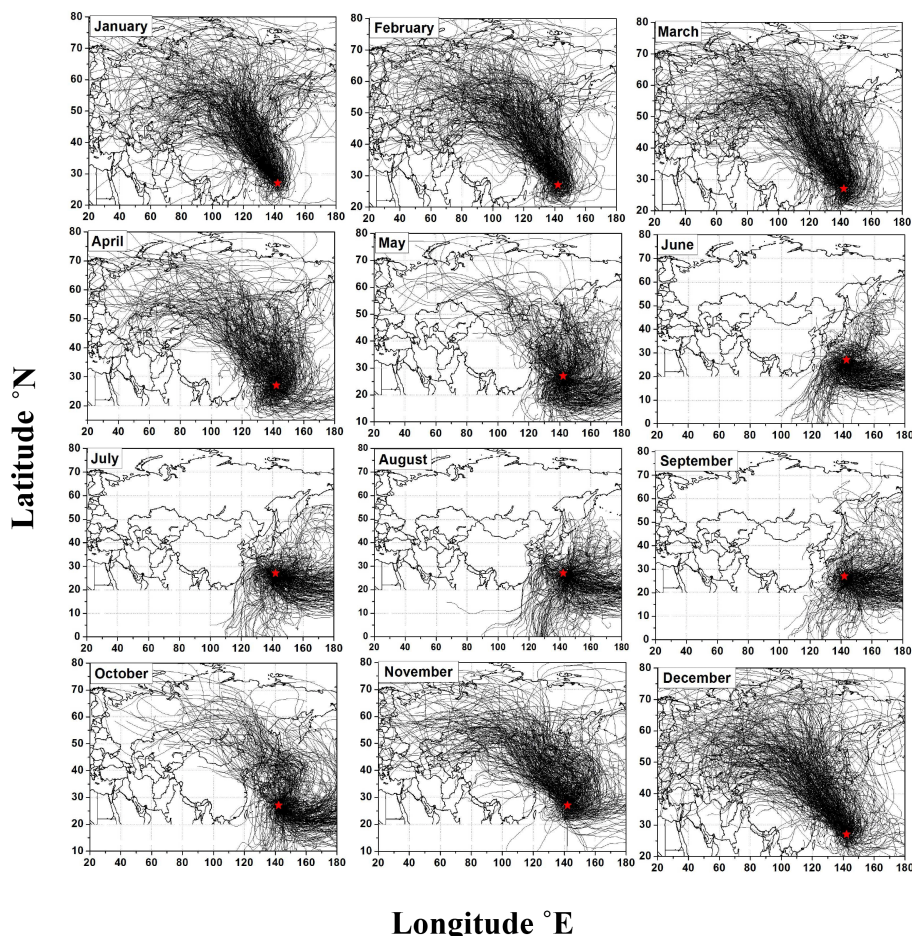
All samples were analyzed at the Institute of Low Temperature Science, Hokkaido University, Japan. The procedure of chemical analysis is as follows: a punch of 20 mm in diameter from each filter sample was extracted with 10 mL organic-free ultrapure water (resistivity of  $> 18.2 \text{ M}\Omega \text{ cm}$ , Sartorius arium 611 UV) and ultrasonicated for 30 min. These extracts were filtered through a disk filter (Millex-GV,  $0.22 \mu\text{m}$  pore size, Millipore) to remove filter debris and particles and were analyzed for major inorganic ions ( $\text{MSA}^{-}$ ,  $\text{Cl}^{-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^{-}$ ,  $\text{Na}^{+}$ ,  $\text{NH}_4^{+}$ ,  $\text{K}^{+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ) using an ion chromatograph (761 Compact IC, Metrohm, Switzerland).

Major anions were separated on a SI-90 4E Shodex column (Showa Denko, Tokyo, Japan) using a mixture of  $1.8 \text{ mM Na}_2\text{CO}_3 + 1.7 \text{ mM NaHCO}_3$  solution at a flow rate of  $1.2 \text{ mL min}^{-1}$  as an eluent and  $40 \text{ mM H}_2\text{SO}_4$  for a suppressor. For cation measurements, a Metrosep C2-150

(Metrohm) column was used by using a mixture of  $4 \text{ mM tartaric acid (C}_4\text{H}_6\text{O}_6) + 1 \text{ mM dipicolinic acid (C}_7\text{H}_5\text{NO}_4)$  solution as eluent at a flow rate of  $1.0 \text{ mL min}^{-1}$ . The injection loop volume was  $200 \mu\text{L}$ . A calibration curve was evaluated using authentic standards along with a sequence of filter samples. The analytical error in duplicate analysis was about 10%. Contributions from the field blanks varied between 0 to 8% and 0 to 2% of real samples for anions and cations, respectively, during the sampling period. The concentrations of all inorganic ions reported here are corrected for field blanks that were collected during the sampling period (2001–2012). A total of 545 samples were used in this study.

## 2.3 Synoptic wind pattern and general meteorology

Figure 2 shows monthly mean wind vectors at 850 mb pressure level over Chichijima Island and its surrounding regions, as obtained from the National Centers for Environmental Prediction (NCEP)/National Center for Atmospheric Research (NCAR) reanalysis (<http://www.esrl.noaa.gov/psd/data/gridded/reanalysis/>); the data have been used to ascer-



**Figure 3.** NOAA HYSPLIT 10-day backward air mass trajectories at 500 m a.g.l. for each month over Chichijima Island during 2001–2012.

tain the synoptic conditions during the study period 2001–2012. It is very clear that from January to April the synoptic winds are stronger, circulation is westerly (from the Asian continent to the Pacific) and the observation site experiences long-range continental aerosols (anthropogenic and dust). The winds are weakening by May/June and the wind direction changes to southeasterly and continues until August/September. The observation site gets pristine marine air masses, low wind speed and also much rainfall during the southeasterly regime. Again the wind starts shifting from southeasterly to northwesterly/westerly by October and becomes stronger towards December and January–April again. Therefore, on the basis of major synoptic meteorological conditions as above, a year is divided into four seasons: winter (December–February), spring (March–May), summer (June–August) and autumn (September–November) over Chichijima Island.

Based on the historical records from 1974 to 2011 (see Fig. S1 in the Supplement) (<http://weatherspark.com/averages/33165/Chichijima-Chichi-Shima-Chubu-Japan>), the temperature typically varies from 16 to 30 °C and is

rarely below 13 °C or above 31 °C over the course of a year. In summer the average daily high temperature is above 28 °C, whereas in the winter the average daily high temperature is below 22 °C. The relative humidity typically ranges from 55 (winter) to 94 % (summer) over the year, rarely dropping below 45 % and reaching as high as 98 %. The highest average wind speed of 4 m s<sup>-1</sup> occurs in spring, when the average daily maximum wind speed is 6 m s<sup>-1</sup>. The lowest average wind speed of 2 m s<sup>-1</sup> occurs in summer, when the average daily maximum wind speed is 4 m s<sup>-1</sup>. In this region, westerly winds dominate in winter and spring and trade winds dominate in summer and autumn.

## 2.4 Backward air mass trajectories

Figure 3 shows daily 10-day backward air mass trajectories arriving over the observation site, Chichijima at 500 m above the ground level, which were computed for each month using the HYSPLIT model, developed by NOAA/ARL (<http://ready.arl.noaa.gov/HYSPLIT.php>) (Draxler and Rolph, 2003), for the study period of 2001–2012. The selection of 500 m altitude for air mass trajectories was due to the po-

tential impact of the air–sea surface interactions within the boundary layer (Zielinski et al., 2014; Rozwadowska et al., 2010). The sampling site Chichijima is in the western North Pacific, located in the outflow region of Asian dusts and polluted air masses from China. At 500 m altitude, all trajectories come from the East Asian countries during winter and spring. Therefore, based on the sampling point (JAXA, 254 m) and source regions, we assumed that 500 m is the minimum suitable altitude to calculate backward air mass trajectories over Chichijima Island. As we discussed above, during the winter and spring months, the air masses originate from Siberia passing over northeastern Asia, whereas in the summer months they mostly originate from the Pacific, where pristine air masses exist.

## 2.5 Evaluation of non-sea salt analysis

The contributions from other sources excluding sea salts are calculated using  $\text{Na}^+$  as a sea spray marker. However, in this study, for better accuracy, non-sea salt components were evaluated from the sea salt (ss)  $\text{Na}^+$  fraction (Bowen, 1979; Becagli et al., 2005).

$$\text{nss-SO}_4^{2-} = [\text{SO}_4^{2-}] - 0.253 \cdot \text{ss-Na}^+, \quad (1)$$

$$\text{nss-Ca}^{2+} = [\text{Ca}^{2+}] - 0.038 \cdot \text{ss-Na}^+, \quad (2)$$

$$\text{nss-K}^+ = [\text{K}^+] - 0.037 \cdot \text{ss-Na}^+, \quad (3)$$

where  $[\text{SO}_4^{2-}]$ ,  $[\text{Ca}^{2+}]$  and  $[\text{K}^+]$  are the total measured TSP mass concentrations and  $\text{ss-Na}^+$  was calculated using the four-equation system reported below and knowing total  $\text{Na}^+$ , total  $\text{Ca}^{2+}$ , the mean  $\text{Ca}^{2+}/\text{Na}^+$  ratio in the crust ( $(\text{Na}^+/\text{Ca}^{2+})_{\text{crust}} = 1.78 w/w$ ; Bowen, 1979) and the mean  $\text{Ca}^{2+}/\text{Na}^+$  ratio in sea water ( $(\text{Ca}^{2+}/\text{Na}^+)_{\text{seawater}} = 0.038 w/w$ ; Bowen, 1979).

$$\begin{aligned} \text{ss-Na}^+ &= \text{Na}^+ - \text{nss-Na}^+ \\ \text{nss-Na}^+ &= \text{nss-Ca}^{2+} \cdot (\text{Na}^+/\text{Ca}^{2+})_{\text{crust}} \\ \text{nss-Ca}^{2+} &= \text{Ca}^{2+} - \text{ss-Ca}^{2+} \\ \text{ss-Ca}^{2+} &= \text{ss-Na}^+ \cdot (\text{Ca}^{2+}/\text{Na}^+)_{\text{seawater}} \end{aligned} \quad (4)$$

Crustal contribution to water-soluble sodium ranged from 0.004 to 0.94 with a mean of  $0.078 \pm 0.071$  during the study period.

