HOKKAIDO UNIVERSITY

Title	Comparison of Amazonian biomass burning and East Asian marine aerosols : Bulk organics, diacids and related compounds, water-soluble inorganic ions, stable carbon and nitrogen isotope ratios
Author(s)	Kundu, Shuvashish; Kawamura, Kimitaka; Lee, Meehye et al.
Relation	大気圏と生物圏の相互利用. 北海道大学低温科学研究所編
Citation	低温科学, 68, 89-100
Issue Date	2010-03-31
Doc URL	https://hdl.handle.net/2115/45168
Type	departmental bulletin paper
File Information	LTS68_014.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

Low Temperatine Science, 68 (2010), 89-100

Comparison of Amazonian biomass burning and East Asian marine aerosols: Bulk organics, diacids and related compounds, water-soluble inorganic ions, stable carbon and nitrogen isotope ratios

Shuvashish Kundu[1,2], Kimitaka Kawamura[1,*], Meehye Lee[3], Tracey W. Andreae[4], András Hoffer[5], Meinrat O. Andreae[4]

Received 5 March 2010; accepted 11March 10, 2010

In this study, biomass burning and marine aerosols collected in the Amazon, Brazil and on an island south of South Korea are compared in terms of chemical characteristics and ageing by the determination of water-soluble organic carbon (WSOC), water-insoluble organic carbon (WIOC), elemental carbon (EC), diacids (C_2-C_{11}) and related compounds (ketoacids and α-dicarbonyls), stable carbon isotopic ratios ($\delta^{13}C$) of total carbon (TC), and nitrogen isotopic ratios ($\delta^{15}N$) of total nitrogen (TN). The concentration ratios of WSOC, WIOC, and EC to aerosol mass are 2-12 times higher in biomass burning aerosols than in marine aerosols. In contrast, concentration ratios of water-soluble cations and anions to aerosol mass are lower by a factor of 0.2-0.6 in biomass burning aerosols than in marine aerosols. Among diacids and related compounds, oxalic acid (C_2) was found to be the most abundant, followed by succinic acid (C_4) in biomass burning aerosols, while malonic acid (C_3) dominated in marine aerosols. Lower relative abundances of C_2-C_4 diacids, unsaturated diacids, and α-dicarbonyls in total diacids and related compounds were observed in biomass burning aerosols than in marine aerosols, whereas those of C_5-C_{11} diacids, branched diacids, multifunctional diacids, and ketoacids were higher in biomass burning aerosols. These results suggest that there are significant differences in the sources and photochemical production pathways of individual diacids and related compounds. While the $\delta^{13}C$ values (−26.5 to −20.5 ‰) of TC and $\delta^{15}N$ values (+6.8 to +26.9 ‰) of TN showed a large variation in marine aerosols, the variations were rather small ($\delta^{13}C$: −26.1 to −23.6 ‰; $\delta^{15}N$: +21.5 to +25.7 ‰) in biomass-burning aerosols. We propose that these $\delta^{13}C$ and $\delta^{15}N$ values can be used to characterize biomass-burning aerosols.

[1] Institute of Low Temperature Science, Hokkaido University, Sapporo 060-0819, Japan
[2] Graduate School of Environmental Science, Hokkaido University, Sapporo 060-0810, Japan
[3] Department of Earth and Environmental Sciences, Korea University, Seoul 136-701, South Korea
[4] Biogeochemistry Department, Max Planck Institute for Chemistry, Mainz, Germany
[5] Department of Earth and Environmental Sciences, University of Pannonia, Veszprém, Hungary
* Corresponding author phone: +81-11-706-5457; fax: +81-11-706-7142; e-mail: kawamura@lowtem.hokudai.ac.jp

1. Introduction

The largest rainforest in the world (~4,000,000 km²) is located in Brazilian Amazonia. It is experiencing one of the highest deforestation rates in the world, which is associated with slash-and-burn techniques for both primary deforestation and seasonal burning of secondary forests and pastures [Fearnside, 1990; Skole et al., 1994]. Biomass burning in Amazonia emits huge amounts of trace gases and aerosols [Crutzen and Andreae, 1990; Crutzen and Goldam-

mer, 1993], which affect global air quality, climate and biogeochemical distribution of nutrients. The Gosan site in Jeju Island, South Korea, is seriously influenced by the pollutant transports from East Asian countries/areas including Siberia, China, Korea and Japan.

Biomass burning is one of the major sources of atmospheric carbonaceous aerosols that are significantly enriched with water-soluble organic carbon (WSOC) [Graham et al., 2002; Kundu et al., 2010a]. Water-soluble and -insoluble carbonaceous fractions become elevated in marine aerosols due to the formation of low-volatility compounds which result from the oxidation of organics in the gas and aqueous phases during a long-range transport [Kundu et al., 2010d, and references therein]. These species together with inorganic aerosol components influence the aerosol climate forcings [Penner et al., 1998, and references therein; Novakov and Corrigan, 1996, and references therein]. It is therefore important to study the carbonaceous and inorganic materials in both biomass burning and marine aerosols. Additionally, comparative knowledge in terms of organic and inorganic composition is essential between biomass burning and marine aerosols for their characterization in the atmosphere.

The ubiquity of diacids and related compounds (ketoacids and α-dicarbonyls) has been discussed for biomass burning aerosols [Allen and Miguel, 1995; Narukawa et al., 1999; Graham et al., 2002; Mayol-Bracero et al., 2002; Gao et al., 2003; Decesari et al., 2006; Falkovich et al., 2005; Kundu et al., 2010b] and for marine aerosols [Kawamura and Usukura, 1993; Kawamura and Sakaguchi, 1999; Baboukas et al., 2000; Mochida et al., 2003a, b; Sempéré and Kawamura, 2003; Legrand et al., 2007]. These studies have also discussed their significant contributions to aerosol mass, their sources, and their chemical formation and degradation in biomass burning and marine aerosols. However, none of these studies has focused on the differences in molecular distribution and chemical composition of diacids and related compounds between biomass burning and marine aerosols.

Diacids and ketoacids account for 2–9% of the water-soluble organic carbon (WSOC) in biomass burning aerosols [Narukawa et al., 1999; Falkovich et al., 2005; Decesari et al., 2006; Kundu et al., 2010a] and for more than 10% of WSOC in remote marine aerosols [Sempéré and Kawamura, 2003]. WSOC in aerosols contributes to the CCN activity [Sherwood, 2002; Andreae et al., 2004; Mircea et al., 2005; Andreae and Rosenfeld, 2008], which affects cloud microphysical properties and hence precipitation patterns and cloud albedo [Kaufman and Fraser, 1997; Ramanathan et al., 2001; Kaufman et al., 2002]. Glutaric acid (a C_5 diacid) has been found to increase the CCN activation ability of ammonium sulfate, a major inorganic species in atmospheric aerosols [Cruz and Pandis, 1997, 1998].

