Size-resolved sulfate and ammonium measurements in marine boundary layer over the North and South Pacific

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Abstract

Marine background levels of non-sea-salt- (nss-) SO_4^{2-} (5.0–9.7 neq m^{-3}), NH_4^+ (2.1–4.4 neq m^{-3}) and elemental carbon (EC) (40 - 80 ngC m^{-3}) in aerosol samples were measured over the equatorial and South Pacific during a cruise by the R/V Hakuho-maru from November 2001 to March 2002. High concentrations of nss-SO_4^{2-} (47–94 neq m^{-3}), NH_4^+ (35–94 neq m^{-3}) and EC (130 - 460 ngC m^{-3}) were found in the western North Pacific near the coast of the Asian continent under the influence of the Asian winter monsoon. Particle size distributions of ionic components showed that the equivalent concentrations of nss-SO_4^{2-} were balanced with those of NH_4^+ in the size range of $0.06 < D < 0.22$ μm, whereas the concentration ratios of NH_4^+ to nss-SO_4^{2-} in the size range of $D > 0.22$ μm were decreased with increase in particle size. We estimated the source contributions of those aerosol components in the marine background air over the equatorial and South Pacific. Biomass burning accounted for the large fraction (80–98% in weight) of EC and the minor fraction (2–4% in weight) of nss-SO_4^{2-}. Marine biogenic source accounted for several tens percents of NH_4^+ and nss-SO_4^{2-}. In the accumulation mode, 70% of particle number existed in the size range of $0.1<D<0.2$ μm. In the size rage of $0.06 < D < 0.22$ μm, the dominant aerosol component of $(NH_4)_2SO_4$ would be mainly derived from the marine biogenic sources.

Key words: Size distribution; Anthropogenic aerosol; Biogenic sulfate; Ammonium sulfate; Elemental carbon.

1. Introduction

Aerosol particles scatter solar radiation directly as well as indirectly (IPCC, 2001). Several studies have been conducted on the spatial and temporal variations of particle number concentrations in the accumulation mode range ($0.1 < D < 1.0$ μm) that effectively scatter the visible rays and provide the largest number of cloud condensation nuclei (CCN). It is necessary to relate the mass concentrations of the chemical components in an aerosol particle that is newly formed in the accumulation mode range to the increase in particle number concentration. In marine air, non-sea-salt- (nss-) SO_4^{2-} is the major component of accumulation mode range aerosols and accounts for the largest number of aerosol particles (O'Dowd and Smith, 1993), while Novakov et al. (1997) suggested that organic matter released from the ocean surface is also an important component of marine aerosol. The global burden of nss-SO_4^{2-} of 0.78 Tg S is distributed as follows: 37% from anthropogenic fossil fuel burning, 36% from volcanoes, 25% from dimethyl sulfide (DMS) produced by marine phytoplankton, and 1.6% from biomass burning (Graf et al., 1997). In the middle latitude of Cape Grim (41°S, 144°E) in the Southern Ocean, the seasonal variation of nss-SO_4^{2-} concentration, which is high in summer during high productive season and low in winter, was consistent with the seasonal variations of DMS and methane sulfonic acid (MSA) aerosol as good indicators of marine biogenic sources (Ayers and Gras, 1991; Ayers et al., 1991). Fitzgerald (1991) summarized that DMS is the most important source of nss-SO_4^{2-} over the remote oceans. On the other hand, Andreae et al. (1999) indicated that the low concentration of DMS over the Southern Ocean could not sustain the background level of nss-SO_4^{2-} (>1.6 neq m^{-3}) during winter when the primary production is low; they further indicated that continental sources must be contributing significantly to the nss-SO_4^{2-} levels. During the First Aerosol Characterization Experiment (ACE 1) above the remote Southern Ocean in summer, it was observed that between 10 and 45% of the SO_4^{2-} particles had coagulated with soot particles even in clean air (Posfai et al., 1999). Posfai et al. concluded that internally mixed soot and nss-SO_4^{2-} particles appear to comprise a globally significant fraction of anthropogenic (or land source) aerosols in the troposphere; this was the case even during summer when the primary production is high.

While many studies have been conducted on the sources of SO_4^{2-} in marine air, few studies were conducted on the sources of NH_4^+ that acts as a counter part of nss-SO_4^{2-} ion in the accumulation mode. Since the concentration of the atmospheric total ammonia (aerosol NH_4^+ + gaseous NH_3) was much lower in the oceanic air over the Pacific than in the air over the land, the land is the major contributor to the total ammonia in the oceanic air (Tsunogai and Ikeuchi, 1968; Tsunogai, 1971). Later works (Quinn et al., 1987; Quinn et al., 1990; Zhuang and Huebert, 1996; Lee et al., 1998; Gibb et al., 1999; Sorensen et al., 2003) estimated the air-sea flux of ammonia by comparing their concentrations in the air and ocean. These studies concluded that ocean surfaces are potential sources of ammonia in marine air. Recently, a source analysis study using the δ15N method reported that NH_4^+ aerosols in remote marine air were mainly derived from marine biological activity and the biogenic NH_4^+ concentration was below 6 neq m^{-3} (Jickells et al., 2003).

