



**Carbonaceous and
nitrogenous
components**

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K. Kawamura

One-year observations of carbonaceous and nitrogenous components and major ions in the aerosols from subtropical Okinawa Island, an outflow region of Asian dusts

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

Ambient aerosol samples (TSP, $n = 50$), collected at subtropical Okinawa Island, Japan, an outflow region of Asian dusts in the western North Pacific, were studied for organic carbon (OC), elemental carbon (EC), water-soluble organic carbon (WSOC), water-soluble total nitrogen (WSTN), water-soluble organic nitrogen (WSON) and major ions to better understand the long-range atmospheric transport and formation and transformation pathways of East Asian aerosols. Concentrations of OC, EC, WSOC, WSTN and WSON ranged from 0.76 to $7.1 \mu\text{g m}^{-3}$ (av. $1.74 \pm 1.03 \mu\text{g m}^{-3}$), 0.07–0.96 $\mu\text{g m}^{-3}$ ($0.28 \pm 0.19 \mu\text{g m}^{-3}$), 0.27–1.9 $\mu\text{g m}^{-3}$ ($0.73 \pm 0.38 \mu\text{g m}^{-3}$), 0.77 to 3.03 $\mu\text{g m}^{-3}$ ($0.58 \pm 0.46 \mu\text{g m}^{-3}$) and 0 to 2.2 $\mu\text{g m}^{-3}$ ($0.12 \pm 0.23 \mu\text{g m}^{-3}$), respectively. The average concentration of OC is higher in growing seasons; spring ($2.36 \mu\text{g m}^{-3}$) and summer ($1.79 \mu\text{g m}^{-3}$). Similarly, the highest concentrations of EC and WSOC were found in spring (av. 0.41 $\mu\text{g m}^{-3}$ and 0.95 $\mu\text{g m}^{-3}$, respectively) followed by winter (0.37 and 0.90 $\mu\text{g m}^{-3}$) whereas the lowest concentrations were found in summer (0.19 and 0.52 $\mu\text{g m}^{-3}$, respectively). In contrast, higher concentrations of WSTN were observed in winter (0.86 $\mu\text{g m}^{-3}$) and lower concentrations were observed in summer (0.37 $\mu\text{g m}^{-3}$) and autumn (0.34 $\mu\text{g m}^{-3}$). Similarly, higher concentrations of WSON were observed in early summer (av. 0.26 $\mu\text{g m}^{-3}$) due to the emission from marine biota. The high OC/EC (av. 7.6) and WSOC/OC (44%) ratios suggest the secondary formation of organic aerosols. The OC/EC ratios, correlation analyses between OC and EC ($r = 0.81$), and OC and MSA^- (0.81) in spring suggest that springtime aerosols are influenced by additional marine and terrestrial biogenic sources. The correlation analyses of Ca^{2+} and TSP in spring suggests a significant influence from dust whereas the higher concentrations of NO_3^- and nss-SO_4^{2-} in winter suggest the influence from anthropogenic sources including biomass burning, vehicular emission and coal combustion. $\text{NH}_4\text{-N/WSTN}$ ratios peaked in winter (0.56), indicating an important contribution of biomass burning to WSTN in cold season. In contrast, higher $\text{NO}_3\text{-N/WSTN}$ ratio in spring than winter suggests that vehicular emissions are significant in spring.

Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Correlation analyses of major ions suggest that NH_4^+ and Ca^{2+} play major role in the neutralization of aerosols forming NH_4HSO_4 , $(\text{NH}_4)_2\text{SO}_4$ and CaSO_4 .

1 Introduction

Aerosols affect the Earth's radiative forcing directly by scattering and absorbing light and indirectly by acting as cloud condensation nuclei (Buseck and Posfai, 1999). The role of atmospheric aerosols in radiative budget, however, has not been well understood in spite of many studies (e.g., Ramanathan et al., 2001). Carbonaceous aerosols (OC and EC) play major role in climate change and health effect (Folinsbee, 1992). Although EC is minor component in carbonaceous aerosols, it has positive radiative forcing at the top of the atmosphere (TOA) and negative radiative forcing at the surface (Ramanathan et al., 2001). Organic aerosols that contain water-soluble species play an important role in climate forcing (Novakov and Penner, 1993) and CCN activity (Saxena et al., 1995). Large amounts of water-soluble organic compounds including dicarboxylic acids are present in the tropospheric aerosols from urban (Kawamura and Kaplan, 1987), rural (Limbeck et al., 2001), marine (Kawamura et al., 2004), Arctic (Kawamura et al., 1996a, 2010) and Antarctic regions (Kawamura et al., 1996b), supporting that they are important chemical constituents in the atmosphere.

Oxygenated organic compounds constitute major part of carbonaceous aerosols. The biomass burning is the important source of water-soluble organic carbon (WSOC) although the oxidation, adsorption, condensation and coagulation accelerate to the formation of WSOC during the atmospheric transport (Sempéré and Kawamura, 2003; Rudich et al., 2007). Inorganic species are also major constituents of the atmospheric aerosols (George et al., 2008; Aggarwal and Kawamura, 2008). The condensation nuclei of cloud and fog droplets represent the mixtures of organic and inorganic species including $(\text{NH}_4)_2\text{SO}_4$. Once it is formed in the environment, the droplets continuously grow to dissolve organic and inorganic species (Seinfeld and Pandis, 1998) and are subjected to wet deposition of water soluble fraction including polar organic compounds

Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



(Facchini et al., 1999), and to cloud processing of volatile organic compounds (Ervens et al., 2008). Recently, Tran et al. (2012) showed that during evaporation of droplets organosulfates and aldols are produced in the presence of H_2SO_4 . They can act as light absorbing products after the evaporation of droplets, suggesting that the inorganic species play an important role in the complicated atmospheric reactions.

About 70 % of carbonaceous aerosols are originated from coal burning in China (Cooke et al., 1999). Large amounts of low quality coal are used for house heating and cooking purposes (Wang et al., 2006). Light absorbing EC and light scattering OC have been abundantly reported in Chinese aerosols (Ho et al., 2007; Cao et al., 2007), which are subjected to the long-range transport over the western North Pacific. Okinawa Island is located in the outflow region of Asian aerosols and on the pathway to the Pacific. Cape Hedo is located on the northern edge of Okinawa and has been used as a supersite of Atmospheric Brown Clouds (ABC) project to study the atmospheric transport of Chinese aerosols and their chemical transformation in East Asia (Takami et al., 2007). In the Asian Pacific region, the East Asian monsoon dominates in winter to spring, whereas the monsoon from the Pacific Ocean dominates in summer to fall (Sato et al., 2009), therefore, continental air masses from East Asian countries including Russia, Mongolia, China, and Korea generally arrive over Okinawa during winter and spring.

In this study, we report, for the first time, one-year observations of OC, EC, WSOC, WSTN and major ions in marine atmospheric aerosol (TSP) samples, collected at Cape Hedo, Okinawa. We calculate water-soluble organic nitrogen (WSON) based on the difference between WSTN and inorganic nitrogen (NO_3^- and NH_4^+). We discuss the seasonal trends of these components and transformations of organic aerosol (OA) during the long-range transport of Asian aerosols. Many studies related to the atmospheric chemistry have been conducted at Cape Hedo (Sato et al., 2009; Wang et al., 2009; Zhang et al., 2003; Jaffe et al., 2005; Verma et al., 2011; Lun et al., 2009; Yamamoto and Kawamura, 2011; Ueda et al., 2011; Arakaki et al., 2006; Handa et al., 2010; Mochida et al., 2010). However, no studies were conducted for a long-term measure-

Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

ment of OC, EC, WSOC, WSTN, WSON and major ions in atmospheric aerosols from Cape Hedo, which is located in the northwestern edge of Okinawa Island and outflow region of Asian dusts.

2 Samples and analytical procedure

2.1 Sampling site and aerosol collection

Using a high-volume air sampler (Kimoto AS-810B) and pre-combusted (450 °C, 4 h) quartz fiber filters (Pallflex 2500QAT, 20 × 25 cm), total suspended aerosol (TSP) samples ($n = 50$) were collected on weekly basis at Cape Hedo Atmosphere and Aerosol Measurement Station (CHAAMS, 26°9' N, 128°2' E) from 2009 October to 2010 October. Figure 1 shows a map of East Asia with the geographical location of Cape Hedo in Okinawa. CHAAMS is located at the northwestern part of Okinawa Island, Japan and it is surrounded by subtropical forest (Yamamoto and Kawamura, 2011) where local anthropogenic emissions are insignificant (Takami et al., 2007). Aerosol filter samples were placed in a preheated glass jar (150 mL) with a Teflon-lined screw cap and stored in darkness at -20 °C until the analysis. Field blanks were also collected at the sampling site.

2.2 Chemical analysis

OC and EC concentrations were measured using a Sunset Laboratory carbon (OC/EC) analyzer following Interagency Monitoring Protected Visual Environments (IMPROVE) thermal/optical evolution protocol (Wang et al., 2005) and presence of carbonate carbon is assumed to be negligible. A filter disk (1.5 cm² punch) was put in quartz boat inside the thermal desorption chamber and stepwise heating was applied in a helium flow at first and then after the initial ramp, helium gas was switched to He/O₂. The evolved CO₂ during the oxidation at each temperature step was measured with non-dispersive infrared (NDIR) detector system. The transmittance of light (red

Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



660 nm) through the filter punch was used for setting up OC/EC split point and thereby OC correction. The analytical errors in duplicate analysis of the filter sample were less than 8 % for OC and 5 % for EC. OC/EC concentrations reported here are corrected for the field blanks.