## 3 Results and discussion

### 3.1 Ion balance

In order to assess the quality of the analysis, we performed an ion balance calculation using major anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ) and cations ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ) assuming that most of the ions are in the solutions. Based on the electro neutrality principle, the sum of total anions ( $\mu\text{eq m}^{-3}$ ) should be equal to the sum of total cations ( $\mu\text{eq m}^{-3}$ ) in the

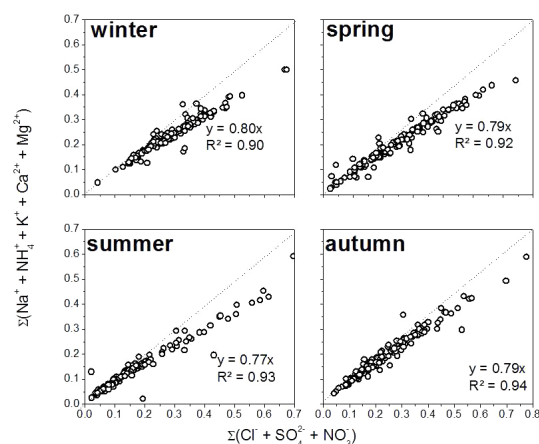


Figure 4. Charge balance of ions ( $\mu\text{eq m}^{-3}$ ) on a seasonal scale.

solutions and this ratio is a good indicator to study the acidity of aerosols over the sampling site. The following equations are used here to calculate the charge balance between cations and anions.

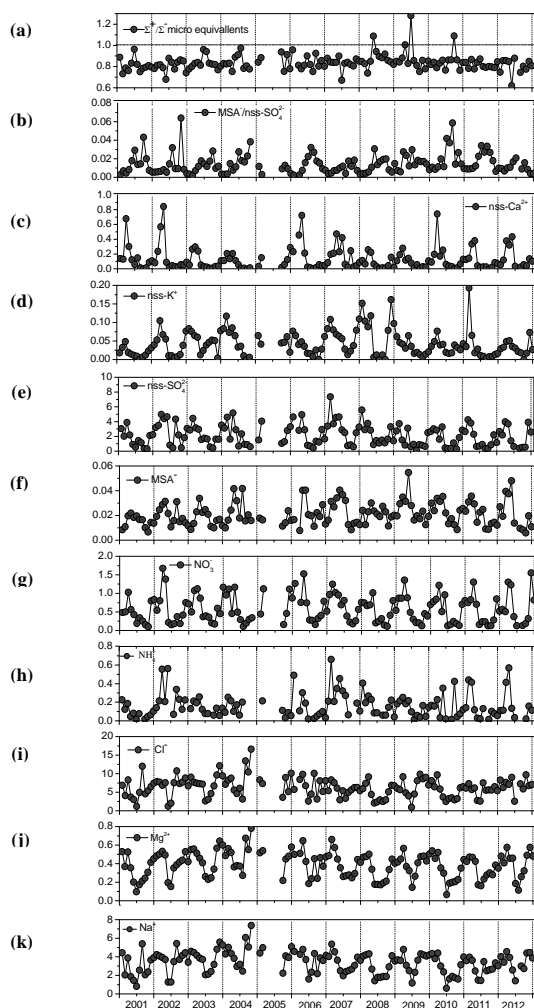
$$\begin{aligned} \text{Cation equivalent}(\Sigma^+) &= \frac{\text{Na}^+}{23} + \frac{\text{NH}_4^+}{18} + \frac{\text{K}^+}{39} \\ &+ \frac{\text{Mg}^{2+}}{12} + \frac{\text{Ca}^{2+}}{20} \end{aligned} \quad (5)$$

$$\text{Anion equivalents}(\Sigma^-) = \frac{\text{SO}_4^{2-}}{48} + \frac{\text{NO}_3^-}{62} + \frac{\text{Cl}^-}{35.5} \quad (6)$$

The relation between anions and cations for different seasons are shown in Fig. 4. We found that correlation coefficients of anions vs. cations were higher than 0.92 for all seasons, which indicates a good quality of data and that ions share a common origin (Zhang et al., 2011). The slopes of linear regression lines for the seasonally stratified data are  $> 1$  with the following order: summer (1.264)  $>$  spring (1.256)  $>$  autumn (1.252)  $>$  winter (1.231). This result suggests that in all seasons, the TSP was apparently acidic. As most of the major ions were measured except for hydrogen ions ( $\text{H}^+$ ), the cation deficits are probably due to the  $\text{H}^+$  ion.

### 3.2 Temporal variations of major inorganic species, $\text{MSA}^-/\text{nss-SO}_4^{2-}$ and $\Sigma^+/\Sigma^-$ ratios

Figure 5 presents temporal variations of major water-soluble ionic species,  $\text{MSA}^-/\text{nss-SO}_4^{2-}$  and  $\Sigma^+/\Sigma^-$  ratios for the period 2001–2012 over the sampling site. All the measured ions showed a clear temporal trend for each year during the study period. The  $\Sigma^+/\Sigma^-$  ratio ( $\mu\text{eq m}^{-3}$ ), which is a good indicator of acidity of aerosols over the environment, ranged from 0.8 to 1.6 with a mean of  $1.2 \pm 0.1$ , demonstrating that aerosol particles are acidic over Chichijima Island (Fig. 5a). The  $\text{MSA}^-/\text{nss-SO}_4^{2-}$  ratio, which can be used as a tracer to assess the contribution of biogenic sources to sulfate in the atmosphere (Savoie and Prospero, 1989), varied between



**Figure 5.** Temporal variations of different measured/derived inorganic ions ( $\mu\text{g m}^{-3}$ ) and mass ratios over the western North Pacific during 2001–2012. Each data point represents 1 month in each year.

0.002 and 0.064 with a mean of  $0.014 \pm 0.01$  and summertime maxima (Fig. 5b).

Sea salt species ( $\text{Cl}^-$  and  $\text{Na}^+$ ) are found as the most abundant ranging from 0.92 to  $16.6 \mu\text{g m}^{-3}$  with a mean of  $6.31 \pm 2.61 \mu\text{g m}^{-3}$  and from 0.61 to  $7.36 \mu\text{g m}^{-3}$  with a mean of  $3.39 \pm 1.20 \mu\text{g m}^{-3}$ , respectively (see Fig. 5i and k). Concentrations of  $\text{nss-SO}_4^{2-}$  varied from 0.09 to  $7.85 \mu\text{g m}^{-3}$  with a mean of  $2.17 \pm 1.53 \mu\text{g m}^{-3}$  (see Fig. 5e), whereas those of nitrate ranged from 0.09 to  $1.17 \mu\text{g m}^{-3}$  (mean  $0.57 \pm 0.37 \mu\text{g m}^{-3}$ ). Although  $\text{NH}_4^+$  was less abundant throughout the sampling period, we found significant levels under the influence of continental air masses in the spring. Its concentrations ranged from 0.01 to  $1.10 \mu\text{g m}^{-3}$  with a mean of  $0.17 \pm 0.16 \mu\text{g m}^{-3}$  (Fig. 5h). Concentrations of  $\text{MSA}^-$ , a marker of biogenic source, varied from 0.006 to  $0.055 \mu\text{g m}^{-3}$  with a mean of  $0.021 \pm 0.009$  (Fig. 5f).  $\text{nss-Ca}^{2+}$  ( $\text{nss-K}^+$ ), a tracer for dust (biomass burning), ranged

from 0.002 to  $0.84 \mu\text{g m}^{-3}$  ( $0.002$  to  $0.19 \mu\text{g m}^{-3}$ ) with a mean of  $0.13 \pm 0.15 \mu\text{g m}^{-3}$  ( $0.04 \pm 0.03 \mu\text{g m}^{-3}$ ) (Fig. 5c, d). Concentrations of  $\text{Mg}^{2+}$  ranged from 0.06 to  $0.78 \mu\text{g m}^{-3}$  with a mean of  $0.40 \pm 0.14 \mu\text{g m}^{-3}$  (Fig. 5j). It is also noteworthy that the sum of all the water-soluble inorganic ions (WSIM) ranged from 2.9 to  $25.7 \mu\text{g m}^{-3}$  with a mean of  $13.1 \pm 4.8 \mu\text{g m}^{-3}$  in Chichijima TSP aerosols for the study period of 2001–2012 (not shown as a figure).