To relate the increase in particle number and nss-SO_4^{2-} aerosol formation in the accumulation mode range, we must identify the nss-SO_4^{2-} formation processes in remote marine air. New particle formation and subsequent coagulation/condensation growth are responsible for the increase in particle number in the accumulation mode range. The heterogeneous reaction of SO_2 with a sea-salt particle and the subsequent aqueous phase oxidation to SO_4^{2-} accounts for more than 60% of the total amount of nss-SO_4^{2-} formation in marine air (Luria and Sievering, 1991). The heterogeneous reaction of SO_2 with cloud droplets is also an important formation process of nss-SO_4^{2-} (Feichter et al., 1996). The formation of nss-SO_4^{2-} by heterogeneous reactions does not increase the particle number.

In order to examine the sources of nss-SO_4^{2-} and NH_4^+ and the relation between those components and particle number in marine air, we analyzed the size distributions of ionic components in aerosol samples collected over the North and South Pacific Ocean.

2. Method

2.1. Marine air sampling

Aerosol sampling was carried out over the North and South Pacific Ocean during the R/V Hakuho-maru cruise KH01-3 from November 2001 to March 2002 (Figure 1). Aerosol samples were collected at the fore of the uppermost deck (17 m above sea level) on the shipboard. We collected the size-segregated aerosols on Nuclepore filters (80-mm diameter) by a low-pressure cascade impactor having 50% cutoff diameters of D > 0.06, 0.13, 0.22, 0.33, 0.52, 0.76, 1.25, 2.5, 3.9, 5.7, 8.5, and 12.1 μm. The ambient air was pumped at a flow rate of 20 L min^{-1}. The sampling pump was automatically stopped to avoid the influence of ship exhaust when the wind was blowing from the stern of the ship. The total collection time for each filter was about 72 h. We collected 14 samples of size-segregated aerosols (sample id. LP_1–LP_14) during the cruise. The aerosol samples collected on the Nuclepore filters were kept in separate petri dishes that were sealed with a tape and stored in an airtight box at room temperature. Thermodynamically unstable NH_4NO_3 is decomposed into the gaseous NH_3 and HNO_3 when the partial pressure of gaseous NH_3 is reduced (Matsumoto and Tanaka, 1996). Since the large fraction of NH_4^+ is combined with SO_4^{2-} and forms $(NH_4)_2SO_4$ or NH_4HSO_4 in marine air (Johansen et al., 1999), we can neglect the loss of NH_4NO_3 on the filter samples collected in marine air.

2.2. Analytical method

The filter samples were placed in polystyrene bottles with a volume of 15 mL, and the water-soluble components were ultrasonically extracted into 10 mL of deionized water (Milli-Q 18MΩ cm) just before chemical analysis. Insoluble components contained in the extracted solutions were filtrated by a membrane filter of 0.4 μm pore size. The major ionic components in the filtrated solutions were analyzed by ion chromatography using a Dionex DX-120 fitted with AG4A/AS4A column system for the anions and CG12A/CS12A column system for the cations. A carbonate/bicarbonate eluent (1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$) and methane sulfonic acid eluent (18 mM, MSA) were used for detecting the major anions (Cl^-, NO_3^-, and SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}), respectively. The overall experimental precision (standard deviation/mean, n = 5) was below 5%.

2.3. Particulate elemental carbon (EC) and particle number

The concentration of elemental carbon (EC) in PM2.5 (D < 2.5 μm) was measured continuously by a thermal technique using an ambient carbon particulate monitor (Rupprecht & Patashnick Co. Inc., Model 5400) at 4-h intervals (Uematsu et al., 2001; Matsumoto et al., 2003). The amounts of carbonaceous substances evolved at 340°C and 750°C were defined as organic carbon (OC) and total carbon (TC), respectively. The difference between the amounts of TC and OC gives the amount of EC (Uematsu et al., 2001). An optical particle counter (OPC, type KC-18, Rion, Inc.) measured the particle number concentrations (D > 0.3, 0.2, 0.15, and 0.1 μm) continuously at a flow rate of 0.3 L min^{-1} through a semiconductive tube (50-cm length) to minimize the loss of particles.

3. Results and discussions

The concentrations of nss-SO_4^{2-}, NH_4^+, and EC are listed in Table 1. The concentration of EC is shown as an average value during the size-segregated aerosol sampling period. The concentration of nss-SO_4^{2-} was calculated from the molar ratio of SO_4^{2-}/Na^+ (0.0607) in seawater. We will classify the aerosol samples into five air mass categories. The ship observation has the advantage of providing the aerosol data at a wide area of ocean in a short period, however, one-shot data by a cruise can not necessarily represent the typical value of each air mass category.

3.1. Trajectory Analysis

The global final (FNL) analysis data was used to conduct backward air trajectory analysis with the HYSPLIT Model (Draxler and Rolph, 2003; Rolph, 2003). In winter, the air mass is frequently transported from the eastern Asian region to the northwestern North Pacific (>25°N) by the Asian winter monsoon. During the collection of samples LP_1 and LP_12, air masses were transported from the Asian continent for at most 25% of collection time of each sample, and from the remote part of the North Pacific for at least 75 % of collection time. The air masses corresponding to LP_1 and LP_12 are the mixture of maritime air and land source air. The air masses corresponding to LP_13 and LP_14 had passed over the Asian continent (and/or the Japanese islands) 3 days before the whole collection time. The air mass corresponding to LP_2 in the subtropical North Pacific had passed over the western coast of North America 10 days before the collection time. The air masses corresponding to LP_3, 4, 5, and 6 over the equatorial and South Pacific had not encountered land for the previous 10 days. The air masses corresponding to LP_7, 8, and 9 had passed over the New Zealand and Australia within 2 days. The R/V Hakuho-maru cruised near the islands in the western subtropical and equatorial Pacific during the collection of samples LP_10 and LP_11.