5 WSOC and WSTN concentrations were measured using a Shimadzu total carbon/total nitrogen analyzer (TOC-V_{CSH}) (Miyazaki et al., 2011). A filter disc (3.14 cm²) was extracted with organic-free pure water under ultrasonication for 15 min. The water extracts were filtrated on a syringe filter (Millex-GV, 0.45 μm, Millipore). Before the analysis, the extracts were acidified with 1.2 M HCl and purged with pure air to remove dissolved inorganic carbon and volatile organics. The analytical error in triplicate
10 analysis of laboratory standards was within 5 % (Miyazaki et al., 2011).

Major cations and anions were measured using an ion chromatograph (761 Compact IC, Metrohm, Switzerland). A sample filter disc (20 mm diameter) was extracted with organic-free pure water (10 mL) under ultrasonication (15 min × 2 times). The extracts
15 were filtrated using a membrane disc filter (Millex-GV, 0.45 μm, Millipore) and injected to IC for measuring major ions. Anions were separated on a SI-90 4E Shodex column (Showa Denko, Tokyo, Japan) by using a mixture of 1.8 mM Na₂CO₃ and 1.7 mM NaHCO₃ at a flow rate of 1.2 mL min⁻¹ as an eluent and 40 mM H₂SO₄ for suppressor. For cation measurements, a Metrosep C2-150 (Metrohm) column was used by using
20 a mixture of 4 mM tartaric acid and 1 mM dipicolinic acid as an eluent at a flow rate of 1.0 mL min⁻¹. The injection loop volume was 200 μL. The analytical errors in duplicate analysis of the authentic standards were within 5 %.

2.3 Estimate of organic matter and secondary organic carbon

Abundances of organic matter (OM) in the atmosphere are generally estimated by multiplying the measured OC concentrations with the conversion factor of 1.6 ± 0.2 for urban and 2.1 ± 0.2 for aged aerosols (Turpin and Lim, 2001). As mentioned above, our sampling site is located in the outflow region of East Asian aerosols and local
25

Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

anthropogenic activities are negligible. During the atmospheric transport, aerosols are subjected to aging processes to result in more oxygenated organic species (Kawamura et al., 2004; Kundu et al., 2010). Thus, it is better to take 2.1 ± 0.2 instead of 1.6 ± 0.2 for the Cape Hedo samples.

5 The contributions of the primary and secondary organic carbon (SOC) to carbonaceous aerosols are calculated by EC-tracer method. EC is used as a tracer of incomplete combustions generated from primary sources (e.g., Turpin and Huntzicker, 1991). The EC- tracer method assumes the relatively constant OC/EC ratios for given area, season and local meteorology because EC and primary OC (POC) typically have the
10 the same sources (Pavuluri et al., 2011). Thus, we can use the minimum OC/EC ratios to estimate the contribution of SOC in the atmospheric aerosol for a specific region of interest (Castro et al., 1999). This method is also applied in several atmospheric researches (Turpin and Huntzicker, 1995; Castro et al., 1999; Pavuluri et al., 2011) although it involves some degree of uncertainty. In this study, the concentrations of SOC
15 and POC were calculated by the following equations,

$$\text{POC} = \text{EC} \times (\text{OC/EC})_{\min} + k \quad (1)$$

$$\text{SOC} = \text{OC}_{\text{meas}} - \text{POC} \quad (2)$$

where $(\text{OC/EC})_{\min}$ is the observed minimum OC/EC ratio during the sampling period,
20 k is a parameter for non-combustion sources contributing to the POC which was assumed to be negligible and OC_{meas} is the measured OC concentration. The minimum OC/EC ratios of 3.5 (winter), 4.2 (spring), 5.5 (summer), and 3.5 (autumn).

2.4 Estimate of sea salt and non-sea salt component

In order to determine whether it is oceanic or continental, the sea salt (ss) and non
25 sea (nss) salt concentrations were calculated using Na as a reference element. The mass concentrations of non-sea salt component X ($M_{\text{nss-x}}$) can be estimated as follows

Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

(George et al., 2008).

$$M_{\text{nss-x}} = M_x - (X/\text{Na})_{\text{sw}} \times M_{\text{Na}},$$

where M_x and M_{Na} mean the total mass loading of X and Na, respectively. $(X/\text{Na})_{\text{sw}}$ represents the mass ratio of species X to Na in seawater. The ratios of X/Na for SO_4^{2-} , K^+ , Ca^{2+} and Mg^{2+} are 0.25, 0.037, 0.038 and 0.12, respectively, assuming that sea salt is the only source of water-soluble Na^+ (Berg and Winchester, 1978). By using above equation, the mass concentrations of sea salt and non-sea salt SO_4^{2-} , K^+ , Ca^{2+} , and Mg^{2+} are calculated.

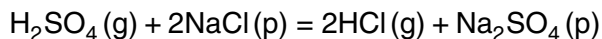
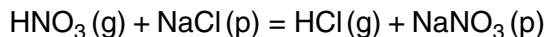
2.5 Estimate of chlorine loss

Chlorine depletion can be estimated using following formula (Yao and Zhang, 2012).

$$\text{Cl}_{\text{loss}} (\mu\text{g m}^{-3}) = 1.798 \times [\text{Na}^+]_{\text{measured}} - [\text{Cl}^-]_{\text{measured}}$$

$$\text{Cl}_{\text{loss}} (\%) = [\text{Cl}_{\text{loss}}]/1.798[\text{Na}^+]_{\text{measured}} \times 100,$$

where $[\text{Na}^+]_{\text{measured}}$ and $[\text{Cl}^-]_{\text{measured}}$ represent measured concentrations of Na^+ and Cl^- in $\mu\text{g m}^{-3}$, respectively. The mass concentration ratio of Cl^- to Na^+ in seawater is 1.798 (George et al., 2008). The following two reactions are associated with the loss process of Cl.



2.6 Backward air mass trajectory analysis

Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4) model (<http://www.arl.noaa.gov/ready/hysplit4.html>) was used to find the source regions of air

22066

masses at Okinawa during one-year campaign (Draxler and Rolph, 2003). 7 day back trajectory analysis at 500 m above the ground was performed every day using the HYSPLIT model. Figure 2 shows the 7 day air mass trajectories for winter, spring, summer and autumn seasons. In spring and winter, Cape Hedo was strongly influenced by continental air masses (Fig. 2a and b). In contrast, in summer, the site was covered with oceanic air masses (Fig. 2c) whereas in autumn it was affected by both oceanic and continental air masses (Fig. 2d). As explained previously, the sampling period is 7 days for each sample. Thus, each sample contains mixed air masses from continent and ocean.

3 Results and discussion

3.1 Aerosols mass loading

The aerosol mass loading at Okinawa ranged from 19.2 to 286 $\mu\text{g m}^{-3}$ with an average of 74.3 $\mu\text{g m}^{-3}$ during one-year observation period. Figure 3 shows the monthly averaged aerosol mass concentrations at Okinawa with error bars denoting the standard deviation. The average mass concentration shows a peak ($109 \pm 69.9 \mu\text{g m}^{-3}$) during spring season (March, April and May) and decrease towards the summer ($44 \pm 36 \mu\text{g m}^{-3}$). The westerly winds are responsible for such a high peak in spring, by uplifting the mineral dusts from the arid regions in China and Mongolia followed by a transport to the Pacific together with pollutants emitted from Chinese cities. During the Asian dust outflow, crustal elements (calcium, iron, aluminium, barium, etc.) are abundant in dust particles and loess deposits (Nishikawa et al., 2000). A good correlation between Ca and TSP ($r = 0.81$) in spring suggests that the spring aerosols are significantly influenced by dust particles from arid regions in China and Mongolia. The air mass back trajectories also demonstrated that in spring, air masses mostly originated from the arid regions of the Asian continent.

3.2 Seasonal variations of carbonaceous and nitrogenous components

Table 1 gives the concentrations of carbonaceous components with statistical summaries in the TSP samples ($n = 50$) collected from Cape Hedo, Okinawa. Their monthly variations are shown in Fig. 3. The average concentrations of OC, EC, WSOC and WSTN ranged from 0.76 to $7.12 \mu\text{g m}^{-3}$ (av. $1.78 \mu\text{g m}^{-3}$), 0.07 – $0.96 \mu\text{g m}^{-3}$ ($0.28 \mu\text{g m}^{-3}$) 0.27 – $1.9 \mu\text{g m}^{-3}$ ($0.73 \mu\text{g m}^{-3}$) and 0.07 – $3.02 \mu\text{g m}^{-3}$ ($0.58 \mu\text{g m}^{-3}$), respectively. Seasonally average concentration of OC was found highest in spring ($2.36 \mu\text{g m}^{-3}$) followed by summer ($1.79 \mu\text{g m}^{-3}$) and winter ($1.53 \mu\text{g m}^{-3}$) whereas the lowest concentration was observed in autumn ($1.42 \mu\text{g m}^{-3}$). Similarly, the highest concentrations of EC and WSOC were also found in spring ($0.41 \mu\text{g m}^{-3}$ and $0.95 \mu\text{g m}^{-3}$) followed by winter (0.37 and $0.90 \mu\text{g m}^{-3}$) whereas the lowest concentrations were found in summer (0.19 and $0.52 \mu\text{g m}^{-3}$).

OC showed higher concentration during winter in Chinese aerosols (Wang et al., 2011; Cao et al., 2007, 2003; Ho et al., 2007) because low quality coals are commonly used for heating and cooking purposes. Very high concentration of OC was reported in winter than spring in urban region of China (Wang et al., 2011). In contrast, we found higher concentration of OC in spring although most of the air parcels come from China, suggesting the additional contribution to OC from biogenic sources because biogenic emissions are significant in spring season (Pavuluri et al., 2010). The springtime maxima concentrations of OC (Fig. 4a) and WSOC (Fig. 4c) suggest that they are formed by extensive photochemical oxidation of various organic precursors including biogenic volatile organic compounds (BVOC) emitted from terrestrial plants. EC also maximized in spring followed by winter, suggesting significant contributions of EC from China through long-range atmospheric transport by westerly winds. Water-insoluble organic carbon (WIOC = OC – WSOC) showed the highest concentration in spring ($1.41 \mu\text{g m}^{-3}$) followed by summer ($1.27 \mu\text{g m}^{-3}$).