The $\delta^{13}C$ of bulk organic carbon has been successfully used to better understand the contributions of marine and continental sources to aerosol carbon [Chesselet et al., 1981; Cachier et al., 1986, 1989; Narukawa et al., 1999, 2008; Turekian et al., 2003]. However, stable carbon and nitrogen isotope ratios in biomass burning and marine aerosols have not previously been studied extensively [Turekian et al., 1998; Kawamura et al., 2004; Kundu et al., 2010a]. Stable carbon and nitrogen isotopic ratios not only provide information about the origins of aerosols but also about the isotopic fractionation that is likely to occur during biomass burning and after the emission of aerosol particles or their gaseous precursors into the atmosphere [Kundu et al., 2010a, c].

In this study, we report on the differences in the chemical (bulk organics, diacids and related compounds and water-soluble inorganic ion) and isotopic composition (stable carbon isotope ratios of total carbon and nitrogen isotope ratios of total nitrogen) of biomass burning and marine aerosols in order to explore the characteristics of these two types of aerosols.

2. Samples and methods

Aerosol sampling was carried out during an intensive biomass burning period (dry season), 16–26 September 2002, at the FNS (Fazenda Nossa Senhora Aparecida) site (10°45′44″ S, 62°21′27″ W, 315 m asl) located in the western province of Rondônia, Brazil [Figure 1a]. Aerosol sampling procedures have been described in detail elsewhere [Hoffer et al., 2006]. Briefly, fine ($PM_{2.5}$) aerosol samples were collected on pre-combusted (~10 h at 600°C) Pallflex quartz fiber filters using a dichotomous virtual impactor [Solomon et al., 1983] mounted on a 10 m high tower.

Total suspended particles (TSP) in the atmosphere were collected at the Gosan site over 2–7 days

throughout the year from April 2003 to April 2004. TSP samples (n=84) were collected on pre-combusted quartz fiber filters using a high volume air sampler (Kimoto AS-810) installed on the roof of a trailer house (~3 m above the ground). The Gosan site is located on a cliff (~71 m asl) at the western tip of Jeju Island (33°29′ N, 126°16′ E). It is approximately 100 km off the south coast of the Korean Peninsula, ~500 km off the east coast of China (Jiangsu province or Shanghai), ~200 km to the west of Kyushu Island, Japan, and ~1000 km off the northeast coast of Taiwan (Figure 1b). The site and its surroundings are covered with grasses but there are no trees. Due to its location and very limited local anthropogenic emissions [Kim et al., 1998], Gosan has been considered as an ideal site to monitor the impact on air quality of the western rim of the North Pacific due to the outflows from East Asia [Carmichael et al., 1996, 1997; Chen et al., 1997]. Gosan was used as a supersite for the ACE-Asia campaign in 2001 [Huebert et al., 2003], and for the PEM-West A and PEM-West B programs conducted between 1991 and 1994 [Hoell et al., 1996, 1997]. It is now used as one of the superstations of the Atmospheric Brown Cloud (ABC) program [Lee et al., 2007]. A more detailed description of this site is given elsewhere [Kim et al., 1998;

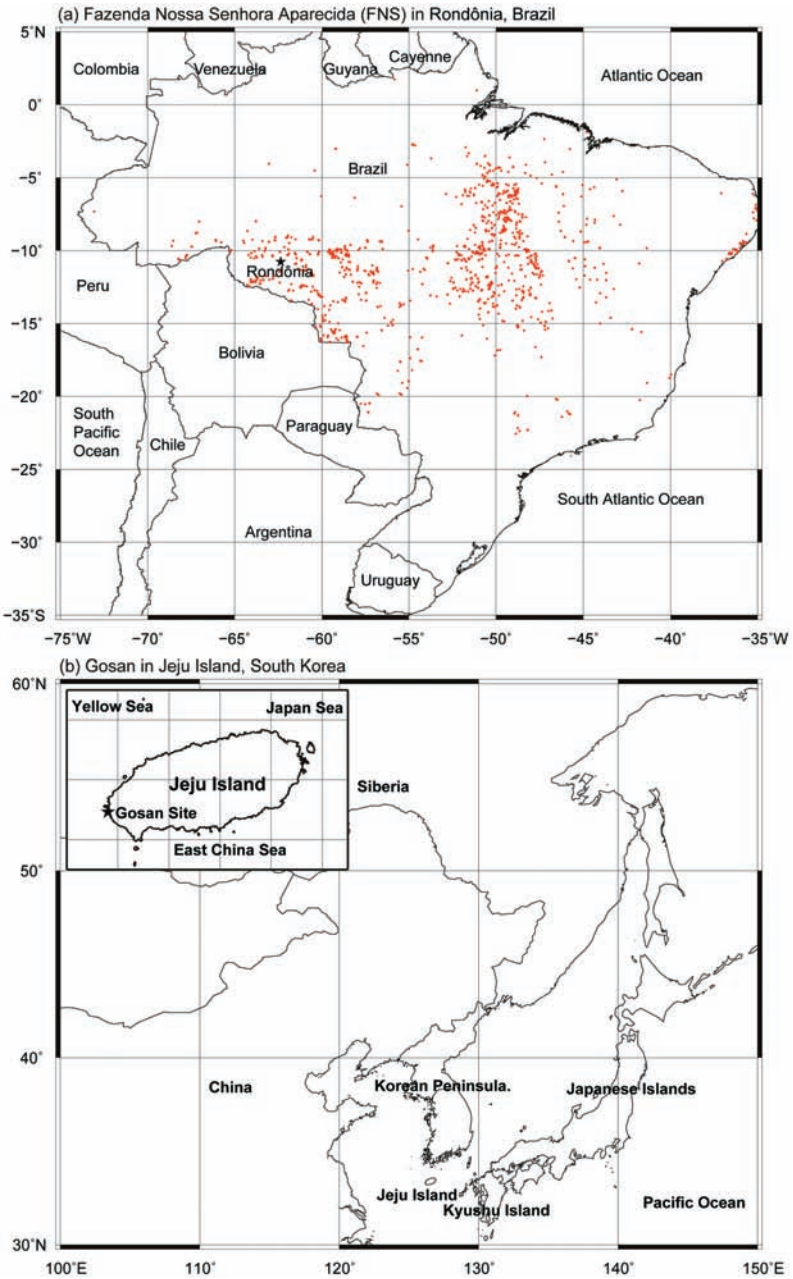

Figure 1 : Map showing geographical location of aerosol sampling site at (a) Fazenda Nossa Senhora Aparecida (FNS) in Rondônia, Brazil and (b) Gosan in Jeju Island, South Korea. A star symbol indicates the FNS and Gosan sites. Fire location data (red dots) are cited from http://dup.esrin.esa.int/ionia/wfa.

Kawamura et al., 2004; Lee et al., 2007].

The concentrations of organic carbon (OC) and elemental carbon (EC) were measured using an OC/EC analyzer (Sunset Laboratory Inc., Portland, OR, USA). The WSOC was measured with a carbon analyzer (Shimadzu, TOC-5000), whereas water-soluble inorganic ions were measured using a Metrohm 761 ion chromatography (IC) system (Metrohm, Herisau, Switzerland). The detailed analytical methods for the measurements of OC, EC, WSOC and water-soluble inorganic ions are described in Kundu et al. [2010a].