### 3.3 Monthly variations of major chemical species and $\text{MSA}^- / \text{nss-SO}_4^{2-}$

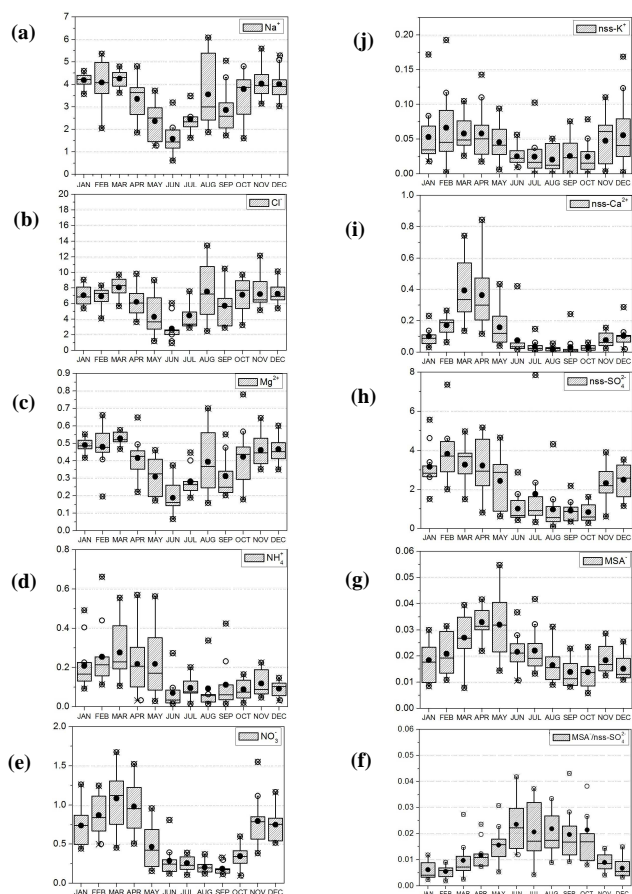
Figure 6 shows box and whisker plots of monthly variations of different chemical species at Chichijima Island in the western North Pacific for the period of 2001–2012. Almost all of the ions showed a clear monthly/seasonal variation with higher concentrations during the long-range atmospheric transport of continental air masses and lower concentrations under the influence of marine air masses. Seasonally averaged concentrations of major ions (mean  $\pm$  SD) during 2001–2012 at Chichijima Island in the western North Pacific are reported in Table 1. The presence of a monthly averaged trend is demonstrated by Theil–Sen slope test (Sen, 1968; Theil, 1950). The results show that these differences are statistically significant with Theil–Sen slope values of less than 0.01.

As illustrated in Fig. 6a and b, sea salt particles are characterized by a gradual increase from autumn to winter, with a peak in early spring (March). Thereafter,  $\text{Na}^+$  and  $\text{Cl}^-$  decreased to a minimum in early summer (June) and again increased toward winter. We found a significantly high concentration during August, probably due to the influence of southeast Asian air masses (see Fig. 3). This trend of sea salts is similar to that of wind speed over the sampling site; that is, higher wind speeds during spring/winter and lower in the summer. This result suggests that the concentrations of sea salts are mainly dependent on wind speed. It is also worth noting that a similar seasonal pattern can also be seen in the concentrations of  $\text{Mg}^{2+}$  (see Fig. 6c), indicating that  $\text{Mg}^{2+}$  comes from the oceanic rather continental sources. This is further supported by the existing correlation between  $\text{Mg}^{2+}$  and  $\text{Na}^+$ . We found a strong correlation ( $R^2 = 0.94$  and slope = 0.117) between  $\text{Mg}^{2+}$  and  $\text{Na}^+$  with the ratio being very close to seawater (0.12).

The seasonal variations of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  are characterized by spring maxima and summer minima.  $\text{NH}_4^+$  concentrations are low throughout the sampling period over Chichijima Island (Fig. 6d, e), probably because the sampling site is far away from the source regions of ammonia over the Asian continent (Boreddy et al., 2014; Matsumoto et al., 2007). The residence time of  $\text{NH}_3$  is of approximately several hours in the marine boundary layer (Quinn et al., 1990) and the concentration of  $\text{NH}_3$  transported from continental to remote marine locations should be considerably low. Interestingly, we found a significantly higher concentration of

**Table 1.** Seasonal mean concentrations of major water-soluble ions (mean  $\pm$  SD) and the Theil–Sen slope value for the seasonal trend during the period 2001–2012 at Chichijima Island in the western North Pacific.

	MSA <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	nss-SO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	nss-K <sup>+</sup>	nss-Ca <sup>2+</sup>	Mg <sup>2+</sup>
Winter	0.02 $\pm$ 0.00	7.10 $\pm$ 0.88	0.78 $\pm$ 0.14	3.06 $\pm$ 0.43	4.12 $\pm$ 0.47	0.19 $\pm$ 0.06	0.05 $\pm$ 0.03	0.12 $\pm$ 0.03	0.48 $\pm$ 0.05
Spring	0.03 $\pm$ 0.01	6.18 $\pm$ 1.20	0.84 $\pm$ 0.15	2.97 $\pm$ 0.89	3.32 $\pm$ 0.59	0.23 $\pm$ 0.10	0.05 $\pm$ 0.02	0.30 $\pm$ 0.12	0.42 $\pm$ 0.07
Summer	0.02 $\pm$ 0.00	4.94 $\pm$ 1.54	0.24 $\pm$ 0.09	1.06 $\pm$ 0.59	2.52 $\pm$ 0.71	0.11 $\pm$ 0.13	0.02 $\pm$ 0.01	0.04 $\pm$ 0.04	0.29 $\pm$ 0.09
Autumn	0.01 $\pm$ 0.00	7.12 $\pm$ 2.61	0.43 $\pm$ 0.11	1.31 $\pm$ 0.42	3.62 $\pm$ 1.06	0.11 $\pm$ 0.05	0.05 $\pm$ 0.04	0.04 $\pm$ 0.03	0.40 $\pm$ 0.11
Theil–Sen slope (2001–2012)									
Slope	0	-0.0067	-0.0004	-0.0045	-0.0048	-0.0002	0.0005	0	-0.0005

**Figure 6.** Box and whisker plots of monthly variations of different measured/derived ionic species ( $\mu\text{g m}^{-3}$ ) and mass ratio for the period 2001–2012 over the western North Pacific.

NO<sub>3</sub><sup>-</sup> than of NH<sub>4</sub><sup>+</sup> over the sampling site, which may result from some additional NO<sub>3</sub><sup>-</sup> sources. The heterogeneous reaction, HNO<sub>3</sub> + NaCl  $\rightarrow$  NaNO<sub>3</sub>, can provide an additional source of NO<sub>3</sub><sup>-</sup> in TSP aerosols (Wu et al., 2006) over the observation site. Furthermore, the low temperature over East Asian regions in winter and spring would favor the shift from the gas phase of nitric acid to nitrate in the particle phase, which could lead to a higher concentration of NO<sub>3</sub><sup>-</sup>

that is transported to the western North Pacific in winter and spring. On the other hand, nss-K<sup>+</sup>, which is derived mainly from biomass burning, was also quite low in Chichijima TSP aerosols, although it shows a higher concentration in winter and spring than in summer and autumn. The seasonal variation of nss-SO<sub>4</sub><sup>2-</sup> showed maxima in the spring/winter and minima in summer (see Fig. 6h), being similar to that of NO<sub>3</sub><sup>-</sup>. This result indicates that the higher levels of nss-K<sup>+</sup> during the winter and spring are mainly associated with the long-range atmospheric transport of anthropogenic/biomass burning particles over the observation site.

The concentrations of nss-Ca<sup>2+</sup> drastically increased in spring when the Asian dusts were transported over the observation site by westerly winds (see Fig. 6i). This result is consistent with the previous studies (Kawamura et al., 2003; Suzuki et al., 2008; Guo et al., 2011) where nss-Ca<sup>2+</sup> increased to a maximum in spring. A strong seasonal variability was found in MSA<sup>-</sup> concentrations with higher values in spring followed by winter and lower values in autumn and summer. This strong seasonal variability in MSA<sup>-</sup> can be ascribed to seasonality of photochemistry, biology, and meteorology. It is worth noting that the mass concentration of MSA<sup>-</sup> showed similar seasonal variation with nss-Ca<sup>2+</sup> and NO<sub>3</sub><sup>-</sup>, although its concentrations are much lower than that those of nss-Ca<sup>2+</sup> and NO<sub>3</sub><sup>-</sup>. This result suggests that there should be a link between dust and biological emissions and NO<sub>3</sub> radicals (see Fig. 6g). This point will be discussed in more details in the subsequent sections. The mass ratio MSA<sup>-</sup> / nss-SO<sub>4</sub><sup>2-</sup> showed a clear, distinct variation characterized by a gradual increase from winter to spring with a peak in summer; it again gradually decreased toward winter (see Fig. 6f). This result illustrates that the contribution of marine biogenic sources to nss-SO<sub>4</sub><sup>2-</sup> was higher in summer, because of higher solar radiation which enhances the biological activity over the sampling site. We also found covariation between the MSA<sup>-</sup> / nss-SO<sub>4</sub><sup>2-</sup> ratio and air temperature, both of which showed a maximum in summer followed by spring and minimum in winter.



**Table 2.** Annual mean concentrations of major inorganic ions (mean  $\pm$  SD) and the Mann–Kendall test for annual trends during 2001–2012 at Chichijima Island in the western North Pacific.