EC and WSOC show similar seasonal variations (Fig. 4b and c), suggesting that they are formed from similar sources. The average highest concentration of primary organic

Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

carbon (POC) is found in spring followed by winter whereas the higher concentration of secondary organic carbon (SOC) was found in spring and summer, as shown in Fig. 4e and f. The highest concentration of SOC was observed in March with an increase toward July. The highest average concentration of SOC in summer may be caused by photochemical oxidation of organic precursors due to the strong solar radiation.

WSTN showed higher concentration during winter ($0.86 \mu\text{g m}^{-3}$) followed by spring ($0.77 \mu\text{g m}^{-3}$) although concentration during spring months is almost constant whereas it showed lower concentration during summer and autumn (0.37 and $0.34 \mu\text{g m}^{-3}$). The higher concentration of WSTN during winter suggests that WSTN is abundantly present in polluted air. Meanwhile, concentrations of water-soluble organic nitrogen ($\text{WSN} = \text{WSTN} - \text{NO}_3\text{-N} - \text{NH}_4\text{-N}$) ranged from 0 to $2.2 \mu\text{g m}^{-3}$ (av. $0.11 \mu\text{g m}^{-3}$). WSON comprised on average 18.9% of WSTN. Marine organisms are probably the main sources of WSON. Terrestrial and marine organisms emitted nitrogenous components, which contain certain amount of WSON (Wang et al., 2013a). Marine bacteria and degraded proteins are the sources of WSON (Wedyan and Preston, 2008). Marine biota also can emit amino acids, urea and proteinaceous materials. WSON is emitted to the atmosphere by bubble bursting process in the ocean surface (Cape et al., 2011). We found higher concentration of WSON in summer (av. $0.21 \mu\text{g m}^{-3}$) followed by spring (0.13) and autumn (0.07) and lowest concentration was in winter (0.06). The summertime maximum of WSON suggests that they are emitted from marine biota.

We found that the contribution of OM to TSP is on average $6.27 \pm 3.7\%$. The highest average contribution of OM to TSP was found in summer (9.5 %) followed by autumn (5.31 %) and spring (4.85 %), and the lowest in winter (4.48 %) (Fig. 5). The contribution of WSOM to TSP was found highest in winter (2.71 %) followed by summer (2.60 %). In contrast, the contribution of WIOM to TSP became highest in summer (6.9 %), suggesting more emission of water-insoluble organic compounds probably from biological sources such as pollens (Fu et al., 2012). The average contribution of EC to TSP was found highest in winter (0.54 %), and lowest in summer (0.42 %). In this study, we found a strong correlation between the OC and EC in winter ($r = 0.93$) and spring (0.81), sug-

Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

[Back](#)

Close

Full Screen / Esc

[Printer-friendly Version](#)

Interactive Discussion



gesting that they are formed from similar sources (Turpin et al., 1991). However, such a strong relation was not found in summer (0.44) and autumn (0.22) (Fig. 6), indicating that OC and EC are derived from different sources. During winter and spring, our sampling site is significantly influenced by anthropogenic activities in East Asian cities, thus we obtained strong correlation between OC and EC. However, in summer, anthropogenic activities are negligible in Cape Hedo, hence the correlation between OC and EC is rather weak.

3.3 Seasonal variations of OC/EC and WSOC/OC ratios

OC/EC ratio has been used to study the emission and transformation characteristics of carbonaceous aerosols (Cao et al., 2003). The OC/EC ratios exceeding 2.0 have been considered to indicate the contribution of secondary organic aerosols (Cao et al., 2003). In our study, OC/EC ratios ranged from 3.5 to 21 with average of 7.6 ± 4.7 . The season-average OC/EC ratios are 4.4 (winter), 5.7 (spring), 12.5 (summer) and 7.7 (autumn). Most of the world's urban OC/EC ratios range from 1 to 4 (Turpin et al., 1991). A ratio of 4.0 is also assumed for emissions from fossil fuel combustion (Koch, 2001). During winter and spring, the average OC/EC ratios are 4.4 and 5.7, respectively. The average OC/EC ratio is still higher in spring than winter although EC showed higher concentration in spring, suggesting that Cape Hedo is influenced by biogenic volatile organic compounds (BVOCs) emitted from local and regional biogenic sources. The OC/EC ratios obtained in this study, except for summer samples, are comparable with those from Mongolia and Chinese cities (Jung et al., 2010; Cao et al., 2007). Compared to the most of the world's urban OC/EC ratios, our summer OC/EC ratio (12.5) is extremely high, suggesting an extra source of OC from the ocean and/or secondary OC via the oxidation of BVOCs is enhanced in summer. Tambunan et al. (2006) showed that the emissions of isoprene and other BVOCs in Okinawa Island maximize in summer. Generally, the emissions of BVOCs are higher in summer (Kim et al., 2005).

Figure 7a shows the monthly variation of OC/EC ratios. In November we found high OC/EC ratio. This may be caused by long-range atmospheric transport of biomass

burning plumes from South East Asia because biomass burning is very common in East Asia in autumn (Wang et al., 2013b). OC/EC ratios from biomass burning give higher values of 5 to 8 (Andreae and Merlet, 2001). We found a strong correlation ($r = 0.87$) between OC and biomass burning tracer (nss- K^+) in autumn, indicating a significant influence of biomass burning on OC. The enhanced OC/EC ratios in Cape Hedo may also be caused by the oxidation of BVOC during long-range atmospheric transport. Cao et al. (2005) showed that aerosols from residential coal combustion contain high OC/EC ratio (12). The average OC/EC ratios for winter (4.4) and spring (5.7) samples are comparable with the value (3.8) reported in 14 Chinese cities (Cao et al., 2007), indicating that our sampling site is significantly influenced by anthropogenic aerosols in winter and spring.

WSOC to OC ratio is useful to discuss the potential sources (Jung et al., 2010). Figure 7b shows the monthly averaged variation of WSOC/OC. The annual average ratio in Cape Hedo was $43 \pm 15\%$ (range, 15 to 90 %). This value is lower than the ratios reported in Mongolian aerosols (31 to 97 %, av. 53 %) (Jung et al., 2010), but similar to those from Christchurch, New Zealand (48 %, Wang et al., 2005), Sapporo, Japan (44 %, Aggarwal and Kawamura, 2008) and from 14 Chinese cities (summer 48 % and winter 40 %, Ho et al., 2007). However, lower WSOC/OC ratios were reported from Gosan, Korea (30 %) during the ABC campaign (Miyazaki et al., 2007), from New Delhi, India (25 %) in nighttime (Miyazaki et al., 2009), and from Tokyo (summer 20 % and winter 35 %, Miyazaki et al., 2006). Mayol-Bracero et al. (2002) found higher WSOC/OC ratios (45–75 %) in biomass burning aerosols over Amazonia. The smoldering combustion of biomass produces WSOC abundantly (Andreae et al., 1996). The WSOC/OC ratio in Okinawa suggests that significant fractions of organic aerosols were derived from atmospheric oxidation of the aerosols derived from biomass burning and fossil fuel combustion.

In contrast, Kawamura et al. (2010) reported the increased ratios of WSOC/TC in the Arctic atmosphere after polar sunrise due to extensive photochemical oxidation of organic precursors. The enhanced WSOC/OC ratios (81 % on average) were

**Carbonaceous and
nitrogenous
components**B. Kunwar and
K. Kawamura

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

also reported for summit Greenland aerosol (Hagler et al., 2007). We found highest WSOC/OC ratios in winter (60 %) followed by spring (45 %) and autumn (41 %). The lowest WSOC/OC ratio was observed in summer (28 %). The lower WSOC/OC ratio may be caused by the sea-to-air emissions of water-insoluble organic compounds that are produced by marine phytoplankton, because the summertime air masses are derived from the oceanic region (Fig. 2c). The highest ratios in winter (60 %) may be due to the enhanced oxidation of primary organic compounds during long-range atmospheric transport and/or gas-to-particle conversion of anthropogenic semi-volatile polar compounds (Kawamura et al., 2010).

Being different from this study, the previous studies in East Asia often showed the wintertime maximum of OC. In Table 3, we compare our OC/EC data with available data from East Asia. The annual average concentration of OC in Cape Hedo is $1.78 \mu\text{g m}^{-3}$, which is about 19 times less than those reported in Mongolia during winter (Jung et al., 2010), 3 to 18 times less than those of Chinese cities (Cao et al., 2007) and approximately 8 times less than those of the Pearl Delta region, China (Cao et al., 2003), Kaohsiung, Taiwan (Lin and Tai, 2001) and Seoul, Korea (Park et al., 2002). The concentration of OC in Cape Hedo is approximately 2 times lower than that of Jeju Island (Lee et al., 2001). The Asian outflow is also important in Jeju Island. As the distance from the Asian cities increases, concentration of OC decreases. Hence, we can say that the concentrations of OC decrease during long-range atmospheric transport via atmospheric dilution and/or dry and wet scavenging. The major sources of carbonaceous components include industrial and vehicular emissions, fossil fuel combustions and biomass burnings in East Asia (Wang et al., 2006).