Analytical procedures for the analyses of diacids and related compounds are described in detail by Kawamura and Ikushima [1993]. Briefly, aliquots of filter samples were extracted with organic free pure water. The extracts were dried and derivatized with 14% borontrifluoride in n-butanol at 100°C. The derived dibutyl esters and dibutoxy acetals were determined using a GC instrument (Hewlett-Packard, HP6890) equipped with a capillary column and FID detector. Authentic diacid dibutyl esters were used as external standards for the peak identification. The compounds were also identified using a GC/mass spectrometer (Thermoquest, Trace MS).

For TC and TN analyses, a small disc (area 0.95 cm^2) was cut off from each filter sample. The disc was put into a tin cup and shaped into a rounded ball using a pair of flat-tipped tweezers. The samples were introduced into the elemental analyzer (EA; model: NA 1500 NCS, Carlo Erba Instruments) using an auto-sampler, and were oxidized in a combustion column packed with chromium trioxide at 1020°C, in which the tin container burns to promote the intensive oxidation of sample materials in an atmosphere of pure oxygen. The combustion products (CO_2 and NO_x) are transferred to a reduction column packed with metallic copper that was maintained at 650°C. Here excess oxygen is removed and nitrogen oxides coming from the combustion column are reduced to molecular nitrogen (N_2). The N_2 and CO_2 derived during this process were isolated on-line using a gas chromatograph and then measured with a thermal conductivity detector. Aliquots of the N_2 and CO_2 gases were then introduced into an isotope ratio mass spectrometer (ThermoQuest, Delta Plus) through an interface (ThermoQuest, ConFlo II). The isotopic composition of $\delta^{13}C$ and $\delta^{15}N$ was determined using the following standard isotopic conversion equations (1) and (2), respectively:

$$\delta^{13}C(‰) = \left[\frac{(^{13}C/^{12}C)_{sample}}{(^{13}C/^{12}C)_{standard}} - 1\right] \times 1000 \quad (1)$$

$$\delta^{15}N(‰) = \left[\frac{(^{15}N/^{14}N)_{sample}}{(^{15}N/^{14}N)_{standard}} - 1\right] \times 1000 \quad (2)$$

Acetanilide was used as an external standard to determine TC, TN and their isotope ratios. The concentrations and isotope ratios reported here are corrected for the field blanks. The reproducibility of TC and TN in atmospheric aerosol samples ranged from 0.7–9% (av. 2.5%) and 1.4–4.8% (av. 3%), whereas the standard deviations of the $\delta^{13}C$ and $\delta^{15}N$ measurements ranged from 0.08–0.24 ‰ (av. 0.12 ‰) and 0.03–0.45 ‰ (av. 0.13 ‰), respectively.

3. Results and discussion

3.1 Molecular composition of diacids, ketoacids and α-dicarbonyls

Straight (C_2-C_{11}) and branched (iC_4, iC_5 & iC_6) chain aliphatic diacids, diacids with additional functional groups (hC_4, kC_3 & kC_4), unsaturated aliphatic diacids (M, mM & F), aromatic diacids (Ph, iPh & tPh), ketoacids (ωC_2-ωC_9, and Pyr), and α-dicarbonyls (Gly and MeGly) were detected in this study. Table 1 presents their concentration ranges and average concentrations together with abbreviations of the compounds.

Figures 2a and b show the molecular distributions of diacids and related compounds in biomass burning and marine aerosol samples. Oxalic acid (C_2) was found as the most abundant species, followed by succinic acid (C_4) in biomass burning aerosols, and malonic acid (C_3) dominated in marine aerosols. Concentrations (700–2060 ng m^{-3}, av. 1360 ng m^{-3}) of oxalic acid (C_2) in biomass burning aerosols are two times higher than those (90–1290 ng m^{-3}, av. 560 ng m^{-3}) in marine aerosols. The dominant presence of oxalic acid (C_2) has been reported in biomass burning aerosols [Kundu et al., 2010b, and references therein] and in remote marine aerosols [Kawamura and Sakaguchi, 1999; Kerminen et al., 2000; Mochida et al., 2003a, b].

The third most abundant species is malonic acid (C_3) in biomass burning aerosol samples followed by glyoxylic acid (ωC_2), glutaric acid (C_5), adipic acid (C_6), phthalic acid (Ph), pyruvic (Pyr), glyoxal (Gly), methylglyoxal (MeGly) and malic acid (hC_4) (Figure 2a). In contrast, succinic acid (C_4) is the third most

Table 1 : Concentrations of diacids, ketoacids and α-dicarbonyls detected in biomass burning aerosols over the FNS site in Rondônia, Brazil and in marine aerosols over the Gosan site in Jeju Island, South Korea.

	Concentrations (ng m^{-3})			
	Biomass burning aerosols (n=15)		Marine aerosols (n=84)	
Name of compound	Range	Average	Range	Average
Saturated n-diacids				
Oxalic, C_2	695-2059	1356	92-1293	458
Malonic, C_3	95-345	188	7-167	58
Succinic, C_4	124-428	277	7-190	48
Glutaric, C_5	3-88	47	0.9-69	13
Adipic, C_6	22-101	47	0.6-19	5
Pimelic, C_7	8-28	15	0.1-11	2
Suberic, C_8	0.07-23	8	0.01-9	2
Azelaic, C_9	9-46	22	0.01-13	4
Sebacic, C_{10}	1-8	4	0.02-4	1
Undecanedioic, C_{11}	0.19-7	3	0.2-9	2
Branched diacids				
Methylmalonic, iC_4	3-16	10	0.3-5	2
Methylsuccinic, iC_5	15-71	42	0.2-12	3
Methylglutaric, iC_6	2-11	6	0.1-5	1
Unsaturated diacids				
Maleic, M	10-56	23	0.1-13	3
Fumaric, F	3-15	9	0.4-12	3
Methylmaleic, mM	3-30	14	0.2-12	3
Phthalic, Ph	25-66	42	0.5-52	10
Isophthalic, iPh	1-5	3	0.01-5	1
Terephthalic, tPh	2-26	12	0.01-30	8
Multifunctional diacids				
Hydroxysuccinic, hC_4	10-44	22	BDL-21	4
Ketomalonic, kC_3	0.14-36	17	0.1-6	1
4-Ketopimelic, kC_7	5-13	9	0.01-21	4
Total diacids	1039-3480	2174	142-1875	636
Ketoacids				
Glyoxylic, ωC_2	65-225	131	6.3-148	34
3-Oxopropanoic, ωC_3	BDL-23	3	0.0-4	1
4-Oxobutanoic, ωC_4	BDL-8	4	BDL-4	0.5
9-Oxononanoic, ωC_9	2-4	2	BDL-6	2
Pyruvic acid, Pyr	12-50	27	0.5-15	4
Total ketoacids	78-309	167	8-170	41
α-Dicarbonyls				
Glyoxal, Gly	19-54	30	0.4-106	4
Methylglyoxal, MeGly	13-43	25	0.9-60	11
Total α-dicarbonyls	31-93	56	2-108	15

Note: BDL means below detection limit.

abundant species in marine aerosols followed by glyoxylic acid (ωC_2), glutaric acid (C_5), methylglyoxal (MeGly), phthalic acid (Ph), terephthalic acid (tPh) and adipic acid (C_6) (Figure 2b). Azelaic acid (C_9) was the most abundant in the range of C_7-C_{11} diacids in both biomass burning and marine aerosols (Figure 2).