	MSA <sup>−</sup>	Cl <sup>−</sup>	NO <sub>3</sub> <sup>−</sup>	nss-SO <sub>4</sub> <sup>2−</sup>	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	nss-K <sup>+</sup>	nss-Ca <sup>2+</sup>	Mg <sup>2+</sup>
2001	0.01 $\pm$ 0.00	5.65 $\pm$ 2.82	0.47 $\pm$ 0.29	1.67 $\pm$ 1.11	2.87 $\pm$ 1.36	0.09 $\pm$ 0.04	0.03 $\pm$ 0.01	0.15 $\pm$ 0.19	0.33 $\pm$ 0.16
2002	0.02 $\pm$ 0.01	6.84 $\pm$ 2.66	0.61 $\pm$ 0.41	2.81 $\pm$ 1.66	3.59 $\pm$ 1.20	0.27 $\pm$ 0.17	0.05 $\pm$ 0.03	0.18 $\pm$ 0.26	0.44 $\pm$ 0.15
2003	0.02 $\pm$ 0.01	7.23 $\pm$ 2.16	0.60 $\pm$ 0.36	2.17 $\pm$ 1.21	3.85 $\pm$ 1.19	0.13 $\pm$ 0.07	0.05 $\pm$ 0.03	0.10 $\pm$ 0.11	0.45 $\pm$ 0.15
2004	0.02 $\pm$ 0.01	8.41 $\pm$ 4.14	0.54 $\pm$ 0.39	2.27 $\pm$ 1.65	4.46 $\pm$ 1.42	0.16 $\pm$ 0.07	0.06 $\pm$ 0.04	0.08 $\pm$ 0.08	0.50 $\pm$ 0.16
2005	0.02 $\pm$ 0.00	7.25 $\pm$ 2.24	0.69 $\pm$ 0.40	2.32 $\pm$ 1.24	4.12 $\pm$ 1.03	0.10 $\pm$ 0.07	0.04 $\pm$ 0.01	0.11 $\pm$ 0.10	0.46 $\pm$ 0.13
2006	0.02 $\pm$ 0.01	6.58 $\pm$ 2.56	0.64 $\pm$ 0.43	2.20 $\pm$ 1.56	3.58 $\pm$ 1.07	0.14 $\pm$ 0.15	0.03 $\pm$ 0.03	0.16 $\pm$ 0.23	0.41 $\pm$ 0.14
2007	0.02 $\pm$ 0.01	5.63 $\pm$ 1.51	0.67 $\pm$ 0.35	2.77 $\pm$ 1.39	3.36 $\pm$ 1.01	0.36 $\pm$ 0.32	0.07 $\pm$ 0.04	0.17 $\pm$ 0.15	0.39 $\pm$ 0.13
2008	0.02 $\pm$ 0.01	4.83 $\pm$ 2.35	0.49 $\pm$ 0.29	2.28 $\pm$ 1.42	2.89 $\pm$ 1.12	0.16 $\pm$ 0.11	0.08 $\pm$ 0.06	0.08 $\pm$ 0.09	0.33 $\pm$ 0.13
2009	0.03 $\pm$ 0.01	6.46 $\pm$ 2.64	0.57 $\pm$ 0.37	1.51 $\pm$ 1.18	3.47 $\pm$ 1.03	0.13 $\pm$ 0.08	0.03 $\pm$ 0.02	0.09 $\pm$ 0.08	0.40 $\pm$ 0.11
2010	0.02 $\pm$ 0.01	5.15 $\pm$ 2.31	0.55 $\pm$ 0.38	1.71 $\pm$ 1.19	2.71 $\pm$ 1.25	0.15 $\pm$ 0.14	0.03 $\pm$ 0.02	0.15 $\pm$ 0.20	0.32 $\pm$ 0.15
2011	0.02 $\pm$ 0.01	5.56 $\pm$ 1.51	0.51 $\pm$ 0.31	1.67 $\pm$ 1.34	2.85 $\pm$ 0.81	0.14 $\pm$ 0.15	0.03 $\pm$ 0.04	0.10 $\pm$ 0.13	0.34 $\pm$ 0.11
2012	0.02 $\pm$ 0.01	7.04 $\pm$ 1.87	0.64 $\pm$ 0.51	2.03 $\pm$ 1.43	3.49 $\pm$ 0.97	0.18 $\pm$ 0.18	0.04 $\pm$ 0.02	0.15 $\pm$ 0.15	0.43 $\pm$ 0.12
Mean	0.02 $\pm$ 0.00	6.39 $\pm$ 1.04	0.58 $\pm$ 0.07	2.12 $\pm$ 0.42	3.44 $\pm$ 0.54	0.17 $\pm$ 0.07	0.05 $\pm$ 0.01	0.13 $\pm$ 0.03	0.40 $\pm$ 0.05
Mann–Kendall non-parametric test (2001–2012)									
Z value	2.34*	−1.71	−1.56	−2.49*	−2.34*	−0.31	0.62*	−2.02*	−2.18*

\* Correlation is significant at the 0.01 level (two-tailed).

### 3.4 Annual variations of different chemical species on a seasonal scale

Annual mean concentrations of major ions (mean  $\pm$  SD) for different seasons during 2001–2012 are reported in Table 2. The presence of an annual average trend is demonstrated by the Mann–Kendall test, results were also reported in Table 2. The Mann–Kendall trend test (Mann, 1945; Kendall, 1975) is one of the widely used non-parametric tests to detect significant trends in time series. In this test, the absolute value of  $Z$  is compared to the standard normal cumulative distribution to define if there is a trend or not at the selected level  $\alpha$  ( $= 0.01$ , in this study) of significance. A positive (negative) value of  $Z$  indicates an upward (downward) trend.

Figure 7 presents the annual variations of selected chemical species for different seasons in the period of 2001–2012. Although there exist some seasonal trends of ions, we could not find any clear annual trends for the species Cl<sup>−</sup>, Mg<sup>2+</sup> and nss-Ca<sup>2+</sup> in all seasons. However, nss-SO<sub>4</sub><sup>2−</sup> and NO<sub>3</sub><sup>−</sup> showed a clear annual trend for all seasons, with an increase from 2001 to 2004 and decrease from 2007 to 2012. Lu et al. (2010) reported that total SO<sub>2</sub> emissions in China increased by 53 % (21.7–33.2 Tg, at an annual growth rate of 7.3 %) from 2000 to 2006, during which period the emissions from power plants were the main sources of SO<sub>2</sub> in China with an increase from 10.6 to 18.6 Tg per year. Geographically, emissions from northern China increased by 85 %, whereas those from the south increased by only 28 %. The growth rate of SO<sub>2</sub> emissions slowed down around 2005 and began to decrease after 2006 mainly due to the wide operation of flue-gas desulfurization (FGD) devices in power plants in response to a new policy of the Chinese government. This change in the SO<sub>2</sub> emissions was exactly recorded in our observations at Chichijima in the western North Pa-

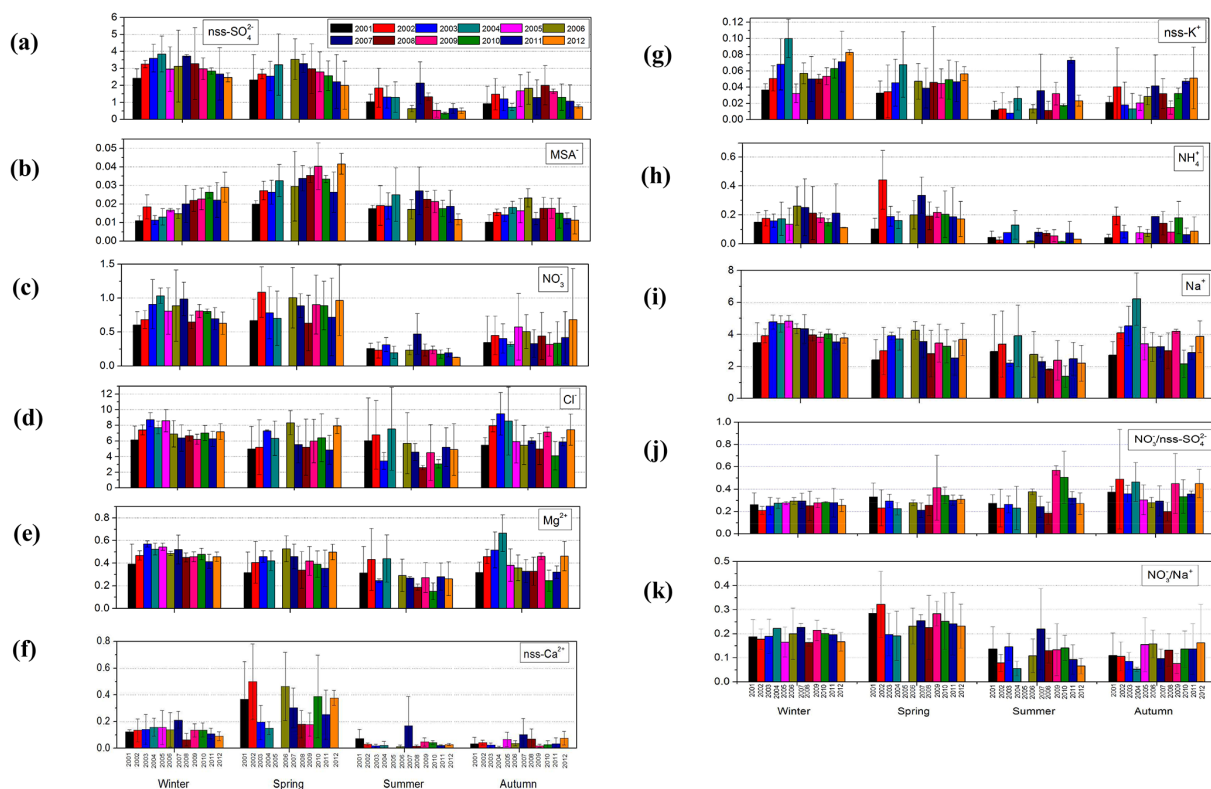
cific; that is, the decreasing trend of SO<sub>4</sub><sup>2−</sup> concentrations over the observation site can be explained by the decrease in SO<sub>2</sub> emissions in China after 2006. Furthermore, these results are supported by the annual variation of nss-SO<sub>4</sub><sup>2−</sup>/Na<sup>+</sup> and nss-NO<sub>3</sub><sup>−</sup>/Na<sup>+</sup> mass ratios (see Fig. 7j and k). The nss-SO<sub>4</sub><sup>2−</sup>/Na<sup>+</sup> ratio showed a clear annual trend in winter and spring with an increase from 2001 to 2004 and a decreasing trend from 2007 to 2012. Therefore, nss-SO<sub>4</sub><sup>2−</sup> concentrations in the western North Pacific are gradually decreasing, because of the suppressed emission of SO<sub>2</sub> over East Asia, especially in China.