3.4 Seasonal variations of inorganic species

The statistical summaries of water-soluble ionic species in the marine aerosol samples from Okinawa are given in Table 2. Their seasonal variations of cations and anions are shown in Fig. 8. The dominant cation in our samples was Na^+ followed by Mg^{2+} and Ca^{2+} . The annual average concentrations of Na^+ , Mg^{2+} and Ca^{2+} are 5.78, 0.71 and

0.66 $\mu\text{g m}^{-3}$, respectively, whose relative contributions to total aerosol mass are 9.3, 1.1 and 0.8 %, respectively. The dominant anion was Cl^- followed by SO_4^{2-} and NO_3^- . Their annual average concentrations are 10.8, 2.4 and 1.6 $\mu\text{g m}^{-3}$, respectively, whose relative contributions to total aerosol mass were 17.1, 3.7 and 2.5 %, respectively. Similarly, the contributions of Na^+ and Cl^- to total ions were on average 26.2 % and 47 %, respectively. Average concentration of Cl^- is 6 times higher than that of OC, suggesting that inorganic loading is very important throughout the whole campaign. MSA^- , a tracer of marine biogenic sources, showed high concentration in spring. This is likely because the air parcels have originated in East Asia and travelled over the urban region, coastal and marine atmosphere before reaching the sampling site and intermixed with coastal and marine aerosols. We found a good positive correlation ($r = 0.81$) between OC and MSA^- , suggesting that some fraction of OC originated from marine sources. Similarly, nss-K^+ , a tracer of biomass burning, showed a good correlation with OC in winter (0.72) and spring (0.65). The stronger correlation in winter than spring suggests that biomass-burning contribution is higher in winter than spring. Most cations and anions showed the highest concentrations in winter months (Fig. 8) and the lowest in summer. Ca^{2+} , a tracer of crustal material, maximized in spring (Fig. 8d).

The relative abundances of NO_3^- , SO_4^{2-} , NH_4^+ in TSP were found to be highest in winter. These results suggest that contributions from fossil fuel combustion, industrial emission, and biomass burning are significant (Kundu et al., 2010) as well as animal excreta (Pavuluri et al., 2011). In contrast, relative abundances of Ca^{2+} in TSP maximized in spring, suggesting a significant influence from crustal dust during spring.

3.4.1 Ion balance

Ion balance calculation is used to evaluate the ion deficit between cations and anions in aerosols (Pavuluri et al., 2011). The following equations are used to calculate the

Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

charge balance between cations and anions.

$$\text{Cation equivalents} = [\text{Na}^+]/23 + [\text{NH}_4^+]/18 + [\text{K}^+]/39 + 2 \times [\text{Mg}^{2+}]/24 + 2 \times [\text{Ca}^{2+}]/40$$

$$\begin{aligned} \text{Anion equivalents} = & 2 \times [\text{SO}_4^{2-}]/96 + [\text{NO}_3^-]/62.04 + [\text{Cl}^-]/35.5 + [\text{Br}^-]/79.9 \\ & + [\text{MSA}^-]/95.1 + 3 \times [\text{PO}_4^{3-}]/94.8 \end{aligned}$$

Average equivalent ratios of total cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+}) to total anions (SO_4^{2-} , NO_3^- , Cl^- , Br^- , MSA^- and PO_4^{3-}) were 0.96 with standard deviation of 0.14 ($n = 50$) as shown in Fig. 9. The slope (0.87) of less than 1 indicates that almost all of the ions had been quantified, although CO_3^{2-} , HCO_3^- , H^+ and organic anions were not determined.

Because the concentration of the ions emitted from the same source or similar reaction pathway should show a good correlation, correlation analyses among the ions would provide indication for their sources. Tables 3, 4, 5, and 6 show the results of correlation analyses of major ions for winter, spring, summer and autumn, respectively. For all the seasons there is a good correlation between Na^+ and Cl^- , indicating that they are derived from the sea spray. During winter, there are strong correlations among Na^+ , K^+ , Mg^{2+} and SO_4^{2-} , further suggesting that K^+ , Mg^{2+} and SO_4^{2-} are of marine origin. NO_3^- , a tracer of anthropogenic source, strongly correlates with NH_4^+ , K^+ , SO_4^{2-} and weakly correlates with Mg^{2+} and Ca^{2+} , suggesting that they are also derived from anthropogenic sources. However, NO_3^- weakly correlated with Mg^{2+} and Ca^{2+} . Hence, K^+ , SO_4^{2-} , Mg^{2+} , and Ca^{2+} should have dual sources, i.e., marine and anthropogenic origin; a point to be discussed in Sect. 3.4.3.

In spring, Na^+ showed a good correlation with K^+ and Mg^{2+} , suggesting that they are formed from same sources or similar reaction pathway. It is of interest to note that there isn't any correlation between Na^+ and NO_3^- , suggesting that NO_3^- is derived from the continental source via a long-range atmospheric transport. However, NO_3^- showed good correlation with K^+ . Ca^{2+} , a tracer of soil dust, showed a good correlation with K^+ ,

Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



indicating that they are both formed from similar sources. It is very meaningful to note that there is no correlation between Ca^{2+} and Na^+ , indicating that the oceanic source of Ca^{2+} is insignificant in spring.

In summer, Na^+ has a strong correlation with Mg^{2+} , indicating a marine source. Similarly Mg^{2+} and Cl^- showed a strong correlation with calcium, suggesting that Ca^{2+} is derived from marine sources in summer. Further, NO_3^- showed a strong correlation with SO_4^{2-} , suggesting that they are formed from similar reaction pathways. Both NO_3^- and SO_4^{2-} come from secondary formation in the atmosphere (Pavuluri et al., 2011).

3.4.2 Sea salt-derived aerosols

Sea salt is the major component in the marine and coastal aerosols (George et al., 2008; Prospero, 2002). Na^+ is used as a tracer to find out the contributions of sea salt to aerosols. The equivalent ratio of Cl^- to Na^+ is 1.16 in seawater. We estimated equivalent ratios of Cl^-/Na^+ in each samples and compared with seawater. Figure 10 presents scatter plots of Na^+ and Cl^- concentration for different seasons. Throughout the year, only few data points are found to locate below the sea water line, indicating that the loss of Cl was insignificant except for spring samples. Cl loss has been observed in many coastal regions and open oceans (Meinert and Winchester, 1977; George et al., 2008; Yao and Zhang, 2012). In some spring samples, estimated chlorine loss was upto 50 %, indicating that vigorous reaction occurs between gaseous HNO_3 and H_2SO_4 , and NaCl to emit gaseous HCl (McInnes et al., 1994).

3.4.3 Sea salt and non-sea salt ions

Ions such as SO_4^{2-} , K^+ , Ca^{2+} , and Mg^{2+} have multiple sources, i.e., oceanic (sea salt: ss) and continental (non sea salt: nss). Besides this, SO_4^{2-} has another oceanic, but nss-source generated by the oxidation of dimethyl sulphide (DMS) that is emitted from the phytoplankton in the sea surface (George et al., 2008; Savoie et al., 1994). However, its contribution is less than 6 % of total SO_4^{2-} in the remote oceanic environment

Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



of the Northern Hemisphere (Savoie et al., 1994). Figure 11 shows the monthly variation of ss and nss species. ss-Mg²⁺ and K⁺ dominate over the nss forms. Interestingly, nss-Ca²⁺ dominated over the ss-Ca²⁺ until May with maxima in March and April while after June it was replaced by the ss-Ca²⁺ (Fig. 11b). Major fraction of Ca²⁺ should be derived from Asian dusts in winter and spring (Kawamura et al., 2004). The percentage of nss-Ca²⁺ to total Ca²⁺ was found highest in winter (62 %) to spring (71.5 %) and decreases towards summer (31.1 %). In spring, the air masses uplift the crustal dust in East Asia and transport over the sampling site. We found strong correlation between nss-Ca²⁺ and TSP ($r = 0.80$) in spring, suggesting that crustal dust from East Asia is the main source of TSP. Similar strong correlation was found between nss-Ca²⁺ and TSP in Gosan site, Jeju Island (Kawamura et al., 2004). However, for the rest of the year, we did not find any good correlation between nss-Ca²⁺ and TSP.

Similarly, the contribution of nss-K⁺ to total K⁺ was found highest in winter (40.6 %) to spring (46.2 %) with a decrease toward summer (37.1 %). K⁺ is a tracer of biomass burning (Kundu et al., 2010) whereas EC is a tracer of incomplete combustions of fossil fuel and biomass burning. We found very strong relationship between the nss-K⁺ and EC ($r = 0.80$) (Fig. 12), indicating that the major fraction of EC is formed by the incomplete biomass burning. The contribution of nss-Mg²⁺ to total Mg²⁺ increased in winter (30.9 %) to spring (35.8 %) and decreased in summer (27.4 %). Because Mg is also found in the crustal dust (Wang et al., 2010), this study again indicates that our sampling site is strongly influenced by crustal elements in spring. Although all the air masses come from the ocean in summer, the loading of sea salt components maximized in winter and spring and became lowest in summer. In winter and spring when westerlies became strong, continental air masses that stayed over the ocean for few days were mixed with marine aerosols according to the backward trajectory analysis.

3.4.4 Anthropogenic aerosols and ionic composition

nss-SO₄²⁻ in the atmosphere is derived from many sources. It can originate from mineral dusts from the desert/arid region, and combustion of fossil fuels. We found

the highest concentration of nss-SO_4^{2-} in winter (av. $1.74 \mu\text{g m}^{-3}$) followed by spring ($1.38 \mu\text{g m}^{-3}$) and the lowest in summer ($0.51 \mu\text{g m}^{-3}$). The higher concentration of nss-SO_4^{2-} in winter and spring suggest that the air quality of Cape Hedo is strongly influenced by fossil fuel combustions and industrial emissions in East Asia via a long-range atmospheric transport. NO_3^- is a tracer of anthropogenic activities and is derived from coal combustions, biomass burning and vehicular emissions (Kundu et al., 2010). We found a positive correlation between NO_3^- and biomass burning tracer (nss-K^+) ($r = 0.65$) in winter, suggesting that NO_3^- is associated with biomass burning. To identify the sources of nitrogenous components, we used $\text{NH}_4\text{-N/WSTN}$ and $\text{NO}_3\text{-N/WSTN}$ ratios. We found that $\text{NH}_4\text{-N/WSTN}$ ratio maximized in winter (0.56) followed by spring (0.42), suggesting that biomass burning is important sources in winter. Similarly, $\text{NO}_3\text{-N/WSTN}$ showed higher ratio in spring (0.51) followed by winter (0.44) and autumn (0.18). Lowest ratios for $\text{NH}_4\text{-N/WSTN}$ (0.07) and $\text{NO}_3\text{-N/WSTN}$ (0.11) were observed in summer due to the lower chance for the continental outflow.