Total diacid concentrations ranged from 1040 to 3480 ng m^{-3} (av. 2170 ng m^{-3}) in biomass burning aerosols versus 140-1880 ng m^{-3} (av. 640 ng m^{-3}) in marine aerosols. Total diacid concentrations in our biomass burning samples are higher than those (220-2610 ng m^{-3}, av. 1160 ng m^{-3}, Graham et al., 2002) reported in aerosol samples collected from the same site during the LBA-EUSTACH campaign in 1999. It is important to note that Graham et al. [2002] detected some of our diacid species and also some additional diacids that have not been detected in our study, including hydroxymalonic acid, 2-hydroxyglutaric acid, and 2-ketoglutaric acid. Our diacid data in marine aerosol are in the same range as that (130-2070 ng m^{-3}, av. 660 ng m^{-3}) reported for the same sampling site for aerosol samples collected between April 2001 and March 2002 [Kawamura et al., 2004]. Similar concentrations (410-1500 ng m^{-3}, av. 850 ng m^{-3}) were reported over the East China Sea for aerosols collected by a ship during the ACE-Asia campaign whereas

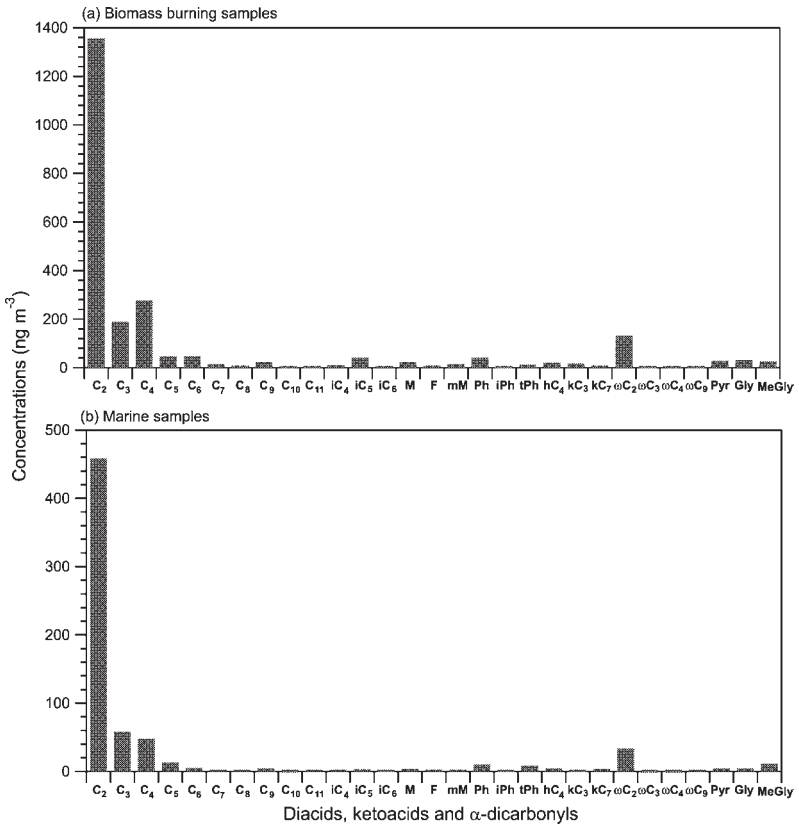

Figure 2 : Molecular distributions of diacids, ketoacids and α-dicarbonyls in (a) biomass burning aerosols and (b) marine aerosols.

much higher concentrations (480–2100 ng m^{-3}, av. 1200 ng m^{-3}) were reported over the Japan Sea [Mochida et al., 2003b]. Total diacid concentrations (6–550 ng m^{-3}, av. 140 ng m^{-3}, Mochida et al., 2003a) in aerosols over Chichi-Jima Island in the western North Pacific, ca. 2000 km away from East Asia, are several times lower than those observed at the Gosan site, suggesting that the Gosan site is strongly influenced by the continental outflow from China, Korea and Japan.

Total ketoacid concentrations ranged from 80 to 310 ng m^{-3} (av. 170 ng m^{-3}) in biomass burning aerosols versus 8–170 ng m^{-3} (av. 40 ng m^{-3}) in marine aerosols. Total dicarbonyl concentrations ranged from 30 to 90 ng m^{-3} (av. 60 ng m^{-3}) in biomass burning aerosols versus 2–110 ng m^{-3} (av. 15 ng m^{-3}) in marine aerosols. Graham et al. [2002] reported two ketoacids, namely glyoxylic and pyruvic acids, whose concentrations ranged from 10–230 ng m^{-3} with the mean value of 80 ng m^{-3} in samples collected from the same site during a biomass burning period (1–29 October 1999). These concentrations in marine aerosols are similar to those (ketoacids: 2–170 ng m^{-3}, av. 50 ng m^{-3}; dicarbonyls: 0.1–85 ng m^{-3}, av. 12 ng m^{-3}) reported for aerosol samples collected at the same site between April 2001 and March 2002 [Kawamura et al., 2004].

Diacids, ketoacids and α-dicarbonyls accounted for 1.5%, 0.1%, and 0.05% of OC, respectively, in biomass burning aerosols and 6.6%, 0.5%, and 0.3%, respectively, in marine aerosols (Table 2). On the other hand, their contributions to WSOC were found to be 2.3%, 0.2%, and 0.08%, respectively, in biomass burning aerosols and 12%, 0.8% and 0.4%, respectively, in marine aerosols (Table 2). The higher contributions of diacids and related compounds to the carbonaceous fraction in marine aerosols than in biomass burning aerosol suggest that marine aerosols are more photochemically aged.

3.2 Aerosol mass and its carbonaceous and ionic components

Table 3 gives a statistical summary of the concentrations of aerosol mass, carbonaceous materials and water-soluble inorganic ion in biomass burning and marine aerosols. Concentrations of carbonaceous materials are significantly higher in biomass burning aerosols than in marine aerosols. On average, EC is higher in biomass burning aerosols than in marine aerosols by a factor of 2, and TC, OC and WSOC are higher by factors of 10–15. Contributions of TC to

Table 2 : Contributions of diacids, ketoacids and α-dicarbonyls to carbonaceous fractions (OC and WSOC) of biomass burning and marine aerosols.

Abundance in bulk carbon (%)	Biomass burning aerosols (n=15)		Marine aerosols (n=84)	
	Range	Average	Range	Average
Organic carbon (OC)				
Total diacids	1.1-2.2	1.5	2-17	6.6
Total ketoacids	0.07-0.2	0.1	0.2-1.2	0.5
Total α-dicarbonyls	0.02-0.1	0.05	0.04-0.7	0.3
Organic carbon (WSOC)				
Total diacids	1.7-3.1	2.3	4.2-26.4	12
Total ketoacids	0.1-0.3	0.2	0.3-2.1	0.8
Total α-dicarbonyls	0.04-0.1	0.08	0.08-1.1	0.4

aerosol mass are an order of magnitude higher in biomass burning aerosols than in marine aerosols. It is interesting to note that although the mean concentration of TN in marine aerosols is similar to that of biomass burning aerosols, the mean contribution of TN to aerosol mass is higher in marine aerosol than in biomass burning aerosols by a factor 2 (Table 3).