In contrast, the annual variation of nss-K<sup>+</sup> showed an increasing trend from 2001 to 2004 and 2006 to 2012, suggesting that biomass burning emissions in East Asia are continuously increasing and transported to the western North Pacific by long-range atmospheric transport. This result is further supported by the study of Verma et al. (2015), who reported long-term measurements of biomass burning organic tracers (levoglucosan, mannosan and galactosan) for the period of 2001–2013 over the same observation site, Chichijima Island. They found a continuous increase in the concentrations of biomass burning tracers from 2006 to 2013, which is mainly caused by enhanced biomass burning in East Asia. It is of interest to note that the annual variations of MSA<sup>−</sup> concentrations have shown a gradual increase from 2001 to 2012 during the winter and spring seasons, indicating that direct transport of MSA<sup>−</sup> from the continental surface to the remote marine locations is continuously increasing. On the other hand, NH<sub>4</sub><sup>+</sup> concentrations showed a gradual decrease from 2006 to 2012 during the winter and spring seasons, whereas in summer and autumn we could not find any clear annual trends in the abundance of NH<sub>4</sub><sup>+</sup>.

**Table 3.** Correlation coefficient matrix among the chemical species for (a) winter, (b) spring, (c) summer, and (d) autumn.

(a) Winter												
	MSA <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	nss-SO <sub>4</sub> <sup>2-</sup>	nss-K <sup>+</sup>	nss-Ca <sup>2+</sup>
MSA <sup>-</sup>	1											
Cl <sup>-</sup>	-.199 <sup>a</sup>	1										
NO <sub>3</sub> <sup>-</sup>	.365 <sup>b</sup>	-.0166	1									
SO <sub>4</sub> <sup>2-</sup>	.481 <sup>b</sup>	-.0125	.689 <sup>b</sup>	1								
Na <sup>+</sup>	-.011	.876 <sup>b</sup>	.209 <sup>a</sup>	.261 <sup>b</sup>	1							
NH <sub>4</sub> <sup>+</sup>	.562 <sup>b</sup>	-.261 <sup>b</sup>	.622 <sup>b</sup>	.821 <sup>b</sup>	0.081	1						
K <sup>+</sup>	.446 <sup>b</sup>	.281 <sup>b</sup>	.568 <sup>b</sup>	.759 <sup>b</sup>	.561 <sup>b</sup>	.744 <sup>b</sup>	1					
Ca <sup>2+</sup>	.303 <sup>b</sup>	.347 <sup>b</sup>	.513 <sup>b</sup>	.478 <sup>b</sup>	.524 <sup>b</sup>	.372 <sup>b</sup>	.533 <sup>b</sup>	1				
Mg <sup>2+</sup>	0.060	.848 <sup>b</sup>	.240 <sup>b</sup>	.291 <sup>b</sup>	.966 <sup>b</sup>	0.124	.589 <sup>b</sup>	.545 <sup>b</sup>	1			
nss-SO <sub>4</sub> <sup>2-</sup>	.496 <sup>b</sup>	-.262 <sup>b</sup>	.677 <sup>b</sup>	.989 <sup>b</sup>	0.116	.835 <sup>b</sup>	.696 <sup>b</sup>	.412 <sup>b</sup>	0.153	1		
nss-K <sup>+</sup>	.520 <sup>b</sup>	-.0155	.518 <sup>b</sup>	.748 <sup>b</sup>	0.107	.829 <sup>b</sup>	.879 <sup>b</sup>	.338 <sup>b</sup>	0.149	.755 <sup>b</sup>	1	
nss-Ca <sup>2+</sup>	.343 <sup>b</sup>	0.052	.480 <sup>b</sup>	.420 <sup>b</sup>	.195 <sup>a</sup>	.380 <sup>b</sup>	.373 <sup>b</sup>	.936 <sup>b</sup>	.229 <sup>a</sup>	.404 <sup>b</sup>	.338 <sup>b</sup>	1
(b) Spring												
	MSA <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	nss-SO <sub>4</sub> <sup>2-</sup>	nss-K <sup>+</sup>	nss-Ca <sup>2+</sup>
MSA <sup>-</sup>	1											
Cl <sup>-</sup>	.199 <sup>a</sup>	1										
NO <sub>3</sub> <sup>-</sup>	.388 <sup>b</sup>	.240 <sup>b</sup>	1									
SO <sub>4</sub> <sup>2-</sup>	.349 <sup>b</sup>	0.089	.619 <sup>b</sup>	1								
Na <sup>+</sup>	.258 <sup>b</sup>	.888 <sup>b</sup>	.418 <sup>b</sup>	.467 <sup>b</sup>	1							
NH <sub>4</sub> <sup>+</sup>	.368 <sup>b</sup>	-.0150	.504 <sup>b</sup>	.710 <sup>b</sup>	0.026	1						
K <sup>+</sup>	.305 <sup>b</sup>	.416 <sup>b</sup>	.703 <sup>b</sup>	.710 <sup>b</sup>	.639 <sup>b</sup>	.474 <sup>b</sup>	1					
Ca <sup>2+</sup>	.236 <sup>b</sup>	.353 <sup>b</sup>	.665 <sup>b</sup>	.485 <sup>b</sup>	.355 <sup>b</sup>	.258 <sup>b</sup>	.516 <sup>b</sup>	1				
Mg <sup>2+</sup>	.382 <sup>b</sup>	.872 <sup>b</sup>	.519 <sup>b</sup>	.416 <sup>b</sup>	.912 <sup>b</sup>	0.105	.660 <sup>b</sup>	.545 <sup>b</sup>	1			
nss-SO <sub>4</sub> <sup>2-</sup>	.418 <sup>b</sup>	-.0008	.609 <sup>b</sup>	.988 <sup>b</sup>	.456 <sup>b</sup>	.770 <sup>b</sup>	.646 <sup>b</sup>	.473 <sup>b</sup>	.362 <sup>b</sup>	1		
nss-K <sup>+</sup>	.294 <sup>b</sup>	-.0082	.539 <sup>b</sup>	.578 <sup>b</sup>	0.034	.631 <sup>b</sup>	.655 <sup>b</sup>	.360 <sup>b</sup>	0.137	.611 <sup>b</sup>	1	
nss-Ca <sup>2+</sup>	.200 <sup>a</sup>	.220 <sup>b</sup>	.621 <sup>b</sup>	.440 <sup>b</sup>	.200 <sup>a</sup>	.256 <sup>b</sup>	.421 <sup>b</sup>	.988 <sup>b</sup>	.404 <sup>b</sup>	.444 <sup>b</sup>	.369 <sup>b</sup>	1
(c) Summer												
	MSA <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	nss-SO <sub>4</sub> <sup>2-</sup>	nss-K <sup>+</sup>	nss-Ca <sup>2+</sup>
MSA <sup>-</sup>	1											
Cl <sup>-</sup>	-.0163	1										
NO <sub>3</sub> <sup>-</sup>	.422 <sup>b</sup>	-.0161	1									
SO <sub>4</sub> <sup>2-</sup>	.425 <sup>b</sup>	0.029	.376 <sup>b</sup>	1								
Na <sup>+</sup>	-.065	.949 <sup>b</sup>	-.049	.192 <sup>a</sup>	1							
NH <sub>4</sub> <sup>+</sup>	.359 <sup>b</sup>	-.0243	.485 <sup>b</sup>	.866 <sup>b</sup>	-.0096	1						
K <sup>+</sup>	0.123	.811 <sup>b</sup>	0.062	.429 <sup>b</sup>	.862 <sup>b</sup>	.513 <sup>b</sup>	1					
Ca <sup>2+</sup>	0.127	.765 <sup>b</sup>	0.148	.258 <sup>b</sup>	.797 <sup>b</sup>	0.195	.776 <sup>b</sup>	1				
Mg <sup>2+</sup>	-.0027	.939 <sup>b</sup>	-.0009	.202 <sup>a</sup>	.980 <sup>b</sup>	-.0046	.885 <sup>b</sup>	.817 <sup>b</sup>	1			
nss-SO <sub>4</sub> <sup>2-</sup>	.535 <sup>b</sup>	-.200 <sup>a</sup>	.455 <sup>b</sup>	.968 <sup>b</sup>	-.0061	.911 <sup>b</sup>	.242 <sup>b</sup>	0.082	-.0039	1		
nss-K <sup>+</sup>	.376 <sup>b</sup>	-.0067	.471 <sup>b</sup>	.666 <sup>b</sup>	-.0007	.876 <sup>b</sup>	.456 <sup>b</sup>	0.212	0.053	.738 <sup>b</sup>	1	
nss-Ca <sup>2+</sup>	.277 <sup>b</sup>	0.006	.259 <sup>b</sup>	0.147	-.0016	.384 <sup>b</sup>	0.151	.601 <sup>b</sup>	0.045	.213 <sup>a</sup>	.266 <sup>a</sup>	1
(d) Autumn												
	MSA <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	nss-SO <sub>4</sub> <sup>2-</sup>	nss-K <sup>+</sup>	nss-Ca <sup>2+</sup>
MSA <sup>-</sup>	1											
Cl <sup>-</sup>	0.007	1										
NO <sub>3</sub> <sup>-</sup>	.517 <sup>b</sup>	0.037	1									
SO <sub>4</sub> <sup>2-</sup>	.554 <sup>b</sup>	0.104	.753 <sup>b</sup>	1								
Na <sup>+</sup>	.249 <sup>b</sup>	.925 <sup>b</sup>	.338 <sup>b</sup>	.217 <sup>b</sup>	1							
NH <sub>4</sub> <sup>+</sup>	.342 <sup>b</sup>	-.0131	.360 <sup>b</sup>	.463 <sup>b</sup>	0.088	1						
K <sup>+</sup>	.410 <sup>b</sup>	.567 <sup>b</sup>	.582 <sup>b</sup>	.734 <sup>b</sup>	.754 <sup>b</sup>	.529 <sup>b</sup>	1					
Ca <sup>2+</sup>	.292 <sup>b</sup>	.505 <sup>b</sup>	.492 <sup>b</sup>	.584 <sup>b</sup>	.629 <sup>b</sup>	.336 <sup>b</sup>	.653 <sup>b</sup>	1				
Mg <sup>2+</sup>	.274 <sup>b</sup>	.895 <sup>b</sup>	.428 <sup>b</sup>	.485 <sup>b</sup>	.970 <sup>b</sup>	0.122	.807 <sup>b</sup>	.637 <sup>b</sup>	1			
nss-SO <sub>4</sub> <sup>2-</sup>	.583 <sup>b</sup>	-.0111	.760 <sup>b</sup>	.970 <sup>b</sup>	.224 <sup>b</sup>	.610 <sup>b</sup>	.626 <sup>b</sup>	.483 <sup>b</sup>	.310 <sup>b</sup>	1		
nss-K <sup>+</sup>	.359 <sup>b</sup>	-.0137	.432 <sup>b</sup>	.667 <sup>b</sup>	0.189	.828 <sup>b</sup>	.738 <sup>b</sup>	.531 <sup>b</sup>	0.230	.699 <sup>b</sup>	1	
nss-Ca <sup>2+</sup>	0.163	0.075	.364 <sup>b</sup>	.442 <sup>b</sup>	0.170	.477 <sup>b</sup>	.343 <sup>b</sup>	.879 <sup>b</sup>	0.180	.434 <sup>b</sup>	.623 <sup>b</sup>	1

<sup>a</sup> Correlation is significant at the 0.05 level (two-tailed). <sup>b</sup> Correlation is significant at the 0.01 level (two-tailed).