3.4.5 Neutralization factor and ionic composition

The acid neutralization capacity of desired cation is estimated by neutralization factor (NF). NO_3^- and SO_4^{2-} , which are formed by secondary oxidation of NO , NO_2 and SO_2 , are major acid-producing anions, whereas Ca^{2+} , Mg^{2+} , NH_4^+ and K^+ are the cations that neutralize acids. The role of Cl^- in acid production is negligible because Cl^- mainly comes from ocean as a sea salt. We calculated NF using following formula (Keene et al., 1986).

$$\text{NF}(\text{Ca}^{2+}) = [\text{nss-Ca}^{2+}]/[\text{NO}_3^-] + [\text{nss-SO}_4^{2-}]$$

$$\text{NF}(\text{Mg}^{2+}) = [\text{nss-Mg}^{2+}]/[\text{NO}_3^-] + [\text{nss-SO}_4^{2-}]$$

$$\text{NF}(\text{K}^+) = [\text{nss-K}^+]/[\text{NO}_3^-] + [\text{nss-SO}_4^{2-}]$$

$$\text{NF}(\text{NH}_4^+) = [\text{NH}_4^+]/[\text{NO}_3^-] + [\text{nss-SO}_4^{2-}]$$

Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



We found that NH_4^+ plays a major role in the neutralization of acidic species. The order of NF is $\text{NH}_4^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+}$. The NF of NH_4^+ and Ca^{2+} were found highest in winter followed by spring, suggesting that all the acidic species were neutralized with CaCO_3 , MgCO_3 and NH_4^+ . Ca^{2+} and SO_4^{2-} show positive correlation ($r = 0.77$), suggesting that these ions mainly exist as CaSO_4 . The mean Ca^{2+} to SO_4^{2-} mass ratio in our samples is 0.53, being similar to the ionic mass ratio of 0.41 in CaSO_4 . NH_4^+ and SO_4^{2-} showed a good correlation ($r = 0.87$) with the mean NH_4^+ to SO_4^{2-} ratio of 0.2, which lies in between the NH_4^+ to SO_4^{2-} mass ratios (0.37) and NH_4^+ to HSO_4^- mass ratio (0.18). This result indicates that the NH_4^+ and SO_4^{2-} are in the form of $(\text{NH}_4)_2\text{SO}_4$ or NH_4HSO_4 and/or the combination of the two forms. Among these two forms, the dominant composition may be NH_4HSO_4 because the measured mass ratios (0.2) is closer to the mass ratio of NH_4HSO_4 rather than that of $(\text{NH}_4)_2\text{SO}_4$.

4 Summary and conclusions

We conducted one-year observation of chemical compositions in aerosol (TSP) samples collected in Okinawa Island, which is located at an outflow region of Asian dusts. The highest aerosol mass loading and highest concentration of nss- Ca^{2+} in spring are caused by strong westerly winds, which uplift the mineral particles from the arid regions in China and Mongolia and then transport over the Pacific.

In contrast to East Asia (wintertime maximum), we found higher concentration of OC in spring (av. $2.36 \mu\text{g m}^{-3}$) than winter (av. $1.53 \mu\text{g m}^{-3}$). Higher concentration of OC was obtained during growing seasons; spring and summer ($1.79 \mu\text{g m}^{-3}$). We also determined WSTN and WSON. Higher concentrations of WSTN were found in winter and higher WSON concentrations were found in summer, suggesting more emissions of water-soluble organic nitrogen from the ocean.

Springtime maxima of OC/EC ratios, MSA^- and correlation coefficients of OC and EC ($r = 0.81$), and MSA^- (0.81) showed that the importance of terrestrial and marine

Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



biogenic sources as well as anthropogenic sources in spring although the contribution from biogenic source is less significant. Similarly, moderate positive correlation between OC and nss-K^+ were found in both winter ($r = 0.72$) and spring (0.65), suggesting that biomass burning contribution is higher in winter season followed by spring.

We found an extremely higher OC/EC ratio and strong correlation between OC and MSA^- (0.71) in summer, further suggesting a strong biogenic emission of OC followed by photochemical formation of SOC in hot season. The highest SOC concentration in July suggests the oxidation of organic compounds under strong solar radiation. Very high WSOC/OC ratios (0.6) in winter suggest the oxidation of anthropogenic primary organic compounds emitted in East Asian countries is still active even in cold season during long-range atmospheric transport, followed by the subsequent gas-to-particle conversion.

The high concentrations of NO_3^- and SO_4^{2-} and high ratios of $\text{NH}_4\text{-N/WSTN}$ in winter suggest that Cape Hedo is strongly influenced by vehicular emission, biomass burning, industrial emission and coal combustion in East Asia. We found a strong correlation between the biomass burning tracer (nss-K^-) and EC ($r = 0.80$), suggesting that major fraction of EC is formed from the incomplete combustion of biomass.

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Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

- Jaffe, D., Prestbo, E., Swartzendruber, P., Penzias, P. W., Kato, S., Takami, A., Hatakeyama, S., and Kajii, Y.: Export of atmospheric mercury from Asia, *Atmos. Environ.*, 39, 3029–3038, 2005.
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Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura**Table 1.** Seasonal variations of mass concentrations of different organic components in aerosols from Cape Hedo, Okinawa.

Components	Concentration in ($\mu\text{g m}^{-3}$)							
	Winter		Spring		Summer		Autumn	
	Range	AV \pm SD	Range	AV \pm SD	Range	AV \pm SD	Range	AV \pm SD
OC	0.83–2.49	1.53 \pm 0.51	1.04–7.12	2.36 \pm 1.71	0.84–3.01	1.79 \pm 0.56	0.76–2.52	1.42 \pm 0.48
EC	0.14–0.59	0.70 \pm 0.51	0.19–0.96	0.41 \pm 0.24	0.07–0.54	0.19 \pm 0.14	0.09–0.38	0.20 \pm 0.09
WSOC	0.45–1.37	0.9 \pm 0.29	0.53–1.88	0.95 \pm 0.40	0.27–1.90	0.52 \pm 0.42	0.29–0.70	0.55 \pm 0.18
WIOC	0.08–1.12	0.63 \pm 0.25	0.51–5.24	1.41 \pm 1.34	0.57–2.29	1.27 \pm 0.41	0.37–1.84	0.89 \pm 0.51
OM	1.66–4.98	3.05 \pm 1.02	2.07–14.2	4.72 \pm 3.42	1.68–6.02	3.59 \pm 1.12	1.52–5.04	2.85 \pm 0.95
WSOM	0.9–2.74	1.80 \pm 0.58	1.06–3.76	1.91 \pm 0.81	0.54–3.80	1.05 \pm 0.85	0.57–1.81	1.12 \pm 0.41
WIOM	0.16–2.24	1.26 \pm 0.51	1.02–10.4	2.82 \pm 2.69	1.14–4.59	2.54 \pm 0.82	0.75–3.69	1.73 \pm 0.81
POC	0.27–1.18	0.72 \pm 0.30	0.38–1.92	0.82 \pm 0.48	0.14–1.08	0.37 \pm 0.28	0.17–0.80	0.42 \pm 0.23
SOC	0.39–1.31	0.81 \pm 0.23	0.65–5.40	1.54 \pm 1.29	0.70–2.18	1.42 \pm 0.37	0.46–2.08	1.01 \pm 0.42

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura**Table 2.** Seasonal variations of ionic species in aerosols from Cape Hedo, Okinawa.

Ions	Concentration ($\mu\text{g m}^{-3}$)							
	Winter		Spring		Summer		Autumn	
	Range	AV \pm SD	Range	AV \pm SD	Range	AV \pm SD	Range	AV \pm SD
Anions								
F ⁻	0.00–0.01	BDL \pm BDL	0.00–0.01	BDL \pm BDL	0.00–0.01	BDL \pm BDL	0.00–0.01	BDL \pm BDL
MSA ⁻	0.01–0.05	0.03 \pm 0.01	0.01–0.05	0.4 \pm 0.02	0.01–0.05	0.02 \pm 0.01	0.01–0.05	0.02 \pm 0.02
Cl ⁻	4.63–26.2	13.9 \pm 6.18	4.63–26.2	12.7 \pm 9.89	3.31–12.1	6.95 \pm 2.84	2.84–26.2	10.8 \pm 8.13
NO ₂ ⁻	0.00–0.00	0.00 \pm 0.00	0.00–0.00	0.00 \pm 0.00	0.00–0.00	0.00 \pm 0.00	0.00–0.00	0.00 \pm 0.00
Br ⁻	0.00–0.01	0.00 \pm 0.00	0.00–0.01	0.00 \pm 0.00	0.00–0.02	0.01 \pm BDL	0.00–0.02	.01 \pm BDL
NO ₃ ⁻	0.86–3.9	2.11 \pm 0.93	0.86–3.9	1.95 \pm 1.42	0.17–3.84	0.79 \pm 0.97	0.17–3.9	1.81 \pm 1.35
PO ₃ ⁻	0.00–0.00	0.00 \pm 0.00	0.00–0.01	BDL \pm BDL	0.00–0.01	BDL \pm BDL	0.00–0.01	BDL \pm BDL
SO ₄ ²⁻	2.34–5.04	3.63 \pm 0.82	0.01–5.04	2.37 \pm 2.04	0.46–5.96	1.29 \pm 1.47	0.01–5.96	2.54 \pm 1.96
Total	7.84–35.2	19.7 \pm 7.94	0.01–25.6	8.32 \pm 7.15	1.67–12.0	4.14 \pm 2.89	1.23–15.0	6.9 \pm 4.08
Cations								
Na ⁺	4.64–12.0	7.57 \pm 2.4	0.01–12.0	5.34 \pm 4.68	2.26–6.35	3.58 \pm 1.3	0.01–12.0	5.19 \pm 3.85
NH ₄ ⁺	0.23–1.51	0.79 \pm 0.41	0.2–1.51	0.74 \pm 0.48	0.00–0.15	0.02 \pm 0.05	0.00–1.51	0.51 \pm 0.53
K ⁺	0.2–0.68	0.44 \pm 0.16	0.01–0.68	0.31 \pm 0.23	0.12–0.43	0.21 \pm 0.09	0.01–0.68	0.3 \pm 0.22
Ca ²⁺	0.3–1.35	0.7 \pm 0.28	0.00–1.35	0.62 \pm 0.49	0.09–0.37	0.18 \pm 0.09	0.00–1.35	0.48 \pm 0.45
Mg ²⁺	0.48–1.48	0.92 \pm 0.32	0.00–1.48	0.6 \pm 0.48	0.24–0.66	0.41 \pm 0.14	0.00–1.48	0.6 \pm 0.48
Total	5.85–17.0	10.4 \pm 3.57	10.3–44.7	20.4 \pm 10.7	6.26–18.2	10.1 \pm 3.82	3.72–35.8	17.7 \pm 9.17