The relative abundances of carbonaceous materials (WSOC, WIOC and EC) and water-soluble inorganic ions to aerosol mass concentrations were also different between biomass and marine aerosols (Figure 3). As seen in Fig. 3, biomass burning aerosols are significantly more enriched with carbonaceous materials than marine aerosols. On average, the ratios of WSOC, WISOC, and EC to aerosol mass are 0.3, 0.2, and 0.2, respectively, in biomass burning aerosols versus 0.02, 0.02, and 0.01, respectively, in marine aerosols.

In contrast, marine aerosols are more enriched with water-soluble cations and anions. Na^+ was the most abundant followed by NH_4^+, Ca^{2+}, Mg^{2+} and K^+ among the cations whereas SO_4^{2-} was the most abundant followed by Cl^-, NO_3^-, $CH_3SO_3^-$ and F^- (Table 3). Higher abundance of SO_4^{2-} suggests that Gosan site is significantly influenced by the continental outflows from East Asia. On average, total cations to aerosol mass ratio is 0.05 in biomass burning aerosols and 0.09 in marine aerosols. Total anions to aerosol mass ratio is 0.03 in biomass burning aerosols and 0.25 in marine aerosols.

The concentrations of carbonaceous and inorganic fractions and their contributions to aerosol

Table 3 : Organic, inorganic and isotopic composition of biomass burning and marine aerosols.

Components	Biomass burning aerosols (n=15)		Marine aerosols (n=84)	
	Range	Average	Range	Average
Bulk analyses ($\mu g\ m^{-3}$)				
Aerosol mass	83-190	110	27-268	82
Total carbon (TC)	23-86	53	0.7-14	5.4
Organic carbon (OC)	20-86	50	1-12	3.7
Water-soluble organic carbon (WSOC)	18-51	31	0.2-7	2.1
Elemental carbon (EC)	0.6-3.6	2.4	0.2-4	1
Total nitrogen (TN)	1.2-4	2.2	0.2-9	2.5
TC/aerosol mass (%)	28-45	46	1.3-16	6.4
TN/aerosol mass (%)	1.4-2.1	1.8	0.7-7	3.2
Ion analyses ($\mu g\ m^{-3}$)				
Na^+	1.6-4.1	2.6	0.2-12	3.5
NH_4^+	0.3-2.2	1.3	0.1-6	1.7
K^+	1-2.9	2	0.03-2	0.5
Mg^{2+}	0.01-0.08	0.04	0.03-2	0.5
Ca^{2+}	0.02-0.2	0.1	0.06-5	0.7
F^-	0.05-0.2	0.1	0.001-0.12	0.02
$CH_3SO_3^-$	0.2-0.6	0.3	0.007-0.3	0.06
Cl^-	0.05-0.4	0.1	0.08-33	6.1
NO_3^-	0.4-4.9	2.1	0.7-20	4.4
SO_4^{2-}	2.2-3.4	2.7	0.4-23	9.3
Isotope analyses (‰)				
$\delta^{13}C$ (TC)	−26.1 to −23.5	−24.7	−26.5 to −20.5	−23.5
$\delta^{15}N$ (TN)	+23.5 to +25.7	+23.5	+6.8 to +26.9	+15.1

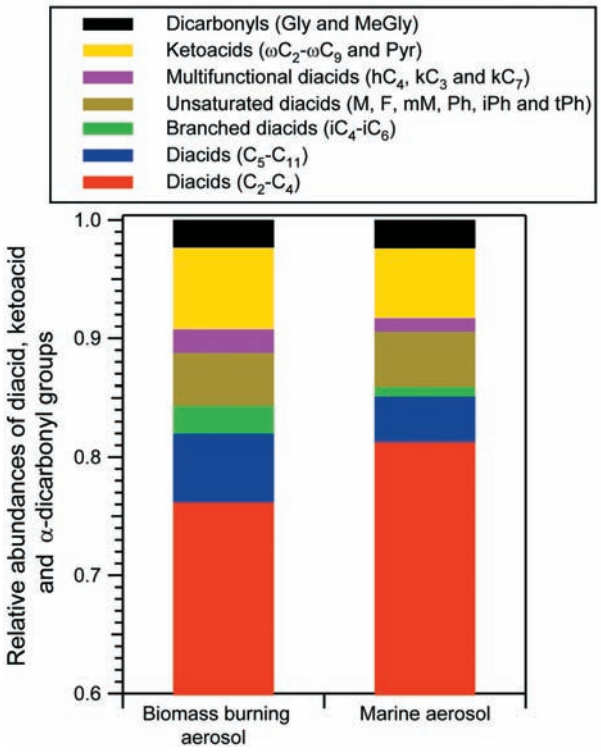

Figure 3 : Contributions of diacids and related compound groups to total molecular organics detected in biomass burning and marine aerosols. The Y axis begins at 60%, because the contributions of lower-molecular-weight diacids (C_2-C_4) in both aerosols account for >60%, thus the relative abundances of other organics can be visualized.

mass concentrations in the size class of $PM_{2.5}$ in marine aerosols can be different from those in total suspended particles (TSP). The contributions of organic carbon (OC), cations, and anions to $PM_{2.5}$ mass concentrations are reported to be 10%, 20%, and 40%, respectively, in Gosan site [Yang et al., 2004] whereas their contributions to TSP mass concentrations are found to be 5%, 10%, and 30%, respectively, in our study of marine aerosols. These results suggest that OC and ions are more enriched in fine particles than in coarse particles.

3.3 Stable carbon and nitrogen isotopic composition of aerosols

The average value of $\delta^{13}C$ for TC in biomass burning aerosols was −24.7 ‰ with a range of −26.1 to −23.5 ‰, while it was −23.5 ‰ in marine aerosols with a range of −26.5 ‰ to −20.5 ‰. The $\delta^{13}C$ values in biomass burning aerosols suggest the predominance of C_3 plant burning over C_4 plant burning as sources of smoke aerosols. The dominant presence of C_3 plants is characterized at the sampling site and its neighboring areas from which smokes are transported [Kundu et al., 2010a]. The average $\delta^{13}C$ value in aerosols collected from the C_3 plant-dominated Santarém region of Brazil was reported to be −25.8 ‰ with a range of −26.9 ‰ to −24.9 ‰ [Martinelli et al., 2002]. The $\delta^{13}C$ values in marine aerosols from Gosan site can be interpreted by a significant contribution of carbonaceous aerosols from continental sources, whose $\delta^{13}C$ are lower than those from marine sources [Cachier et al., 1986]. This result is consistent with the fact that Gosan site is seriously influenced by continental outflows almost throughout the year [Kundu et al., 2010c]. Air masses are significantly transported to the Gosan site from eastern and northeastern China in spring, East China, China Sea and Pacific Ocean in summer, and northeastern China in autumn and winter [Kundu et al., 2010c].