**Figure 7.** Annual variations of different chemical species ( $\mu\text{g m}^{-3}$ ) on a seasonal scale over the sampling period of 2001–2012.

### 3.5 Correlation analyses among the inorganic ions

In order to find the crucial information about sources of ions, we performed a correlation analysis among the ions for different seasons (see Table 3) because the ion concentrations emitted from the same source or similar reaction pathway should show a good correlation between them. Tables 3a, b, c, and d show the results of correlation analyses of major ions for winter, spring, summer, and autumn, respectively, during the study period. In all seasons, we found strong correlation (excellent correlation during summer and autumn) among  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Cl}^-$ , indicating that these ions have a similar source and mainly come from sea spray. Although  $\text{NH}_4^+$  concentrations are low throughout the sampling period, it shows good correlation with  $\text{SO}_4^{2-}$  during all seasons.

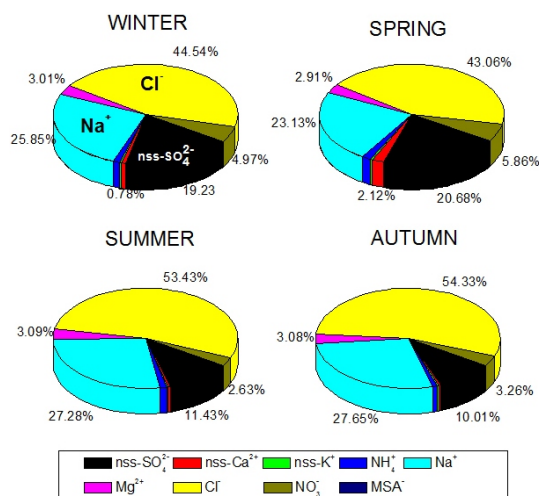
During winter,  $\text{nss-K}^+$ , a tracer of biomass burning source, strongly correlates with  $\text{nss-SO}_4^{2-}$ , whereas  $\text{NO}_3^-$ , a tracer of anthropogenic source, correlates with  $\text{NH}_4^+$ ,  $\text{Na}^+$ , and  $\text{nss-K}^+$  with a relatively strong correlation coefficient ( $r > 0.55$ ), suggesting that they are derived from biomass burning and anthropogenic sources in the Asian continent, respectively. In spring,  $\text{Ca}^{2+}$  shows relatively strong correlation with  $\text{NO}_3^-$  ( $r = 0.62$ ) and moderate correlation with  $\text{Mg}^{2+}$ ,  $\text{nss-K}^+$ , and  $\text{nss-SO}_4^{2-}$ , indicating that they are derived from similar sources or reaction pathways. It is important to note that  $\text{Na}^+$  moderately correlated with acetic ions ( $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ )

during spring, whereas no correlation in summer reveals that chloride loss is prominent in spring than in summer and that  $\text{NH}_3$  and  $\text{HNO}_3$  probably react with sea salt particles in the marine atmosphere.

### 3.6 Percent contribution of major ions to total WSIM

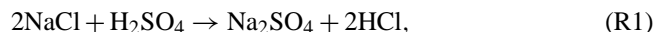
The percent contributions of individual inorganic species to the total WSIM are shown as a pie chart in Fig. 8 for the different seasons. Among all the inorganic species, sea salt ( $\text{NaCl}$ ) is a major contributor to the WSIM, followed by  $\text{nss-SO}_4^{2-}$  and  $\text{NO}_3^-$  during all seasons.  $\text{Na}^+$  and  $\text{Cl}^-$  together contributed  $\sim 70$ , 66, 80 and 82 % to the total WSIM for winter, spring, summer and autumn, respectively, whereas  $\text{nss-SO}_4^{2-}$  contributed  $\sim 26$ , 24, 11 and 10 %, respectively. The  $\text{nss-Ca}^{2+}$  shows a significant contribution (about 2 %) to WSIM in spring, indicating a long-range atmospheric transport of Asian dusts over the observation site. Similarly,  $\text{Mg}^{2+}$  contributed to the total WSIM by about 3 % in all seasons.

We found a significant depletion of chloride during winter and spring, probably due to the atmospheric mixing of anthropogenic pollutants such as  $\text{SO}_2$ ,  $\text{NO}_3$ , etc. (Boreddy et al., 2014). Figure 9a and b show the monthly and seasonal variations of the  $\text{Cl}^-/\text{Na}^+$  mass ratio during the study period. The monthly averaged  $\text{Cl}^-/\text{Na}^+$  ratio varied from 1.58 to 2.05 with a mean value of  $1.79 \pm 0.15$ . Although the mean mass ratio is almost equal to that of seawater (1.8), we found

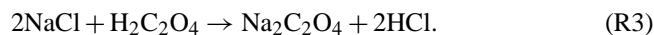


**Figure 8.** Percentage contribution of major ions to total water-soluble ions for different seasons.

significant chlorine loss in the winter and spring samples. Atmospheric processing of anthropogenic pollutants/minerals and their mixing with sea salt particles during the long-range atmospheric transport are probably responsible for the chlorine loss. On the other hand, acid displacement also plays an important role in chloride depletion over the marine environment through the following reactions:

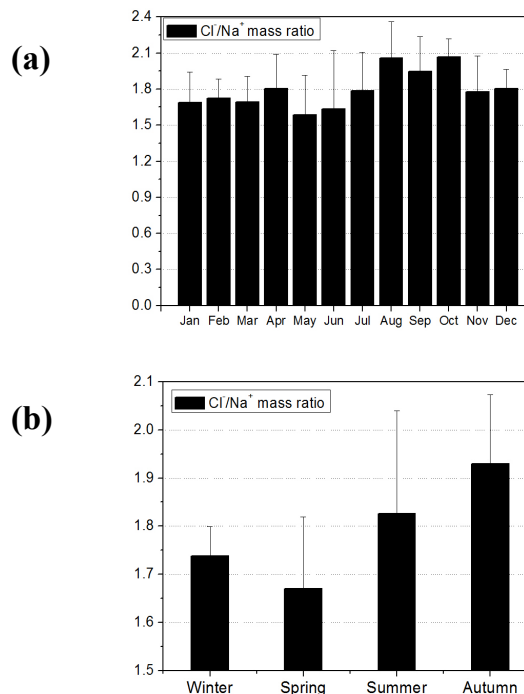


Furthermore, Mochida et al. (2003) reported high abundance of oxalic acid in the Chichijima TSP aerosols in spring. Oxalic acid may be internally mixed with dust-derived minerals. Previous studies of Asian dust showed that oxalate was largely mixed with dust particles (Sullivan and Prather, 2007). Therefore, it is reasonable to assume that the spring-time chlorine loss over the western North Pacific was most likely due to the displacement of  $\text{Cl}^-$  with oxalate through the following reaction:



In contrast, during the summer and autumn, we found an excess of chloride over the observation site, because of some additional source of chloride added to the TSP aerosols.

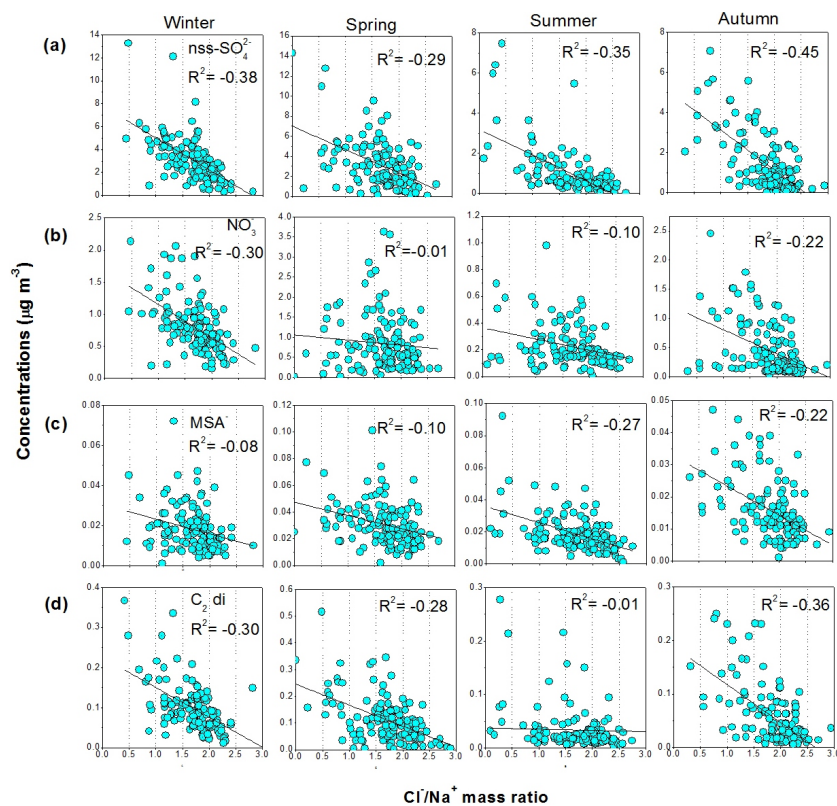
In order to investigate which acids are responsible for the depletion of chloride, we performed regression analysis between the  $\text{Cl}^-/\text{Na}^+$  mass ratio and acidic species,  $\text{nss-SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{MSA}^-$  and oxalic acid for different seasons during 2001–2012 as shown in Fig. 10. The regression analysis was verified by *t* test. The results show that the differences between the  $\text{Cl}^-/\text{Na}^+$  mass ratio and acidic species are statistically significant with a two-tailed *P* value that is  $\leq 0.001$