3.2. Concentrations under the influence of the Asian winter monsoon (LP_1, 12, 13, and 14)

Increased concentrations of NH_4^+ and nss-SO_4^{2-} were observed in LP_13 (35 and 47 neq m^{-3}, respectively) and LP_14 (94 and 94 neq m^{-3}, respectively) north of 25°N, whereas those of LP_1 and LP_12 did not exhibit any increase. The annual average, maximum, and minimum concentrations of NH_4^+ and nss-SO_4^{2-} around the Pacific Ocean are summarized in Table 2. The concentrations of LP_13 and LP_14 were two times higher than the average concentrations at Haha-jima Island (27°N, 140°E), which were affected by the transport from Asian anthropogenic sources during the winter season (Matsumoto et al., 1998). EC is a good indicator of land source aerosols (fuel burning and/or biomass burning); it primarily exists in the accumulation mode range (Seinfeld and Pandis, 1998; Kaneyasu and Murayama, 2000). The EC concentrations of 130–210 ng m^{-3} during the periods corresponding to LP_1, 12, and 13 were comparable to the average of 180 ng m^{-3} at Chichi-jima Island (27°N, 142°E), which was affected by Asian anthropogenic substances during the March–May period (Matsumoto et al., 2003). The EC concentration of LP_14 (460 ng m^{-3}) was close to the maximum concentration of 590 ng m^{-3} at Chichi-jima Island. The concentration ratios of EC (ng C m^{-3})/nss-SO_4^{2-} (ng S m^{-3}) of LP_14 and LP_13 were 0.31 and 0.17, respectively. Similar ratios were found for the air mass under the Asian anthropogenic influence at Chichi-jima Island (0.24 = 180 ng EC m^{-3}/736 ng S m^{-3}) and Amami Island (29°N, 128°E) over the East China Sea (0.42 = 470 ng BC m^{-3}/1120 ng S m^{-3}) (Matsumoto et al., 2004; Kaneyasu and Takada, 2004). Black carbon (BC), a carbonaceous aerosol like soot particle, is measured by an optical method. The concentration of BC measured by aethalometer was slightly lower (17%) than that of EC with high correlation (r=0.92) in the urban air (Rice, 2004). Those ratios of EC(or BC)/nss-SO_4^{2-} found under the anthropogenic influence of the East Asia were close to the global burden ratio of BC to nss-SO_4^{2-} (0.2 = 0.06 Tg BC/0.29 Tg S) derived from anthropogenic fossil fuel burning, which is calculated by using the global model results of Graf et al. (1997) and Reddy and Boucher (2004). We will use this ratio as a concentration ratio of EC/nss-SO_4^{2-} derived from the anthropogenic fuel burning transported over the ocean for a long time (section 3.7.3).

The size distributions of nss-SO_4^{2-} and NH_4^+ were shown in Figure 2. The particle size of concentration peak of nss-SO_4^{2-} was consistent with that of NH_4^+ in the accumulation mode. The large fraction of nss-SO_4^{2-} in the accumulation mode would exist as $(NH_4)HSO_4$ or $(NH_4)_2SO_4$. The equivalent ratios of NH_4^+ to nss-SO_4^{2-} in the accumulation mode range were shown in Figure 3-a. The higher NH_4^+/nss-SO_4^{2-} ratios were found in the higher loadings of nss-SO_4^{2-} that would be largely derived from the anthropogenic sources. The NH_4^+/nss-SO_4^{2-} ratio of 1 was found over the full size range in the accumulation mode of LP_14. The NH_4^+/nss-SO_4^{2-} ratios of LP_12 and LP_13 in the size range of D> 0.22 μm were decreased with increase in particle size. It is likely that the urban type air is enriched with land source NH_3 and can neutralize anthropogenic nss-SO_4^{2-}, since the equivalent concentrations of NH_4^+ in the accumulation mode were higher than those of nss-SO_4^{2-} in urban air of Tokyo (Ooki and Uematsu, 2005). The concentration of land source NH_3 would be reduced with transport time over the ocean. When the anthropogenic SO_2 has remained after the reduction of land source NH_3 over the ocean, a part of newly formed anthropogenic nss-SO_4^{2-} was added on the size range of D > 0.22 µm. It is supposed that the formation processes of nss-SO_4^{2-} added on D>0.22 µm are condensation of H_2SO_4 onto the pre-existing particle, and/or heterogeneous reaction of SO_2 with cloud droplet and subsequent oxidation.

3.3. Subtropical North Pacific (LP_2)

We found a high concentration of EC (290 ng m^{-3}) during the LP_2 sampling period, while the concentrations of NH_4^+ (1.9 neq m^{-3}) and nss-SO_4^{2-} (4.2 neq m^{-3}) were an order of magnitude lower than those of samples under the Asian winter monsoon influence.