The average $\delta^{15}N$ value of TN for biomass burning aerosols was +23.5 ‰ with a range of +23.5 to +25.7 ‰, whereas it was +15.1 ‰ with a range of +6.8 to +26.9 ‰ for marine aerosols. Our average $\delta^{15}N$ value in biomass burning aerosol samples is higher by 12-13 ‰ than those (10.6–11.5 ‰) reported in atmospheric aerosol samples collected from Santarém and Piracicaba regions in Brazil where major sources of aerosols were unburned vegetation tissues [Martinelli et al., 2002]. Higher $\delta^{15}N$ values in biomass burning aerosols could be interpreted by the fact that $\delta^{15}N$ of aerosol particles produced from the vegetation burns are higher than the source vegetation [Turekian et al., 1998]. The significant $\delta^{15}N$ variability in marine aerosols is due to the contributions of nitrogenous species from different sources in Gosan site because different air masses are transported from different sources. This variability can also be explained by an enhanced atmospheric processing of nitrogenous species during a long-range transport including oxidation of NO_x to HNO_3 and the subsequent gas-to-particle conversion via the reactions with NH_3, sea salts and dust particles [Kundu et al., 2010c].

Stable carbon and nitrogen isotope data of both marine and biomass burning aerosols are plotted in Figure 4. The figure shows that the isotopic signals of biomass burning aerosols are completely different from the marine aerosols, which are influenced by outflows from East Asian countries and marine air masses from the Pacific Ocean.

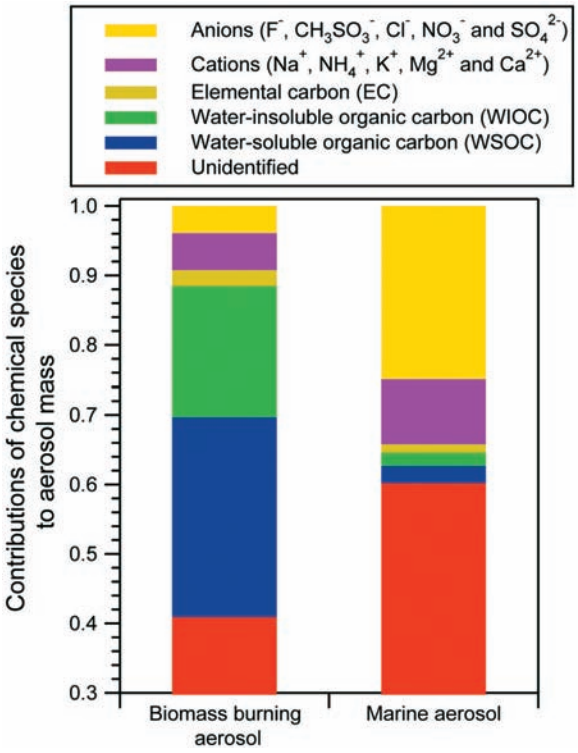

Figure 4 : Contributions of detected chemical components to aerosol mass concentrations of biomass burning and marine aerosols.

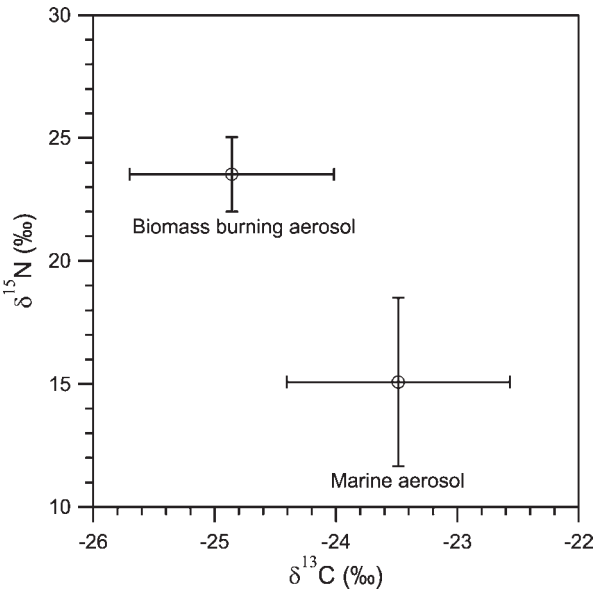

Figure 5 : δ^{13}C of total carbon (TC) versus δ^{15}N of total nitrogen (TN) in biomass burning and marine aerosols.

4. Conclusions

Biomass burning aerosol samples from the Fazenda Nossa Senhora Aparecida (FNS) site in Rondônia, Brazil and marine aerosols from the Gosan site, Jeju Island, were analyzed for bulk organics (TC, OC, WSOC, and EC) and water-soluble inorganic ions. They were also analyzed for molecular organics including diacids, ketoacids and α-dicarbonyls, stable carbon isotopic ratios of TC, and nitrogen isotopic ratios of TN. A chemical mass closure approach demonstrates that biomass burning aerosols are enriched with carbonaceous materials (WSOC, WIOC and EC) whereas marine aerosols are enriched with water-soluble cations and anions. This study shows that molecular distributions of diacids and related compound as well as their contributions to total diacids and related compounds differ between biomass burning and marine aerosols. Several times higher contributions of diacids and related compound-carbon to OC and WSOC in marine aerosols than in biomass burning aerosols suggest that marine aerosols are more chemically aged. This study demonstrates that the δ^{13}C values of TC and δ^{15}N values of TN in biomass burning are quite different from those in marine aerosols influenced by pollution from the East Asian Continent.

Acknowledgements

This research was supported in part by the Japanese Ministry of Education, Science, Sport and Culture (MEXT) through grant-in-aid number 19204055 and also carried out within the framework of the Smoke, Aerosols, Clouds, Rainfall, and Climate (SMOCC) project, a contribution to the Large-Scale Biosphere-Atmosphere Experiment in Amazonia (LBA). The authors gratefully acknowledge financial support by the European Commission (contract No. EVK-CT-2001-00110 SMOCC) and by the Max Planck Society. Financial support to S. K. by the MEXT is also acknowledged.

References

Allen, A. G., and A. H. Miguel, Biomass burning in the Amazon-Characterization of the ionic component of aerosols generated from flaming and smoldering rainforest and savanna, *Environ. Sci. Technol.*, **29**, 486-493, 1995.

Andreae, M. O., D. Rosenfeld, P. Artaxo, A. A. Costa, G. P. Frank, K. M. Longo, and M. A. F. Silva-Dias, Smoking rain clouds over the Amazon, *Science*, **303**, 1337-1342, 2004.

Andreae, M. O., and D. Rosenfeld, Aerosol-cloud-precipitation interactions. part 1. The nature and sources of cloud-active aerosols, Earth-Science Reviews, 89, 13-41, 2008.

Baboukas, E. D., M. Kanakidou, and N. Mihalopoulos, Carboxylic acids in gas and particulate phase above the Atlantic Ocean, *J. Geophys. Res.*, **105**, 14459–14471, 2000.

Cachier, H., P. Buat-Menard, M. Fontugne, and R. Chesselet, Long-range transport of continentally-derived particulate carbon in the marine atmosphere: evidence from stable carbon isotope studies, *Tellus*, **38B**, 161, 1986.

Cachier, H., M. P. Brémond, and P. Buat-Ménard, Carbonaceous aerosols from different tropical biomass burning sources, *Nature*, **340**, 371–373, 1989.

Carmichael, G. R., Y. Zhang, L.-L. Chen, -S. M. Hong, and H. Ueda, Seasonal variation on aerosol composition at Cheju Island, Korea, *Atmos. Environ.*, **30**, 2407–2416, 1996.

Carmichael, G. R., -S. M. Hong, H. Ueda, -L. L. Chen, K. Murano, J. K. Park, Y. Lee, C. Kang, and S. Shim, Aerosol composition at Cheju Island, Korea, *J. Geophys. Res.*, **102**, 6047–6061, 1997.

Chen, L. -L., G. R. Carmichael, -S. M. Hong, H. Ueda, S. Shim, C. H. Song, Y. P. Kim, R. Arimoto, J. Prospero, D. Savoie, K. Murano, J. K. Park, H. -G. Lee, and C. Kang, Influence of continental outflows on the aerosol composition at Cheju Island, South Korea, *J. Geophys. Res.*, **102**, 28551–28574, 1997.

Chesselet, R., M. Fontugne, P. Buat-Menard, U. Ezat, and C. E. Lambert, The origin of particulate organic carbon in the marine atmosphere as indicated by its stable carbon isotopic composition, *Geophys. Res. Lett*, **8**, 345, 1981.

Crutzen, P. J., and M. O. Andreae, Biomass burning in the tropics: Impact on atmospheric chemistry and biogeochemical cycles, *Science*, **250**, 1669–1678, 1990.

Crutzen, P. J., and J. G. Goldammer (Eds.), *Fire in the environment: The Ecological, Atmospheric, and Climatic Importance of vegetation fires*, John Wiley, New York, 1993.

Cruz, C. N., and S. N. Pandis, A study of the ability of secondary organic aerosol to act as cloud condensation nuclei, *Atmos. Environ.*, **31**, 2205–2214, 1997.

Cruz, C. N., and S. N. Pandis, The effect of organic coatings on the cloud condensation nuclei activation of inorganic atmospheric aerosol, *J. Geophys. Res.*, **103**, 13111–13123, 1998.

Decesari, S., S. Fuzzi, M. C. Facchini, M. Mircea, L. Emblico, F. Cavalli, W. Maenhaut, X. Chi, G. Schkolnik, A. Falkovich, Y. Rudich, M. Clayes, V. Pashynska, G. Vas, I. Kourtchev, R. Vermeylen, A. Hoffer, M. O. Andreae, E. Tagliavini, F. Moretti, and P. Artaxo, Characterization of the organic composition of aerosols from Rondônia, Brazil, during the LBA-SMOCC 2002 experiment and its representation through model compounds, *Atmos. Chem. Phys.*, **6**, 375–402, 2006.

Falkovich, A. H., E. R. Graber, G. Schkolnik, Y. Rudich, W. Maenhaut, and P. Artaxo, Low molecular weight organic acids in aerosol particles from Rondônia, Brazil, during the biomass-burning, transition and wet periods, *Atmos. Chem. Phys.*, **5**, 781–797, 2005.

Fearnside, P. M., Fire in the tropical rain forests of the Amazon Basin, *in Fire in the Tropical Biota (Ecological Studies 84)*, edited by J. G. Goldammer, pp 106–115, Springer-Verlag, New York, 1990.

Gao, S., D. A. Hegg, P. V. Hobbs, T. W. Kirchstetter, B. I. Magi, and M. Sadilek, Water-soluble organic components in aerosols associated with savanna fires in southern Africa: Identification, evolution, and distribution, *J. Geophys. Res.*, **108**, 8491, doi:10.1029/2002JD002324, 2003.

Graham, B., O. L. Mayol-Bracero, P. Guyon, G. C. Roberts, S. Decesari, M. C. Facchini, P. Artaxo, W. Maenhaut, P. Koll, and M. O. Andreae, Water-soluble organic compounds in biomass burning aerosols over Amazonia-1. Characterization by NMR and GC-MS, *J. Geophys. Res.*, **107**, 8047, doi:10.1029/2001JD000336, 2002.

Hoell, J. M., D. D. Davis, S. C. Liu, R. Newell, M. Shipham, H. Akimoto, R. J. McNeal, R. J. Bendura, and J. W. Drewry, Pacific Exploratory Mission-West A (PEM-WEST A): September-October 1991, *J. Geophys. Res.*, **101**, 1641–1653, 1996.

Hoell, J. M., D. D. Davis, S. C. Liu, R. E. Newell, H. Akimoto, R. J. McNeal, and R. J. Bendura, The Pacific Exploratory Mission-West Phase B: February-March, 1994, *J. Geophys. Res.*, **102**, 28223–28239, 1997.

Hoffer, A., A. Gelencsér, M. Blaszó, P. Guyon, P. Artaxo, and M. O. Andreae, Diel and seasonal variations in the chemical composition of biomass burning aerosol, *Atmos. Chem. Phys.*, **6**, 3505–3515, 2006.

Huebert, B. J., T. Bates, P. B. Russel, G. Y. Shi, Y. J. Kim, K. Kawamura, G. Carmichael, and T. Nakajima, An overview of ACE-Asia: Strategies for quantifying the relationships between Asian aerosols and their climate impacts, *J. Geophys. Res.*, **108**, 8633, doi:10.1029/2003JD003550, 2003.

Kaufman, Y. J., and R. S. Fraser, The effect of smoke particles on clouds and climate forcing, *Science*, **277**, 1636–1639, 1997.

Kaufman, Y. J., D. Tanre, and O. Boucher, A satellite view of aerosols in the climate system, *Nature*, **419**, 215–223, 2002.

Kawamura, K., and K. Ikushima, Seasonal Changes in the distribution of dicarboxylic acids in the urban atmosphere, *Environ. Sci. Technol.*, **27**, 2227–2235, 1993.

Kawamura, K., and K. Usukura, Distribution of low molecular weight dicarboxylic acids in the North Pacific aerosol samples, *J. Oceanogra.*, **49**, 271–283, 1993.

Kawamura, K., and F. Sakaguchi, Molecular distributions of water soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropic, *J. Geophys. Res.*, 3501–3509, 1999.

Kawamura, K., M. Kobayashi, N. Tsubonuma, M. Mochida, T. Watanabe, and M. Lee, Organic and inorganic compositions of marine aerosols from East Asia: Seasonal variations of water soluble dicarboxylic acids, major ions, total carbon and nitrogen, and stable C and N isotopic composition, In: Geochemical Investigation in

Earth and Space Science; A Tribute to Issac R. Kaplan (eds. R. J. Hill et al.), *The Geochemical Society*, Publication Series No.9, Elsevier, 243–265, 2004.

Kerminen, V. -M., C. Ojanen, T. Pakkanen, R. Hillamo, M. Aurela, J. Merilainen, Low-molecular weight dicarboxylic acids in an urban and rural atmosphere, *J. Aerosol. Sci.*, **31**, 349–362, 2000.

Kim, Y. P., S. -G. Shim, K. C. Moon, C. -G. Hu, C. H. Kang, and K. Y. Park, Monitoring of air pollutants at Kosan, Cheju Island, Korea, during March-April 1994, *J. Appl. Meteorol.*, 1117–1126, 1998.