**Figure 9.** Variation of the  $\text{Cl}^-/\text{Na}^+$  mass ratio on (a) monthly and (b) seasonal scales.

for each season during the study period. For all seasons,  $\text{nss-SO}_4^{2-}$  moderately correlated with the  $\text{Cl}^-/\text{Na}^+$  mass ratios with negative correlation coefficients ( $R^2$ ) of 0.38, 0.29, 0.35 and 0.45 for winter, spring, summer, and autumn, respectively, whereas  $\text{NO}_3^-$  moderately correlated during winter ( $R^2 = -0.30$ ), weakly correlated in autumn ( $R^2 = -0.22$ ) and has no correlation in spring and summer. These results suggest that sulfate has more responsibility for the chloride depletion than nitrate.

On the other hand, the biogenic tracer,  $\text{MSA}^-$ , moderately correlated during summer ( $R^2 = -0.29$ ) and has weak correlation in winter and spring. Freshly emitted  $\text{MSA}^-$  and  $\text{H}_2\text{SO}_4$  (from oceanic biological productivity associated with the upwelling of nutrient rich water) also contribute little to the chloride depletion by coating with sea salt, especially in summer. Interestingly, during spring, the  $\text{Cl}^-/\text{Na}^+$  mass ratio did not correlate with  $\text{NO}_3^-$  or  $\text{MSA}^-$  but weakly correlated with  $\text{nss-SO}_4^{2-}$ . These results suggest that some other organic acids, such as oxalic acid (because of its high abundance during spring), are responsible for the chloride depletion during spring. In fact, we found that oxalic acid significantly correlate with the chlorine loss in winter ( $-0.30$ ), spring ( $-0.28$ ) and autumn ( $-0.36$ ) (see Fig. 10d). These results confirm that oxalic acid plays an important role in a chlorine loss.



**Figure 10.** Relations between chloride depletion ( $\text{Cl}^-/\text{Na}^+$  mass ratio) and acidic species (a)  $\text{nss-SO}_4^{2-}$ , (b)  $\text{NO}_3^-$ , (c)  $\text{MSA}^-$ , and (d) oxalic acid ( $\text{C}_2 \text{ di}$ ) for different seasons over the western North Pacific.

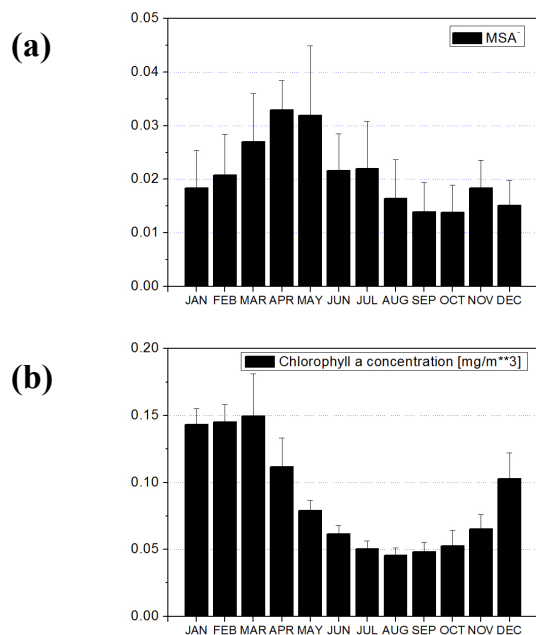
### 3.7 Which biological source is more important as a contributor to $\text{MSA}^-$ ?

To better identify which biological source is a more significant contribution to  $\text{MSA}^-$ , we compared the monthly mean variation of  $\text{MSA}^-$  with chlorophyll *a* ( $\text{Chl } a$  ( $\text{mg m}^{-3}$ ), a satellite-derived biogenic tracer) during the study period as shown in Fig. 11.  $\text{Chl } a$  concentrations were downloaded from the MODIS (Moderate Resolution Imaging Spectroradiometer) Aqua satellite over the region of  $140\text{--}145^\circ \text{E}$ ,  $25\text{--}30^\circ \text{N}$  for the period July 2002–December 2012. We found a clear monthly/seasonal variation in  $\text{Chl } a$  concentration, which gradually increased from autumn to early spring and then decreased from mid spring to summer. Surprisingly, a similar seasonal pattern can also be seen in the concentrations of  $\text{nss-Ca}^{2+}$  (see Fig. 6i), indicating that there should exist a possible link between the long-range transport of Asian dusts (or a springtime bloom) and the ocean productivity in the western North Pacific. The production of algal blooms may quickly respond to dust deposition (nutrients) over the surface ocean (Gabric et al., 2004). By changing the phytoplankton productivity, dusts can act as important source of DMS production (Jickells et al., 2005). However, the mechanisms of marine phytoplankton response to a dust

input from the atmosphere still face numerous uncertainties, a subject of scientific discussion.

Ramos et al. (2005) observed the massive Saharan dust storms along with algal bloom in the North Atlantic in August 2004. Bishop et al. (2002) observed an increase in chlorophyll *a* over a couple of weeks in the North Pacific after passage of a Gobi desert dust cloud. Springtime bloom in the northern East China Sea and Japan Sea was observed by TOMS (Total Ozone Mapping Spectrometer) and SeaWiFS (Sea-viewing Wide Field-of-view Sensor) satellites to be initiated 1 month earlier than usual, being correlated with an Asian dust event in association with precipitation. Such events lead to a supply of bioavailable iron and induce a deepening of the critical depth, which results in an early initiation of the bloom (Jo et al., 2007). On the other hand, Gabric et al. (2004) revealed that the dust storms in Australia (2002–2003) lead to advection of large dust plumes over the Southern Ocean, and observed a coherence between optical characteristics of the Southern Ocean atmosphere and dust loading by satellite and field data on surface ocean chlorophyll *a*. Therefore, it is noteworthy that the transported atmospheric dust particles can act as a fertilizer to stimulate the production of microscopic marine plants (plankton/algae blooms).

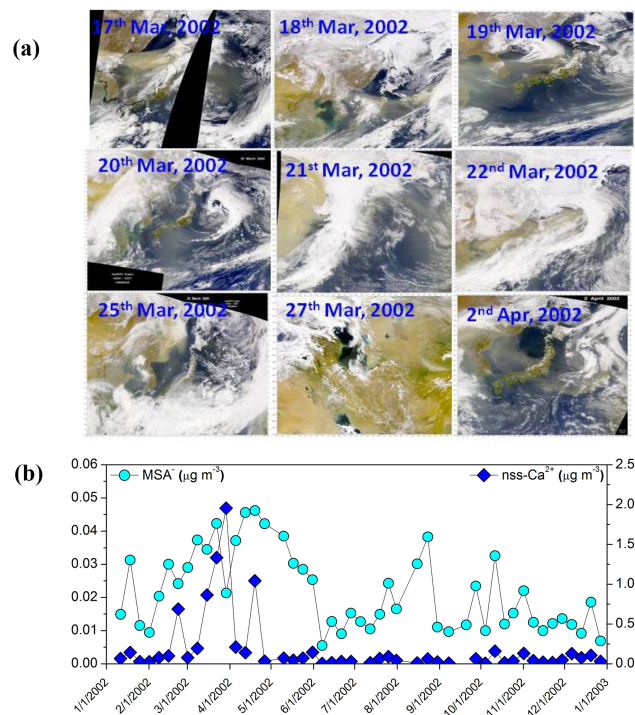
As discussed in Sect. 3.3, the monthly variation of  $\text{MSA}^-$  gradually increased from winter to spring, with a peak in



**Figure 11.** Monthly mean variation of (a)  $\text{MSA}^-$  ( $\mu\text{g m}^{-3}$ ) and (b) chlorophyll *a* concentrations for the study period. Chlorophyll *a* concentrations were downloaded from the MODIS Aqua satellite over the region 140–145° E, 25–30° N for the study period.

April, and gradually decreased towards summer and autumn months. Interestingly,  $\text{MSA}^-$  reached a maximum in April, whereas chlorophyll *a* reached a maximum in March, although both are tracers for marine biological activity. It is also important to mention that the highest concentration of  $\text{MSA}^-$  was observed 1 month after the Asian dust deposition over the ocean surface, suggesting that there may be a time lag between the dust deposition and DMS emissions. Therefore, we assume that there are two possible sources for higher  $\text{MSA}^-$  concentrations in winter/spring over Chichijima Island: (1) direct transport of  $\text{MSA}^-$  from the continental sources, such as industrial emissions (Lu et al., 2010), terrestrial higher plants (Pavuluri et al., 2013), and forest floors (Miyazaki et al., 2012); and (2) springtime bloom of phytoplankton over the western North Pacific.