3.4. Equatorial and South Pacific background level (LP_3, 4, 5, and 6)

The nss-SO_4^{2-} and NH_4^+ concentrations of LP_3, 4, 5, and 6 (5.0–9.7 neq m^{-3} and 2.1–4.4 neq m^{-3}, respectively) were comparable to the minimum concentration of nss-SO_4^{2-} at Fanning (4°N, 159°W) in the equatorial Pacific (Prospero et al., 1985) and the average concentrations at Baring Head (41°S, 174°E) in New Zealand (Allen et al., 1997) (Table 2). The average concentrations of EC (40–50 ng m^{-3}) of LP_4, 5, and 6 in the South Pacific were close to the background level of BC (26–40 ng C m^{-3}) in the equatorial and South Pacific (Kaneyasu and Murayama, 2000), while the concentration of LP_3 (80 ng m^{-3}) in the equatorial Pacific was somewhat higher than the background level. The EC(ngC m^{-3})/nss-SO_4^{2-}(ngS m^{-3}) concentration ratios of 0.52, 0.42, 0.55, and 0.50 (LP_3, 4, 5, and 6, respectively) were somewhat higher than those of LP_13 and 14 which are largely derived from the anthropogenic sources. The concentration peaks of nss-SO_4^{2-} were found in the accumulation mode (LP_3, 4, and 5) and in the size range of 0.76<D<1.25 µm (LP_6) (Figure 2). The average equivalent ratio of NH_4^+/nss-SO_4^{2-} in the marine background air was shown in Figure 3-b with other reports. In marine background air (present study; Sievering et al., 1999; Neususs et al., 2000), the equivalent concentration ratios of NH_4^+/nss-SO_4^{2-} were close to 1 in the smallest size range (around 0.1 µm diameter) and decreased with increase in particle size. In the smallest size range, a large fraction of nss-SO_4^{2-} aerosol exists as $(NH_4)_2SO_4$. At a remote site in the Antarctic the cation/anion ratios were high (~1) in the size ranges of D < 0.15 µm and D > 0.53 µm and low in the size range of 0.15 < D < 0.53 µm (Kerminen et al., 2001). Kerminen et al. concluded that the smaller size range (D < 0.15 µm) of nss-SO_4^{2-} resulted due to the homogeneous reaction and subsequent coagulation/condensation growth, and the enrichment of nss-SO_4^{2-} in the size range of 0.15 < D

< 0.53 μm was caused by the aqueous phase oxidation of SO_2 in cloud droplets. By using the thermal decomposition method of O'Dowd et al. (1997), it was also found that $(NH_4)_2SO_4$ (or NH_4HSO_4) was the predominant component in the size range of D < 0.14 μm in the Southern Ocean (53–57°S, 55–60°W).

3.5. Concentrations under the influence of the Oceania land source (LP_7, 8, and 9)

The R/V Hakuho-maru cruised near the coasts of New Zealand and Australia during the sampling periods of LP_7, 8, and 9. The concentrations of NH_4^+ (7.0–9.3 neq m^{-3}) and nss-SO_4^{2-} (7.5–15 neq m^{-3}) were slightly higher than those of the marine background level, however, EC concentrations (40 ng m^{-3}) were similar to marine background level . The concentration ratios of EC (ngC m^{-3})/nss-SO_4^{2-} (ngS m^{-3}) of LP_7, 8, and 9 were 0.21, 0.33, and 0.17, respectively. Size distributions of nss-SO_4^{2-} and NH_4^+ were similar to other marine air samples.

3.6. Subtropical and equatorial western Pacific (LP_10 and 11)

The concentrations of NH_4^+ and nss-SO_4^{2-} were marine background level, while EC showed high concentration values of 240 ng m^{-3} (LP_10) and 1100 ng m^{-3} (LP_11). The extremely high EC concentration of LP_11 was possibly derived from biomass burning and was comparable to the EC concentration under the influence of Siberian forest fires (1300 ng C m^{-3}) at Rishiri Island (Hayano et al., 2004). The EC(ngC m^{-3})/nss-SO_4^{2-}(ngS m^{-3}) concentration ratio (=12) of LP_11 was close to the global burden ratio of biomass burning (BC/nss-SO_4^{2-} = 15), which was calculated from the global model results (Graf et al., 1997; Reddy and Boucher, 2004). We will use this ratio as a concentration ratio of EC/nss-SO_4^{2-} derived from the biomass burning transported over the ocean for a long time (section 3.7.3).

3.7. Source analysis of nss-SO_4^{2-}, NH_4^+, EC, and particle number in the marine background air over the equatorial and South Pacific.