Kundu, S., K. Kawamura, T. W. Andreae, A. Hoffer, and M. O. Andreae, Diurnal variation in the water-soluble inorganic ions, organic carbon and isotopic compositions of total carbon and nitrogen in biomass burning aerosols from the LBA-SMOCC campaign in Rondônia, Brazil, *J. Aerosol. Sci.*, **41**, 118–133, 2010a.

Kundu, S., K. Kawamura, T. W. Andreae, A. Hoffer, and M. O. Andreae, Molecular distributions of dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls in biomass burning aerosols: Implications for photochemical production and degradation in smoke layers, *Atmos. Chem. Phys.*, **10**, 2209–2225, 2010b.

Kundu, S., K. Kawamura, and M. Lee, Seasonal variation of the concentrations of nitrogenous species and their nitrogen isotopic ratios in aerosols at Gosan, Jeju Island: Implications for atmospheric processing and source changes of aerosols, under revision in *J. Geophys. Res. -Atmos.*, 2010c.

Kundu, S., K. Kawamura, and M. Lee, Seasonal variations of diacids, ketoacids, and α-dicarbonyls in marine aerosols at Gosan, Jeju Island: Implications for their formation and degradation during long-range transport and sources, under revision in *J. Geophys. Res. -Atmos.*, 2010d.

Lee, M., M. Song, K. J. Moon, J. S. Han, G. Lee, and K. -R. Kim, Origins and chemical characteristics of fine aerosols during the northeastern Asia regional experiment (Atmospheric Brown Cloud-East Asia Regional Experiment 2005), *J. Geophys. Res.*, **112**, doi:10.1029/2006JD008210, 2007.

Legrand, M., S. Preunkert, T. Oliveira, C. A. Pio, S. Hammer, A. Gelencsér, A. Kasper-Giebl, and P. Laj, Origin of C_2-C_5 dicarboxylic acids in the European atmosphere inferred from year-around aerosol study conducted at a west-east transect, *J. Geophys. Res.*, **112**, D23S07, doi:10.1029/2006JD008019, 2007.

Martinelli, L. A., P. B. Camargo, L. B. L. S. Lara, R. L. Victoria, and P. Artaxo, Stable carbon and nitrogen isotopic composition of bulk aerosol particles in a C4 plant landscape of southeast Brazil, *Atmos. Environ.*, **36**, 2427, 2002.

Mayol-Bracero, O. L., P. Guyon, B. Graham, G. Roberts, M. O. Andreae, S. Decesari, M. C. Facchini, S. Fuzzi, and P. Artaxo, Water-soluble organic compounds in biomass burning aerosols over Amazonia-2. Apportionment of the chemical composition and importance of the polyacidic fraction, *J. Geophys. Res.*, **107**, 8091, doi:10.1029/2001JD000522, 2002.

Mircea, M., M. C. Facchini, S. Decesari, F. Cavalli, L. Emblico, S. Fuzzi, A. Vestin, J. Rissler, E. Swietlicki, G. Frank, M. O. Andreae, W. Maenhaut, Y. Rudich, and P. Artaxo, Importance of the organic aerosol fraction for modeling aerosol hygroscopic growth and activation: a case study in the Amazon basin, *Atmos. Chem. Phys.*, **5**, 3111–3126, 2005.

Mochida, M., A. Kawabata, K. Kawamura, H. Hatsushika, and K. Yamazaki, Seasonal variation and origins of dicarboxylic acids in the marine atmosphere over the western North Pacific, *J. Geophys. Res.*, **108**, 4193, doi:10.1029/2002JD002355, 2003a.

Mochida, M., K. Kawamura, N. Umemoto, M. Kobayashi, S. Matsunaga, H. -J. Lim, B. J. Turpin, T. S. Bates, and B. R. T. Simoneit, Spatial distributions of oxygenated organic compounds (dicarboxylic acids, fatty acids, and levoglucosan) in marine aerosols over the western Pacific and off the coast of East Asia: Continental outflow of organic aerosols during the ACE-Asia campaign, *J. Geophys. Res.*, **108**, 8638, doi:10.1029/2002JD003249, 2003b.

Narukawa, M., K. Kawamura, N. Takeuchi, and T. Nakajima, Distribution of dicarboxylic acids and carbon isotopic compositions in aerosols from 1997 Indonesian forest fires, *Geophys. Res. Lett.*, **26**, 3101–3104, 1999.

Narukawa, M., K. Kawamura, S. -M. Li, and G. W. Bottenheim, Stable carbon isotopic ratios and ionic composition of the high-Arctic aerosols: An increase in $\delta^{13}C$ values from winter to spring, *J. Geophys. Res. -Atmospheres*, *113*, doi: 10.1029/2007JD008755, 2008.

Novakov, T., and C. E. Corrigan, Cloud condensation nucleus activity of the organic component of biomass smoke particles, *Geophys. Res. Lett.*, **23**, 2141–2144, 1996.

Penner, J. E., C. C. Chuang, and K. Grant, Climate forcing by carbonaceous and sulfate aerosols, *Clim. Dyn.*, **14**, 839–851, 1998.

Ramanathan, V., P. J. Crutzen, J. T. Kiehl, and D. Rosenfeld, Atmosphere-Aerosols, climate, and the hydrological cycle, *Science*, **294**, 2119–2124, 2001.

Sempéré, R., and K. Kawamura, Trans-hemispheric contribution of C_2-C_{10} α,ω-dicarboxylic acids, and related polar compounds to water-soluble organic carbon in the western Pacific aerosols in relation to photochemical oxidation reactions, *Global. Biogeochem. Cycles*, **17**, 1069, doi:10.1029/2002GB001980, 2003.

Sherwood, S., A microphysical connection among biomass burning, cumulus clouds, and stratospheric moisture, *Science*, **295**, 1272–1275, 2002.

Skole, D. L., W. H. Chomentowski, W. A. Salas, and A. D. Nobre, Physical and human dimensions of deforestation in Amazonia, *Bioscience*, **44**, 314–322, 1994.

Solomon, P. A., J. L. Moyers, and R. Fletcher, High-Volume Dichotomous Virtual Impactor for the Fractionation and Collection of Particles According to Aerodynamic Size, *Aerosol Sci. Technol.*, **2**, 455, 1983.

Turekian, V. C., S. Macko, S. D. Ballentine, R. J. Swap, and M. Garstang, Causes of bulk carbon and nitrogen isotope fractionations in the products of vegetation burns: laboratory studies, *Chemical Geology*, **152**, 181, 1998.

Turekian, V. C., S. A. Macko, and W. C. Keene, Concentrations, isotopic compositions, and sources of size resolved, particulate organic carbon and oxalate in near-surface marine air at Bermuda during spring, *J. Geophys. Res. -Atmos.*, *108*, 4157, doi:10.1029/2002JD 002053, 2003.

Yang, H., J. Xu, W. Wu, C. H. Wan, and J. Z. Yu, Chemical characterization of water-soluble organic aerosols at Jeju Island collected during ACE-Asia, *Environ. Chem.*, **1**, 13–17, doi:10.1071/EN04006, 2004.