Note: BDL means below detection limit ($0.001 \mu\text{g m}^{-3}$).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura**Table 3.** OC and EC concentrations and OC to EC mass ratios in atmospheric aerosols from different locations in East Asia.

Location	Period	Size	Concentrations ($\mu\text{g m}^{-3}$)		OC/EC	References
			OC	EC		
Mongolia	Nov 2007–Jan 2008	PM _{2.5}	31.8	6.7	4.7	Jung et al. (2010)
Beijing	Winter	PM _{2.5}	27.2	7.1	3.7	Cao et al. (2007)
Beijing	Summer	PM _{2.5}	17.2	4.6	4.4	Cao et al. (2007)
Jinchang	Winter	PM _{2.5}	23	5	4.5	Cao et al. (2007)
Jinchang	Summer	PM _{2.5}	8.1	1.6	5.9	Cao et al. (2007)
Gangzhou	Winter	PM _{2.5}	41.1	14.5	2.8	Cao et al. (2007)
Gangzhou	Summer	PM _{2.5}	10.6	3.2	3.6	Cao et al. (2007)
Hong Kong	Winter	PM _{2.5}	11.2	5.8	2	Cao et al. (2007)
Hong Kong	Summer	PM ₁₀	7.3	3.6	2.1	Cao et al. (2007)
Hong Kong, PU, China	Nov–Feb 2000–2001	PM _{2.5}	12.0	6.86	> 2	Ho et al. (2003)
Hong Kong, KT, China	Nov–Feb 2000–2001	PM _{2.5}	10.1	5.05	> 2	Ho et al. (2003)
Hong Kong, HT, China	Nov–Feb 2000–2001	PM _{2.5}	5.52	1.36	> 3	Ho et al. (2003)
PRD regions., China	Jan–Feb 2002	PM _{2.5}	14.7	6.1	2.4	Cao et al. (2003)
Taiwan	Nov 1998–Apr 1999	PM ₁₀	14.5	6.1	2.4	Lin and Tai (2001)
Seoul, Korea	27 Nov–9 Dec 1999	PM _{2.5}	15.2	7.3	2.2	Park et al. (2002)
Gosan (Jeju Island)	Dec 1996	PM _{2.5}	4.41	0.43	10	Lee et al. (2001)
Gosan (Jeju Island)	Mar 1996	PM _{2.5}	2.97	0.32	9.3	Lee et al. (2001)
Gosan (Jeju Island)	Jan 1997	PM _{2.5}	3.31	0.23	14	Lee et al. (2001)
Gosan (Jeju Island)	Sep 1997	PM _{2.5}	3.56	0.42	8.5	Lee et al. (2001)
Gosan (Jeju Island)	Dec 1997	PM _{2.5}	2.6	0.34	7.7	Lee et al. (2001)
Cape Hedo, Okinawa	Oct 2009–Oct 2010	TSP	1.78	0.28	7.7	This Study

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Carbonaceous and
nitrogenous
components**B. Kunwar and
K. Kawamura**Table 4.** Correlation coefficients (r) of major ions in winter aerosols from Cape Hedo, Okinawa.

Ions	Na ⁺	NH ₄ ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl [−]	NO ₃ [−]	SO ₄ ^{2−}
Na ⁺	1							
NH ₄ ⁺	0.54	1						
K ⁺	0.88	0.84	1					
Ca ²⁺	0.41	0.39	0.48	1				
Mg ²⁺	0.98	0.59	0.91	0.49	1			
Cl [−]	0.97	0.44	0.82	0.45	0.96	1		
NO ₃ [−]	0.48	0.85	0.74	0.51	0.55	0.35	1	
SO ₄ ^{2−}	0.77	0.85	0.89	0.46	0.79	0.64	0.83	1

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura**Table 5.** Correlation coefficients (r) of major ions in spring aerosols from Cape Hedo, Okinawa.

	Na ⁺	NH ₄ ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl [−]	NO ₃ [−]	SO ₄ ^{2−}
Na ⁺	1							
NH ₄ ⁺	−0.34	1						
K ⁺	0.87	−0.28	1					
Ca ²⁺	0.31	−0.38	0.62	1				
Mg ²⁺	0.94	−0.33	0.96	0.57	1			
Cl [−]	0.91	−0.23	0.85	0.38	0.87	1		
NO ₃ [−]	0.47	−0.46	0.51	0.23	0.42	0.51	1	
SO ₄ ^{2−}	0.28	−0.21	0.63	0.85	0.50	0.48	0.40	1

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura**Table 6.** Correlation coefficients (r) of major ions in summer aerosols from Cape Hedo, Okinawa.

	Na ⁺	NH ₄ ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
Na ⁺	1							
NH ₄ ⁺	0.22	1						
K ⁺	0.38	0.12	1					
Ca ²⁺	0.45	0.05	0.92	1				
Mg ²⁺	0.88	0.14	0.74	0.75	1			
Cl ⁻	0.97	0.26	0.30	0.32	0.83	1		
NO ₃ ⁻	-0.20	0.06	0.76	0.72	0.22	-0.31	1	
SO ₄ ²⁻	0.00	-0.10	0.85	0.86	0.39	-0.13	0.92	1

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura**Table 7.** Correlation coefficients (r) of major ions in autumn aerosols from Cape Hedo, Okinawa.

	Na ⁺	NH ₄ ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl [−]	NO ₃ [−]	SO ₄ ^{2−}
Na ⁺	1							
NH ₄ ⁺	0.03	1						
K ⁺	0.93	0.12	1					
Ca ²⁺	0.71	0.32	0.86	1				
Mg ²⁺	0.98	0.12	0.97	0.80	1			
Cl [−]	0.96	−0.10	0.85	0.58	0.92	1		
NO ₃ [−]	0.43	0.70	0.56	0.69	0.52	0.20	1	
SO ₄ ^{2−}	0.74	0.44	0.84	0.89	0.81	0.54	0.83	1

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Carbonaceous and
nitrogenous
components**

B. Kunwar and
K. Kawamura

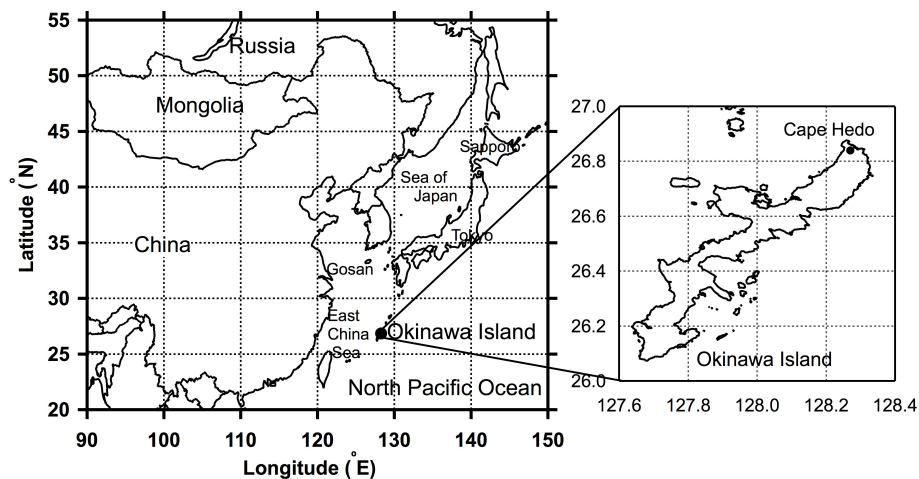


Fig. 1. Map showing the geographical region of Cape Hedo, Okinawa, where sampling was performed.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