3.7.1 nss-SO_4^{2-}

The concentrations of nss-SO_4^{2-} (5.0–9.7 neq m^{-3}) of LP_3, 4, 5, and 6 over the equatorial and South Pacific were close to the average concentration (8.6 neq m^{-3}) at Cape Grim over the Southern Ocean in February when the marine biological activity is high (Andreae et al., 1999). Even in the marine background air over the Southern Ocean during the high productive period, between 10 and 45% of nss-SO_4^{2-} particle were coagulated with land source soot particle (Posfai et al., 1999). It is possible that nss-SO_4^{2-} particles coagulated with soot have been distributed to the wide area of the southern hemisphere. Since the marine background level of EC was found in the South Pacific, we assumed that between 10 and 45% of nss-SO_4^{2-} in mass concentration of LP_3, 4, 5, and 6 has been coagulated with EC derived from the land sources (anthropogenic fuel burning and biomass burning). The concentration of nss-SO_4^{2-} coagulated with EC in the accumulation mode, [nss-SO_4^{2-}]$_{EC}$, was estimated to be 0.4 - 3.9 neq m^{-3}. We estimated the source contributions of nss-SO_4^{2-} in the accumulation mode based on the equations (1) - (4) in section 3.7.3. The concentration range of fuel burning nss-SO_4^{2-} was estimated to be 0.3 - 3.7 neq m^{-3} (Table 3). Biomass burning was a minor fraction (2-4%) of nss-SO_4^{2-}. Since the source of volcanic sulfur is 2.7 times higher than the biomass burning in the southern hemisphere (Graf et al., 1997), volcanic nss-SO_4^{2-} may account for several percents (approximately, 6 - 11%) of nss-SO_4^{2-}. The contribution of marine biogenic source of nss-SO_4^{2-} is roughly estimated to be 42 - 80% by subtracting the contributions of fuel burning, biomass burning, and volcano sources from the total concentration of nss-SO_4^{2-}.

3.7.2. NH_4^+

Considering the residence time of NH_3 and the chemical characteristics of NH_4^+ in marine air, NH_4^+ associated with marine biogenic nss-SO_4^{2-} aerosols in remote marine air has been produced over the ocean. Anthropogenic air masses contain a large amount of SO_2 and its oxidation product H_2SO_4. Land source NH_3 immediately reacts with H_2SO_4 and produces NH_4^+ salt during the transport path from the land to the ocean. The residence time of NH_3 is around several hours in the marine boundary layer (Quinn et al., 1990). The concentration of NH_3 transported from land sources to remote marine air should be considerably low. Biogenic nss-SO_4^{2-} aerosols in remote marine air are exposed to NH_3 generated over the ocean within the time scale of its residence time (several hours). The equivalent ratio of NH_4^+/nss-SO_4^{2-} in the accumulation mode of anthropogenic aerosol (LP_13), which has been transported over the ocean for 3 days, was 0.73. Similar ratio of 0.68 was reported over the western North Pacific under the Asian anthropogenic influence (Matsumoto et al., 2004). Assuming that the NH_4^+/nss-SO_4^{2-} ratio of anthropogenic (land source) aerosol transported over the ocean is 0.73, the concentration ranges of land source NH_4^+ associated with anthropogenic fuel burning nss-SO_4^{2-} is calculated by 0.73×[nss-SO_4^{2-}]$_{fb}$. The concentration of land source NH_4^+ and marine biogenic NH_4^+ over the marine background air (LP_3, 4, 5, and 6) were estimated to be 0.2 - 2.7 neq m^{-3} and 0.3 - 3.6 neq m^{-3}, respectively.

We will estimate the sea-air flux of NH_3 to sustain the concentration of marine biogenic NH_4^+. The marine boundary layer (MBL) height over the Southern Ocean (40°S, 77°E) from December to March was 500m (Koga and Tanaka, 1996). Katoshevski et al., (1999) used the MBL height of 1000m in their box model study. The residence time of NH_4^+ aerosol was estimated to be 4.2 days in a general circulation model (Adams et al., 1999). Using the marine boundary layer height of 500 - 1000 m and the residence time of NH_4^+ aerosol of 4.2 days, a sea-air NH_3 flux of 0.04 – 0.9 μmol m^{-2} day^{-1} is needed to sustain the biogenic NH_4^+ aerosol concentration. The sea-air NH_3 flux in April–May was reported to be 1.8–15 μmol m^{-2} day^{-1} over the Pacific Ocean (170°W, 37°N–11°S) , where the concentrations of seawater NH_4^+ (0.2–0.7 μM) and chlorophyll-a (0.19–0.22 μg L^{-1}) were high (Quinn et al., 1990). Quinn et al. implied that the sea-air NH_3 flux of around 10 μmol m^{-2} day^{-1} in the equatorial Pacific where a high concentration of chlorophyll-a (0.25 μg L^{-1}) exists in the surface water was about an order of magnitude higher than that in the region where this concentration was below 0.1 μg L^{-1}. In the South Pacific (160°W, 0–46°S), we measured low concentrations of NH_4^+ (<0.07 μM) and chlorophyll-a (0.05–0.3 μg L^{-1}) in the surface water (KH01-3 cruise report, 2002). It seems that the lowest level of marine biogenic NH_4^+ (0.3 - 3.6 neq m^{-3}) generated over the oligotrophic subtropical South Pacific can be maintained by the sea-air flux of biogenic NH_3 at the same region.

3.7.3. EC

The total concentration of EC is described by the sum of the anthropogenic fuel burning (fb) EC, $[EC]_{fb}$, and biomass burning EC, $[EC]_{bb}$, in equation (1). The total concentration of land source nss-SO_4^{2-} coagulated with EC is described by the sum of the anthropogenic fuel burning nss-SO_4^{2-}, $[nss\text{-}SO_4^{2-}]_{fb}$, and biomass burning nss-SO_4^{2-}, $[nss\text{-}SO_4^{2-}]_{bb}$, in equation (2).

$$[EC] = [EC]_{fb} + [EC]_{bb} \qquad (1)$$

$$[nss\text{-}SO_4^{2-}]_{EC} = [nss\text{-}SO_4^{2-}]_{fb} + [nss\text{-}SO_4^{2-}]_{bb} \qquad (2)$$

The concentration ratios of $[EC]_{fb}/[nss\text{-}SO_4^{2-}]_{fb}$ and $[EC]_{bb}/[nss\text{-}SO_4^{2-}]_{bb}$ in land source aerosols that were transported over the ocean for a long time would be close to their global burden ratios in equations (3) and (4).

$$[EC]_{fb}/[nss\text{-}SO_4^{2-}]_{fb} = 0.2 \qquad (3)$$

$$[EC]_{bb}/[nss\text{-}SO_4^{2-}]_{bb} = 15 \qquad (4)$$

The concentration ranges of $[EC]_{fb.}$, $[nss\text{-}SO_4^{2-}]_{fb}$, $[EC]_{bb}$ and $[nss\text{-}SO_4^{2-}]_{bb}$ can be calculated by the substitutions $[nss\text{-}SO_4^{2-}]_{EC}$ (ngS m^{-3}) and [EC] (ngC m^{-3}). The percentages of biomass burning EC and fuel burning EC were estimated to be 80 - 98% and 2 - 20%, respectively (Table 3).

3.7.4. Particle number

We considered that $(NH_4)_2SO_4$ in the size range of $0.06 < D < 0.22$ μm is mainly derived from the marine biogenic sources in the marine background air. Nuclei particle grows to a size of D ~ 0.2 μm within 3 days in marine air, which have a low concentration of pre-existing particle (D ~ 0.3 μm) below 10 cm^{-3} (Lin et al., 1992). The average particle number of D > 0.3 μm was low (10 ±8 cm^{-3}) in the marine background air of our study. Even though anthropogenic nss-SO_4^{2-} accounted for several tens percents of the total mass concentration of nss-SO_4^{2-}, marine biogenic $(NH_4)_2SO_4$ newly produced over the ocean would account for the larger fraction of

$nss\text{-}SO_4^{2-}$ in the smaller size range (i.e. $0.06 < D < 0.22$ μm) rather than the land source $nss\text{-}SO_4^{2-}$ aged beyond 10 days over the ocean. Particle number concentration in the size range of $0.1 < D < 0.2$ μm accounted for 70% of the total number concentration in the size range of $0.1 < D < 5$ μm (165 cm^{-3}). Since the marine biogenic NH_3 was used to produce marine biogenic $(NH_4)_2SO_4$ particle in the size range of $D<0.22$ μm, not only the emission of biogenic sulfur (DMS) from the sea surface but also the emission of marine biogenic ammonia would be one of important factors to increase the particle number in marine air.

4. Conclusion

Size-segregated aerosol samples were collected over the North and South Pacific during a cruise by the R/V Hakuho-maru from November 2001 to March 2002. We measured the concentrations of major ionic components and elemental carbon (EC). In the North Pacific, $nss\text{-}SO_4^{2-}$ was fully neutralized by NH_4^+ near the coast of the Asian continent where there is highly affected by anthropogenic sources (LP_14). The equivalent concentration ratio of NH_4^+/ $nss\text{-}SO_4^{2-}$ was decreased with increase in particle size in the accumulation mode under the influence of the Asian winter monsoon (LP_12 and 13). Like the anthropogenic air mass, the ratio of NH_4^+/$nss\text{-}SO_4^{2-}$ in the marine background air of South Pacific was decreased with increase in particle size. In the accumulation mode, the particle number of $0.1<D<0.2$ μm, which would mainly exist as $(NH_4)_2SO_4$ particle, accounted for 70% of total particle number (165 cm^{-3}). We calculated the source contributions of $nss\text{-}SO_4^{2-}$, NH_4^+, and EC in the marine background air of equatorial and South Pacific. Biomass burning accounted for the large fraction (80 - 98% in weight) of EC and the minor fraction (2 - 4% in weight) of $nss\text{-}SO_4^{2-}$. The concentration range of marine biogenic NH_4^+ was roughly estimated to be 0.3 - 3.6 neq m^{-3}. The lowest level of marine biogenic NH_4^+ can be sustained by the sea-air flux of NH_3 even in the oligotrophic sub-tropical South Pacific. Since the large fraction of NH_4^+ in the size range of $0.06<D<0.22$ μm existed as $(NH_4)_2SO_4$, it is possible that the emission of marine biogenic NH_3 as well as DMS to the atmosphere is one of important factors to produce new particles over the ocean.

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Figure captions

Figure 1. Ship track of R/V Hakuhou-maru. Labeled numbers denote aerosol sample id.

Figure 2. Size distributions of nss-SO_4^{2-} (——) and NH_4^+ (– – -).

Figure 3. Equivalent ratios of NH_4^+ to nss-SO_4^{2-} a) under the influence of the Asian winter monsoon of LP_1 (——), LP_12 (···········), LP_13 (——), and LP_14 (······), and b) in the marine background air (1) Portugal (Neususs et al., 2000), (2) present study that is the average of LP_3, 4, 5 and 6, (3) Southern Ocean (Sievering et al., 1999).

Table 1 The concentrations of NH_4^+ and nss-SO_4^{2-} in the total size range and in the accumulation mode range (in parentheses), and of EC in the size range of D < 2.5 μm averaged for size-segregated aerosol sampling period.