Another factor that could affect  $\text{MSA}^-$  concentrations is the concentration of  $\text{NO}_3$  radicals, which are among the key oxidants for MSA production. A polluted air mass with higher  $\text{NO}_x$  concentrations gives higher MSA yields relative to  $\text{SO}_2$  from DMS oxidation (Yin et al., 1990). Under prevailing westerly polluted winds, significant amount of anthropogenic  $\text{NO}_x$  can be transported from East Asia over the western North Pacific, which could enhance the MSA concentrations relative to the less polluted pristine air masses. Similar results are reported elsewhere (Yin et al., 1990; Jensen et al., 1991; Mihalopoulos et al., 1992; Gao et al., 1996). Furthermore, temperature is also an important factor to control the  $\text{MSA}^-$  concentrations through the mech-



**Figure 12.** (a) The SeaWiFS images that captured the large Asian dust storm visible over the Sea of Japan and North Pacific during 17 March–2 April 2002. (b) Temporal variations of  $\text{MSA}^-$  and  $\text{nss-Ca}^{2+}$  concentrations during 2002 over the western North Pacific. The black regions in (a) are the gaps between consecutive SeaWiFS viewing swaths and represent areas where no data were collected.

anism of DMS oxidation by hydroxyl radicals (Arimoto et al., 1996). In the present study, we found lower concentrations of  $\text{MSA}^-$  during summer and autumn months, when ambient temperature is higher, demonstrating that lower temperature may lead to higher MSA concentration in this region. However, the MSA concentrations in the marine atmosphere could be affected by multiple processes related to primary productivity, such as spatial variability of phytoplankton species, air–sea exchange rates of DMS, and different oxidation pathways of DMS. In addition, variations in environmental conditions such as temperatures, precipitation patterns, sea ice conditions, winds and ocean currents could also control the concentrations of MSA (Gao et al., 1996).

To further clarify the relations between  $\text{MSA}^-$  and  $\text{nss-Ca}^{2+}$ , we examined the intense Ca episodes during the study period (March 2002), which can be related to variations in  $\text{MSA}^-$  as shown in Fig. 12 as a typical example. Figure 12a shows the SeaWiFS (flying aboard Orbview-2) images, which captured the large Asian dust storms over the North Pacific during 17 March–2 April 2002. Dust storms originate in the deserts of northern China and Mongolia. The East Asian dust storm appears to have diminished somewhat on 20 March 2002, as compared to previous days. However, there seems to be a new batch of dust rising toward the left

**Table 4.** Mean concentrations of major water-soluble species at Chichijima Island from 2001 to 2012 and those at several other remote marine locations in the Pacific.

Location (data set)	$\text{NO}_3^-$	$\text{nss-SO}_4^{2-}$	$\text{MSA}^-$	References
Present study				
Chichijima (2001–2012)	$0.58 \pm 0.07$	$2.12 \pm 0.42$	$0.02 \pm 0.00$	
Other remote marine locations				
Fanning Island (1981–1986)	$0.16 \pm 0.08$	$0.67 \pm 0.27$	$0.04 \pm 0.01$	Savoie et al. (1989)
Nauru	$0.16 \pm 0.09$			Savoie et al. (1989)
Funafuti	$0.10 \pm 0.07$			Savoie et al. (1989)
American Samoa (1983–1987)	$0.11 \pm 0.05$	$0.34 \pm 0.14$	$0.02 \pm 0.01$	Savoie et al. (1989)
Rarotonga	$0.12 \pm 0.08$			Savoie et al. (1989)
Midway (1981–2000)	$0.29 \pm 0.16$	$0.56 \pm 0.45$	$0.02 \pm 0.01$	Prospero and Savoie (2003)
N. Caledonia (1983–1985)		0.42	0.02	Savoie and Prospero (1989)

side of this image. This scene spans from eastern Asia across Japan and over the western North Pacific, where the dust was partly entrained by a low-pressure system.

On the other hand, possible variations of  $\text{MSA}^-$  concentrations related to the East Asian dusts are shown in Fig. 11b. Interestingly, we found higher levels of  $\text{MSA}^-$  after the Asian dust deposition over the ocean surface. This evidence strongly reveals that Ca episodes supply the nutrients to significantly stimulate plankton blooms accompanied by statistically significant variations in  $\text{MSA}^-$  concentrations in the atmosphere few days after the episodes. This result also demonstrates that Asian dusts can act as an important source of macro and micro nutrients including iron for phytoplankton and thus sea–air emission of DMS over the western North Pacific.

### 3.8 Comparison of major inorganic ions over the Pacific

The mean concentrations of  $\text{NO}_3^-$ ,  $\text{nss-SO}_4^{2-}$ , and  $\text{MSA}^-$  at Chichijima during the period 2001–2012 are compared to those from several other remote marine sites in the Pacific, as summarized in Table 4. Results from the Chichijima data show that mean  $\text{NO}_3^-$  and  $\text{nss-SO}_4^{2-}$  are higher than those from other remote marine locations. The mean concentration of nitrate ( $0.58 \mu\text{g m}^{-3}$ ) at Chichijima is more than 4 times higher than from other remote marine sites (Fanning, Nauru, Funafuti, American Samoa, Rarotonga, and N. Caledonia) and more than twice higher than that from Midway. Moreover, concentrations of  $\text{nss-sulfate}$  at Chichijima ( $2.12 \mu\text{g m}^{-3}$ ) are 4 times higher than at Fanning, Midway, and N. Caledonia and more than 7 times higher than those from American Samoa and Norfolk. The mean concentration of  $\text{MSA}^-$  ( $0.02 \mu\text{g m}^{-3}$ ) at Chichijima is comparable to those from other remote marine locations (see Table 4). These results suggest a similarity to those of the oceanic biological productivity in the North Pacific.

In contrast, the mean  $\text{MSA}^-$  concentration at Fanning in the equatorial Pacific is about twice higher ( $0.044 \mu\text{g m}^{-3}$ ) than that of Chichijima. Savoie and Prospero (1989) have found high biological productivity is associated with the upwelling of nutrient-rich water near the equatorial divergence, with mean DMS levels of  $3.8 \text{ nmol L}^{-1}$  in the surface ocean. They also documented that in the oligotrophic regions, the mean concentrations of  $\text{MSA}$  in the air and DMS in the sea water vary over the narrow range from 0.02 to  $0.03 \mu\text{g m}^{-3}$  and 1.4 to  $1.7 \text{ nmol L}^{-1}$ , respectively.

The mean concentration ratio ( $\text{MSA}^- / \text{nss-SO}_4^{2-}$ ) at Chichijima is 0.02, which is lower than those of other remote marine locations by a factor of 5–7, indicating a substantial impact from continentally derived sulfate. At the tropical stations, American Samoa and Fanning Island,  $\text{MSA}$  and  $\text{nss-SO}_4^{2-}$  ratios exhibit similar values with mean ratios of 0.07 and 0.06, respectively, indicating the cleanest locations in regard to the continental inputs (Arimoto et al., 1987). This result further supports our assumption that Asian dusts can act as an important source of nutrients that stimulate DMS production in the ocean surface following their emission to the marine atmosphere over the western North Pacific. However, it is rather less important that yields of  $\text{MSA}$  from DMS oxidation are enhanced as a function of temperature (Hynes et al., 1986).

## 4 Summary and conclusions

We conducted a 12-year observation of water-soluble inorganic ions in TSP aerosols from the remote marine location of Chichijima Island in the western North Pacific. Long-term observation of marine aerosols provides the following findings.

1. Water-soluble inorganic ions in the TSP aerosols are dominated by sea salt particles ( $\text{Na}^+$  and  $\text{Cl}^-$ ), which

contributed about 75 % to the total WSIM followed by anthropogenic species such as  $\text{nss-SO}_4^{2-}$  and  $\text{NO}_3^-$ .

- Sea salt components showed prominent peaks in autumn and winter months and reached a minimum in spring and summer probably due to the variations in wind speed over the observation site.  $\text{nss-SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{nss-K}^+$  showed higher concentrations in winter and spring due to the atmospheric long-range transport of anthropogenic pollutants and biomass burning emissions in East Asia. Although  $\text{NH}_4^+$  concentrations are relatively low throughout the sampling period over Chichijima Island, they showed prominent peaks in spring and winter months. The concentrations of  $\text{nss-Ca}^{2+}$  in TSP drastically increased in spring when the Asian dusts are transported over the observation site.
- Interestingly, concentrations of  $\text{nss-SO}_4^{2-}$  during winter and spring decreased from 2007 to 2012 probably due to the decrease in  $\text{SO}_2$  emissions in China after 2006. A similar trend was seen in the concentrations of  $\text{NO}_3^-$  during the study period. In contrast, the concentration of  $\text{nss-K}^+$  showed continuous increase from 2001 to 2004 and 2006 to 2012, suggesting that biomass burning emissions in East Asia increased, followed by the atmospheric transport to the western North Pacific. On the other hand,  $\text{MSA}^-$  concentrations during winter and spring continuously increased from 2001 to 2012, indicating that direct continental transport of Asian dust followed by springtime bloom in the ocean play an important role on the annual variation of  $\text{MSA}^-$  concentrations over the western North Pacific.
- We also found there is a time lag between the measured concentrations of  $\text{MSA}^-$  in the aerosols and satellite-derived biological tracer (chlorophyll *a*), suggesting that variability of phytoplankton, sea-air exchange rate of DMS emissions, and other environmental conditions can play an important role in controlling the concentrations of  $\text{MSA}^-$  over the observation site.

This study provides a long-term record (2001–2012) of water-soluble species in TSP aerosols on Chichijima Island, in the western North Pacific, and focuses on the impact of long-range transport of Asian dusts and anthropogenic pollutants from East Asia on the distributions of water-soluble ionic species. This impact has changed suddenly over the last decade and is becoming a challenge for the assessment of future climate effects of Asian aerosols over the western North Pacific. We believe that this study has further implications regarding the radiative forcing and climate models over the oceanic regions.

**The Supplement related to this article is available online at doi:10.5194/acp-15-6437-2015-supplement.**

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