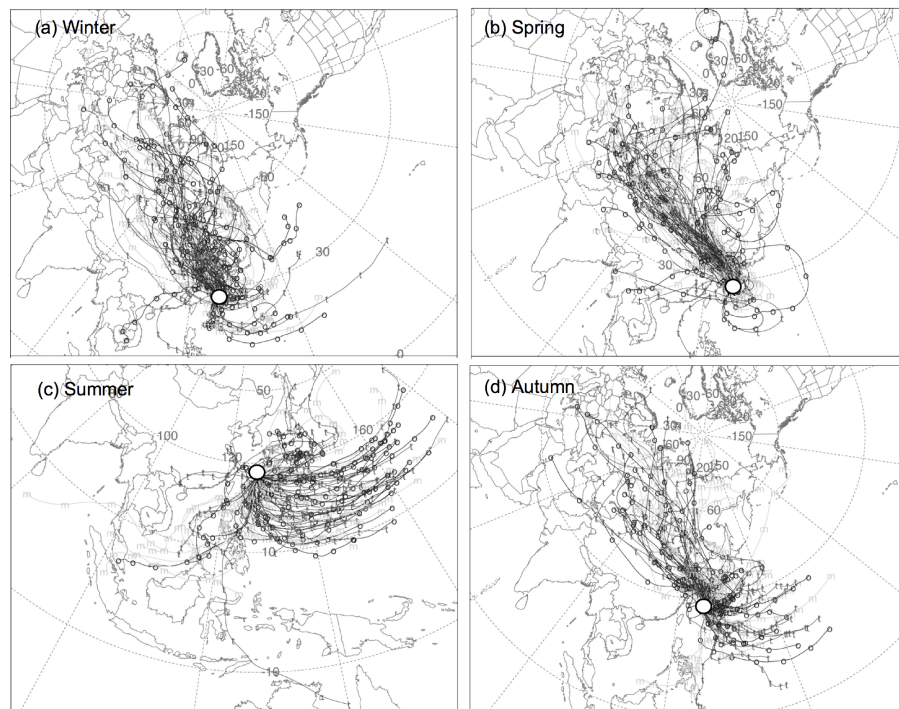
**Carbonaceous and
nitrogenous
components**B. Kunwar and
K. Kawamura

Fig. 2. Seven-day backward trajectory analysis for four seasons; **(a)** winter (December, January and February), **(b)** spring (March, April and May), **(c)** summer (June, July and August), and **(d)** autumn (September, October and November). Backward trajectories at 500 m above ground level were drawn with the NOAA HYSPLIT model.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Carbonaceous and
nitrogenous
components**

B. Kunwar and
K. Kawamura

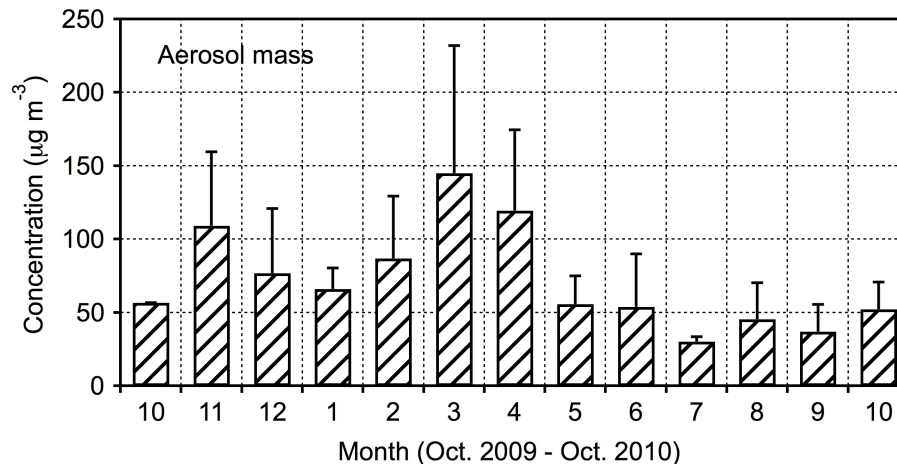


Fig. 3. Average monthly variation of aerosol mass loading in ambient aerosols collected in Cape Hedo, Okinawa.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Carbonaceous and nitrogenous components

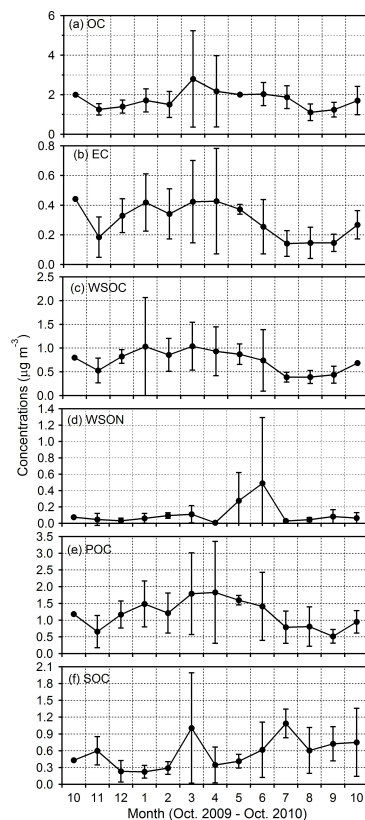
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Fig. 4. Seasonal variation in concentrations of **(a)** organic carbon (OC), **(b)** elemental carbon (EC), **(c)** water soluble organic carbon (WSOC), **(d)** water soluble organic nitrogen (WSON), **(e)** primary organic carbon (POC), and **(f)** secondary organic carbon (SOC) in ambient aerosols collected in Cape Hedo, Okinawa.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

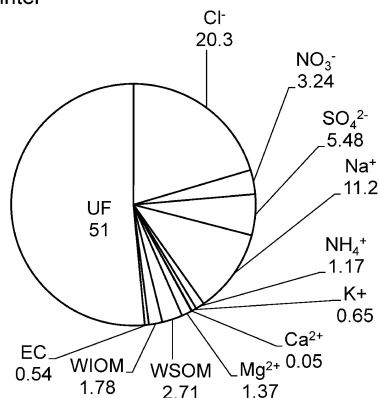
Printer-friendly Version

Interactive Discussion

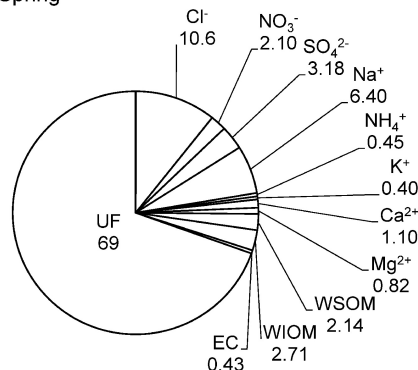
Carbonaceous and nitrogenous components

B. Kunwar and
K. Kawamura

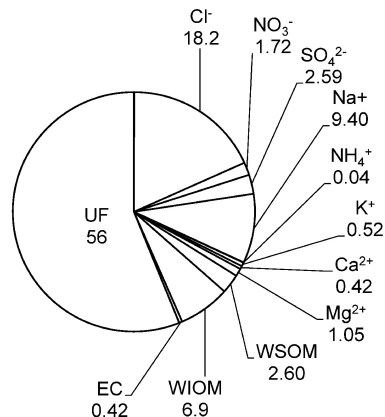
(a) Winter



(b) Spring



(c) Summer



(d) Autumn

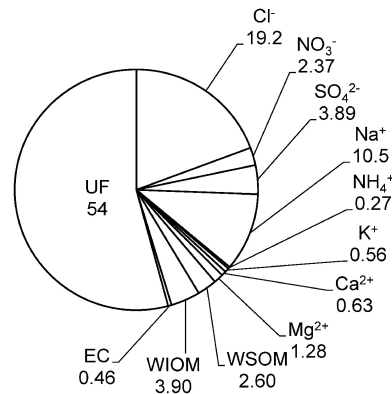


Fig. 5. Average relative abundances (%) of water-soluble organic matter (WSOM), water insoluble organic matter (WIOM), elemental carbon (EC), and major ions in ambient aerosols collected in Cape Hedo, Okinawa. UF is unanalysed fraction.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

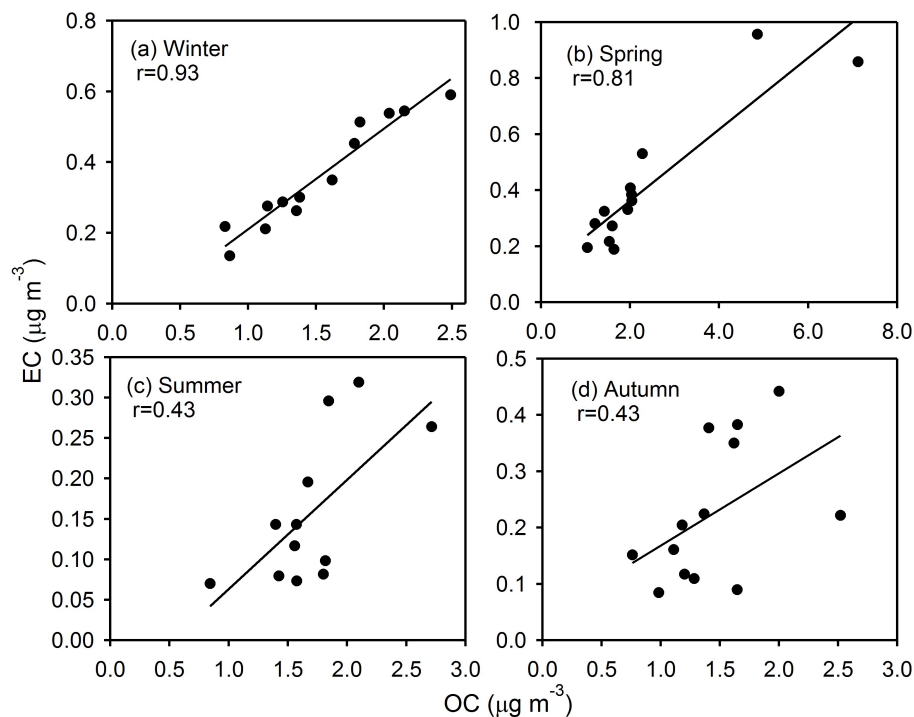
**Carbonaceous and
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Fig. 6. Correlation analysis between elemental carbon (EC) and organic carbon (OC) in ambient aerosol samples collected from Cape Hedo Okinawa.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Carbonaceous and nitrogenous components