Sample ID	NH_4^+ (neq m^{-3})	nss-SO_4^{2-} (neq m^{-3})	EC (ng C m^{-3})	EC/nss-SO_4^{2-*} (ngC m^{-3}/ngS m^{-3})
LP_1	2.0 (1.8)	6.1 (5.9)	210	2.2
LP_2	1.9 (1.7)	4.2 (4.1)	290	4.3
LP_3	4.4 (4.0)	9.7 (8.8)	80	0.52
LP_4	4.1 (3.2)	7.4 (7.2)	50	0.42
LP_5	2.6 (2.3)	5.7 (5.2)	50	0.55
LP_6	2.1 (1.7)	5.0 (4.3)	40	0.50
LP_7	7.6 (6.3)	12 (11)	40	0.21
LP_8	7.0 (5.7)	7.5 (7.5)	40	0.33
LP_9	9.3 (8.5)	15 (12)	40	0.17
LP_10	6.2 (5.4)	7.3 (6.4)	240	2.1
LP_11	4.2 (3.7)	5.6 (5.1)	1100	12
LP_12	5.8 (5.4)	10 (9.0)	140	0.88
LP_13	35 (33)	47 (43)	130	0.17
LP_14	94 (79)	94 (83)	460	0.31

*The concentration ratio of EC (PM 2.5) to nss-SO_4^{2-} in the total size range.

Table 2 Marine aerosol concentrations around the Pacific Ocean

Site		nss-SO_4^{2-} (neq m^{-3})			NH_4^+ (neq m^{-3})		
		Avg.*	Max.**	Min.**	Ave.*	Max.**	Min.**
Present study (Background)	S. Pacific (LP_3–6)	7.0	9.7	5.0	3.3	4.4	2.1
Present study (Monsoon)	N. Pacific (LP_13 and 14)	70	94	47	64	94	35
Mawson[a]	Antarctic (66ºS, 140ºE)	1.8	5.6 (Jan.)	0.2 (Jun.–Jul.)	0.89	3.5 (Jan.)	0.17 (Jun.–Jul.)
Baring Head[b]	S. Pacific (41ºS, 174ºE)	5.2	3.8 (Jun.–Feb.)	2.4 (Jul.–Aug.)	4.1	3.3 (Jun.–Feb.)	2.2 (Sep.–Nov.)
Cape Grim[c]	S. Ocean (40ºS, 144ºE)	-	8.6 (Feb.)	1.6 (Jul.)	-	-	-
Samoa[d]	N. Pacific (14ºS, 171ºW)	7.8	8.8 (Sep.–Nov.)	6.6 (Jun.–Aug.)	-	-	-
Fanning[e, f]	N. Pacific (4ºN, 159ºW)	13	18 (Oct.–Nov.)	8.2 (Jan.)	-	-	-
Oahu[e]	N. Pacific (21ºN, 158ºW)	7.8	10 (Feb.–Jun.)	5.8 (Jul.–Jan.)	-	-	-
Haha-Jima[g]	N. Pacific (27ºN, 140ºE)	36	50 (Nov.–May)	12 (Jul.–Oct.)	14	21 (Nov.–May)	2.4 (Jul.–Oct.)
Midway[e, f]	N. Pacific (28ºN, 177ºW)	12	16 (Feb.–Jun.)	6.4 (Jul.–Jan.)	-	-	-
Shemya[e]	N. Pacific (53ºN, 174ºE)	26	68 (Feb.–Jun.)	14 (Jul.–Jan.)	-	-	-

Except for present study; *Annual average, **Average concentrations during the maximum (minimum) period.

[a]Savoie et al. (1993), [b]Allen et al. (1997), [c]Andreae et al. (1999), [d]Savoie et al. (1994), [e]Prospero et al. (1985), [f]Saltzman et al. (1983), [g]Matsumoto et al. (1998).

Table 3. The concentrations of nss-SO_4^{2-} (neq m^{-3}) and NH_4^+ (neq m^{-3}) in the accumulation mode, and EC (ngC m^{-3}) in PM2.5 over the equatorial and South Pacific. 'F.b.-', 'B.b.-', and 'Bio-' denote the sources of 'anthropogenic fuel burning', 'biomass burning', and 'marine biogenic', respectively.

Sample ID	nss-SO_4^{2-} with EC*	F.b.-SO_4^{2-}	B.b.-SO_4^{2-}	Bio-NH_4^+	F.b.-EC	B.b.-EC
LP_3	0.9 - 3.9	0.6 - 3.7	0.28 - 0.33	1.3 - 3.6	1.8 - 12	68 - 78
	(10 - 45)**	(6.3 - 42)	(3.2 - 3.7)	(33 - 90)	(2.2 - 15)	(85 - 98)
LP_4	0.7 - 3.3	0.5 - 3.1	0.17 - 0.20	1.0 - 2.8	1.7 - 9.9	40 - 48
	(10 - 45)	(7.2 - 43)	(2.3 - 2.8)	(30 - 88)	(3.3 - 20)	(80 - 97)
LP_5	0.5 - 2.3	0.3 - 2.1	0.18 - 0.20	0.7 - 2.0	1.0 - 6.8	43 - 49
	(10 - 45)	(6.0 - 42)	(3.5 - 4.0)	(31 - 90)	(2.0 - 14)	(86 - 98)
LP_6	0.4 - 1.9	0.3 - 1.8	0.14 - 0.16	0.3 - 1.5	0.8 - 5.7	34 - 39
	(10 - 45)	(6.2 - 42)	(3.3 - 3.8)	(21 - 88)	(2.1 - 14)	(86 - 98)

*The concentration of nss-SO_4^{2-} (in the accumulation mode) associated with land source EC, based on the assumption that between 10 and 45% of nss-SO_4^{2-} in weight concentration has been coagulated with land source EC.

**The values in parentheses are percentage (%) of each source to the total concentration in the accumulation mode.

Each value was calculated based on equations (1) - (4).

$$[\text{nss-}SO_4^{2-}]_{bb} = ([EC] - 0.2[\text{nss-}SO_4^{2-}]_{EC})/14.8,$$

$$[EC]_{fb} = [EC] - [EC]_{bb} = [EC] - 15[\text{nss-}SO_4^{2-}]_{bb}$$

The concentration of bio-NH_4^+ was calculated by subtracting the concentration of land source NH_4^+ from the total concentration of NH_4^+.

$$[\text{land source } NH_4^+] = 0.73[\text{nss-}SO_4^{2-}]_{fb}$$

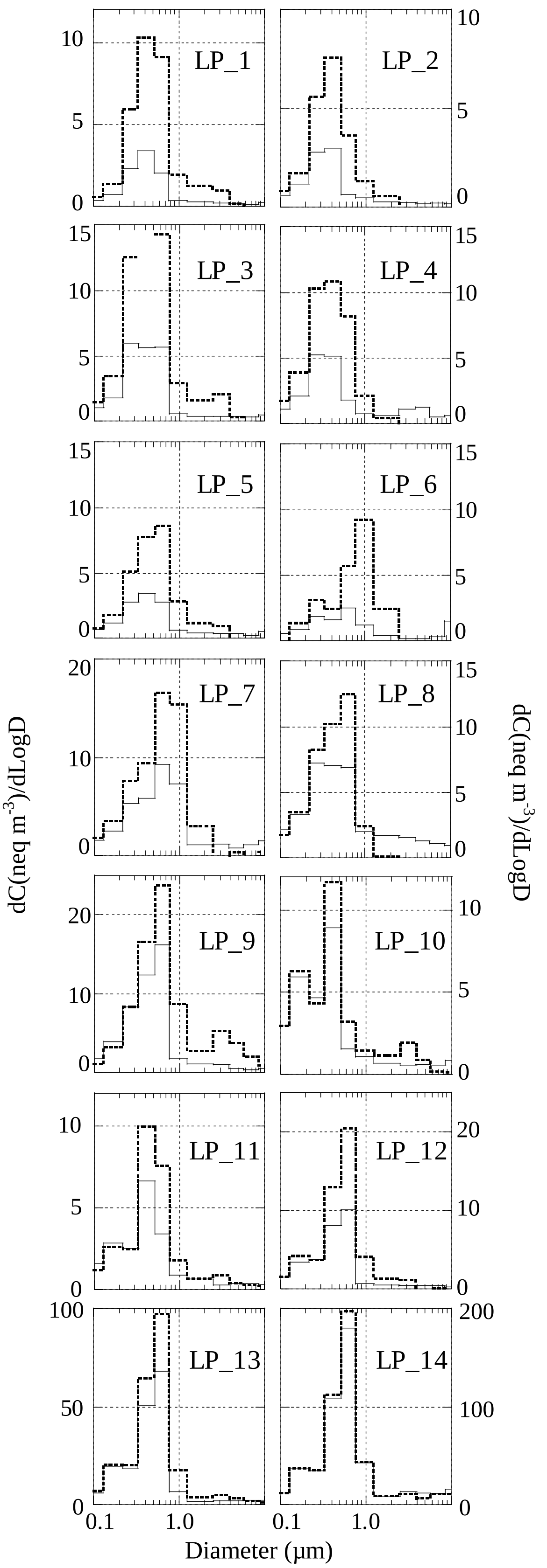

Figure 2 Size distributions of nss-SO_4^{2-} (··········) and NH_4^+ (——).

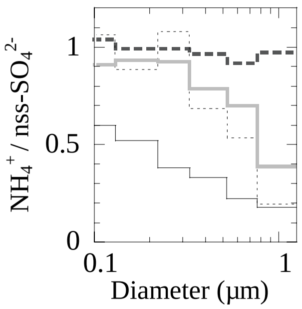

Figure 3-a. Equivalent ratios of NH_4^+ to nss-SO_4^{2-} under the influence of the Asian winter monsoon of LP_1 (——), LP_12 (┈┈┈), LP_13 (——), and LP_14 (······).

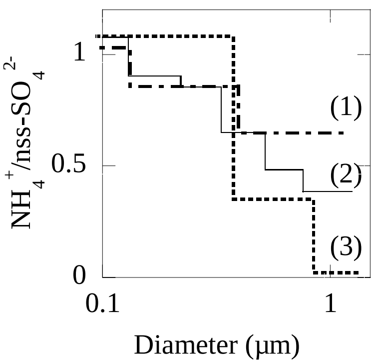

Figure 3-b. Equivalent ratios of NH_4^+ to nss-SO_4^{2-} in the marine background air (1) Portugal (Neususs et al., 2000), (2) present study that is the average of LP_3, 4, 5 and 6, (3) Southern Ocean (Sievering et al., 1999).