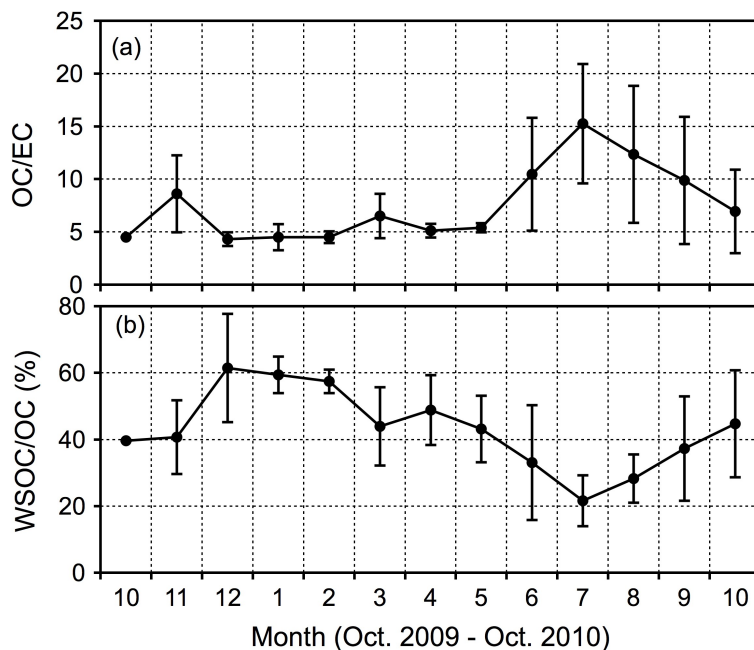
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Fig. 7. Monthly average variations of concentration ratios of **(a)** organic carbon (OC) to elemental carbon (EC), and **(b)** water soluble organic carbon (WSOC) to organic carbon (OC) in ambient aerosols collected from Cape Hedo Okinawa during October 2009 to October 2010.

Carbonaceous and nitrogenous components

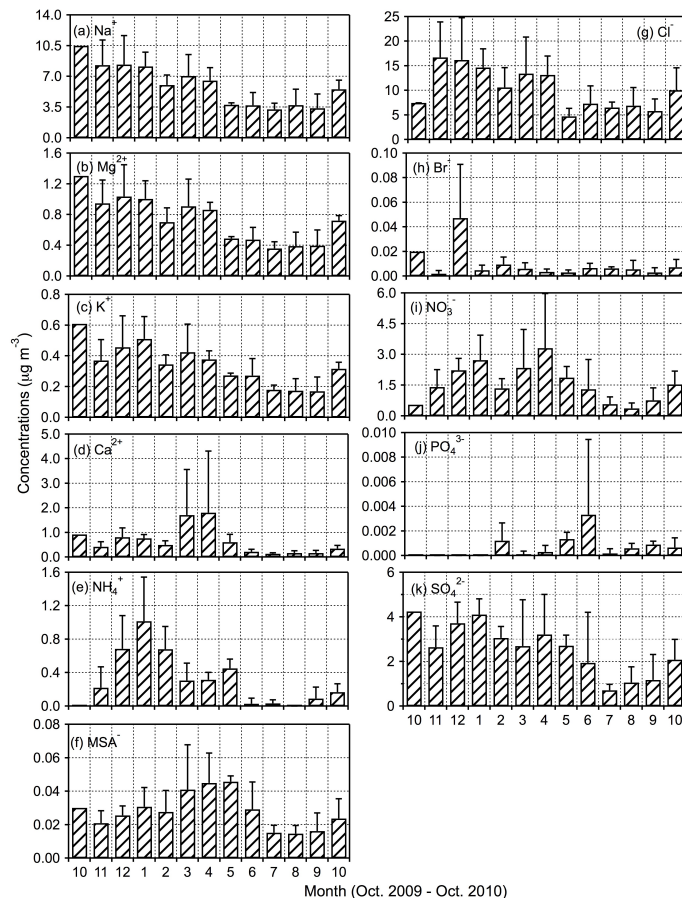
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Fig. 8. Monthly average variations in concentrations of major ions **(a)** Na^+ , **(b)** Mg^{2+} , **(c)** K^+ , **(d)** Ca^{2+} , **(e)** NH_4^+ , **(f)** MSA^- , **(g)** Cl^- , **(h)** Br^- , **(i)** NO_3^- , **(j)** PO_4^{3-} , and **(k)** SO_4^{2-} in the ambient aerosols collected from Cape Hedo, Okinawa.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

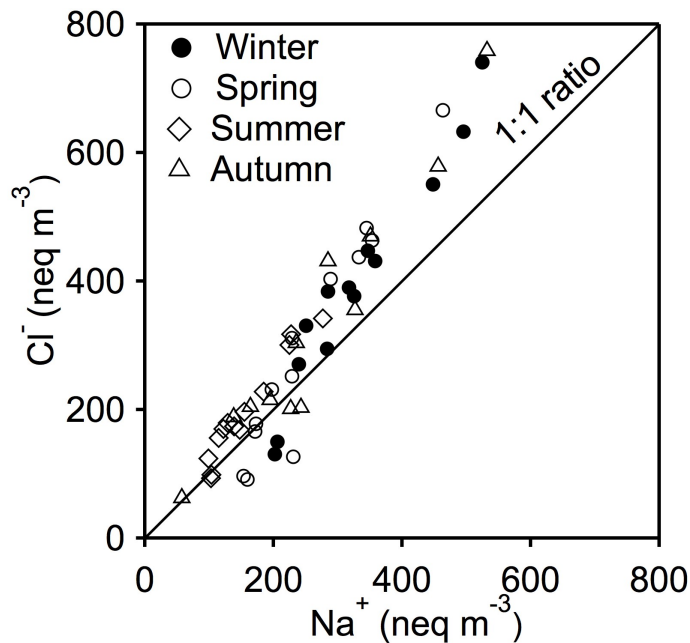
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nitrogenous
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Fig. 10. Scatter plot showing variation of Na^+ and Cl^- with respect to sea water line in ambient aerosols collected from Cape Hedo, Okinawa.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Carbonaceous and nitrogenous components

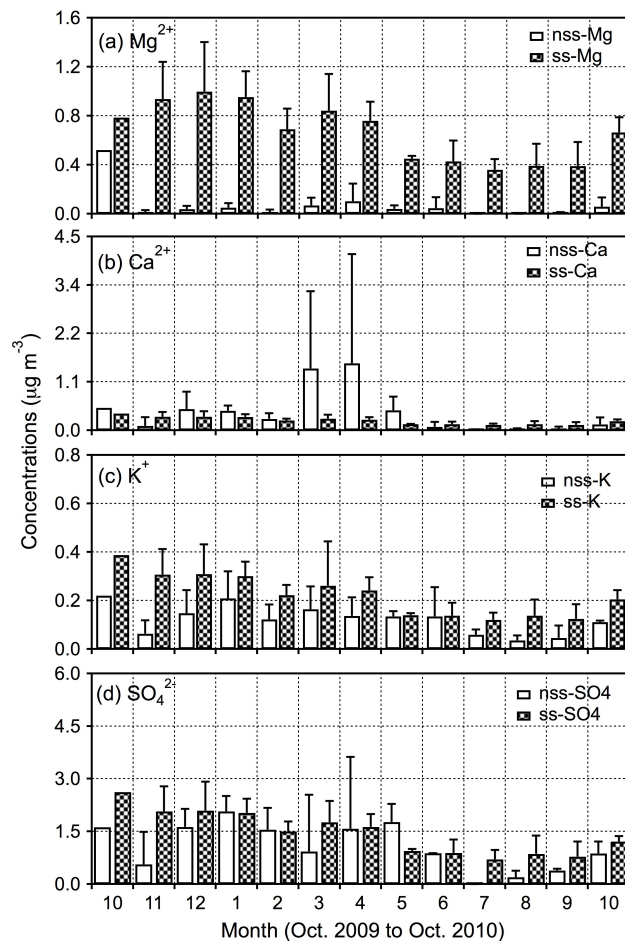
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Fig. 11. Estimated mass concentration of sea salt (ss) and non-sea salt (nss) component of **(a)** Mg^{2+} , **(b)** Ca^{2+} , **(c)** K^+ , and **(d)** SO_4^{2-} in ambient aerosols collected from Cape Hedo, Okinawa.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

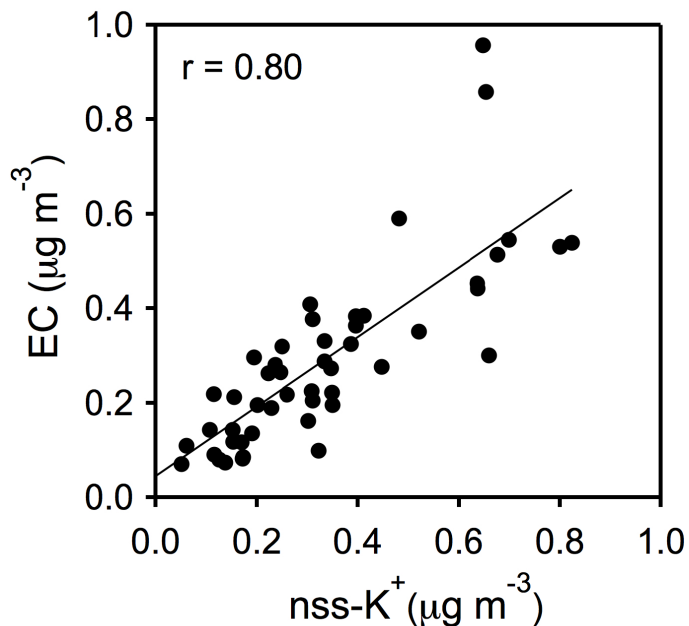
**Carbonaceous and
nitrogenous
components**B. Kunwar and
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Fig. 12. Correlation analysis between nss-K and EC in ambient aerosols collected from Cape Hedo, Okinawa.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion