Stable hydrogen isotope ratios of *n*-alkanes in atmospheric aerosols from Okinawa, Japan

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Abstract

Molecular compositions of *n*-alkanes and their stable hydrogen isotope ratios (δD) were studied in atmospheric aerosols collected from Cape Hedo, Okinawa, Japan, to better understand the long-range atmospheric transport of organic aerosols from the Asian continent. The δD values of the C_{22}–C_{33} *n*-alkanes range from –201 to –115‰, being similar to those of typical fossil fuels and contemporary higher plant leaf waxes in Far East Asia. A correlation between the δD values and the carbon preference index (CPI) suggests that these *n*-alkanes originated from fossil fuel combustion residues and/or terrestrial higher plant waxes. The concentrations of fossil fuel-derived *n*-alkanes increased from mid-November 2009 to February 2010, which is consistent with the enhanced emission of coal-burning aerosols during the winter in China. δD values of the fossil fuel-derived *n*-alkanes (–174 ± 7‰) in the atmospheric aerosols from Okinawa are much lower (by up to 95‰) than those from Tokyo and Sapporo, Japan, suggesting that they are derived from multiple sources in East Asia and are delivered by complex transport processes.

1. Introduction

Atmospheric aerosols contain more than several thousand organic compounds, including *n*-alkanes, polycyclic aromatic hydrocarbons (PAHs), fatty acids, alkanols and water soluble sugars, mono- and dicarboxylic acids (Graedel et al., 1986). One fourth of global primary carbonaceous aerosols are generated in China (Streets et al., 2004), of which approximately 70% are from coal burning (Cooke et al., 1999). Previous studies have reported large amounts of combustion-derived organic compounds in aerosols from both urban and remote ocean sites in the East Asia-Pacific region, suggesting long-range atmospheric transport of pollutants from East Asian cities to the Pacific (Simoneit et al., 2004; Sato et al., 2007; 2008; Wang et al., 2009a, b). However, our knowledge of their sources and transport is still limited compared to integrated information of inorganic pollutants (e.g., Murano et al., 2000; Takami et al., 2007).

Homologous series of *n*-alkanes are one of ubiquitous components found in atmospheric aerosols (Simoneit et al., 1977). These compounds are directly emitted from biological and anthropogenic sources and can be long-range transported by winds because of their chemical stability and low vapor pressure. In general, *n*-alkanes ranging from C_{10} to C_{35} with no carbon number preference are emitted from various anthropogenic activities including fossil fuel combustion (mainly petroleum and coal) and biomass burning (Simoneit, 1984; Standley and Simoneit, 1987; Wang and Kawamura, 2005; Simoneit 2006; Schimidl et al., 2008a, b). In contrast, C_{25} to C_{35} *n*-alkanes with a strong odd carbon number predominance are primarily derived from terrestrial

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higher plant waxes (Eglington and Hamilton, 1967).

The carbon preference index (CPI) of *n*-alkanes has been often used to evaluate the anthropogenic contribution to atmospheric aerosols (e.g., Schefuß et al., 2003) because the CPI values of *n*-alkanes in higher plant waxes are generally larger than 5 (Eglinton and Hamilton, 1963; Mazurek and Simoneit, 1984), whereas those of fossil fuel-derived *n*-alkanes are close to unity (Simoneit and Mazurek, 1982; Kawamura and Kaplan, 1991). However, this interpretation contains much uncertainty because the CPI values of *n*-alkanes vary significantly in natural higher plants (1.4–40.3; Collister et al., 1994; Chikaraishi and Naraoka, 2003).

Recently, Yamamoto and Kawamura (2010) reported a strong negative correlation ($r^2 = \sim 0.76$) between the hydrogen isotopic compositions (δD) of C_{29} and C_{31} *n*-alkanes and the CPI values in urban aerosols from Tokyo. The relation is stronger than those observed between the δ^{13}C and the CPI of the *n*-alkanes, suggesting that the δD values of *n*-alkanes are potentially useful in estimating the relative contribution of terrestrial higher plants to fossil fuel sources. Further, the δD values of *n*-alkanes in fossil fuels exhibit much larger variations than their stable carbon isotope (δ^{13}C) do following their hydrogen sources and post depositional processes (Li et al., 2001; Schimmelmann et al., 2004; Xiong et al., 2005; Tuo et al., 2006; Kikuchi et al., 2010). Thus, the δD ratios of *n*-alkanes in atmospheric aerosols are expected to provide additional information about their sources and source regions.

In this study, we present δD values of *n*-alkanes in marine aerosols from Okinawa, Japan, where polluted air masses are transported from China by the Asian monsoon during winter (Sato et al., 2008). The ultimate objective of the study is to better understand the sources and transport pathways of anthropogenic *n*-alkanes in atmospheric aerosols from Okinawa.

2. Materials and methods

2.1. Aerosol sampling

Aerosol sampling was performed at Cape Hedo Atmosphere and Aerosol Measurement Station (CHAAMS, 26.9°N, 128.2°E) located at the north-western edge of Okinawa Island, Japan (Fig. 1). Air pollution from local anthropogenic activities are likely to be negligible because the northern part of the Okinawa Island is mostly covered with subtropical rain forests, and there is no major industry. Aerosol sampling was conducted on a weekly basis from 27 October 2009 to 13 April 2010. Total suspended particulate samples ($n = 25$) were collected on pre-combusted quartz filters (Pallflex 2500QAT, 20 cm × 25 cm) using a high-volume air sampler (Kimoto AS-810B) for 7 days at a flow rate of 60 m³/h. After the sampling, the filter was placed in a clean glass jar with a Teflon-lined screw cap, transported to the laboratory and stored in a freezer (–20℃) until analysis. Total aerosol mass was measured by weighing the filter before and after the aerosol sampling. Although the aerosol mass was not corrected for the contribution of sea salt, moisture was removed by placing the filter samples in a desiccator before weighing.

2.2. Extraction and separation of *n*-alkanes

n-Alkanes were extracted by using the method described in Yamamoto and Kawamura (2010). Briefly, a portion of the sample filter was extracted using DIONEX ASE-200 three times at 100℃ and 1000 psi
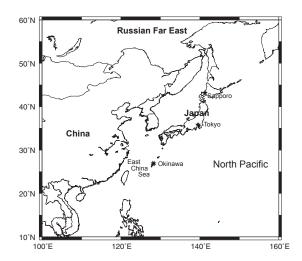

Fig. 1. Map showing the location of Cape Hedo, Okinawa, Japan.

for 5 min with 0.1 M KOH-methanol solution (10 ml) and by subsequent ultrasonication with dichloromethane (10 min × 3). The extracts were combined and concentrated under vacuum and then divided into neutral and acidic fractions. The aliphatic hydrocarbons (including *n*-alkanes) were separated from the neutral fraction using a silica gel column chromatography (1% H_2O deactivated) by elution with 1.5 ml of *n*-hexane.

Concentrations of *n*-alkanes were quantified by using a gas chromatograph/flame ionization detector (GC/FID, Hewlett-Packard 6890 GC) equipped with an on-column injector and a CP-Sil 5 CB fused silica capillary column (60 m × 0.32 mm i.d., 0.25 μm film thickness). Helium was used as a carrier gas. The GC oven temperature was programmed from 50 to 120℃ at 30℃/min, then to 310℃ at 5℃/min and held isothermally for 25 min. Authentic C_{29} and C_{32} *n*-alkanes were used as external standards for this quantification. The carbon preference index (CPI) is calculated as follows:

$$CPI = 0.5 \times [\Sigma(C_{25}-C_{35}) \text{odd} / \Sigma(C_{24}-C_{34}) \text{even} + \Sigma(C_{25}-C_{35}) \text{odd} / \Sigma(C_{26}-C_{36}) \text{even}],$$

where C is the abundance of each *n*-alkane (Bray and Evans, 1961).

Structural identification of *n*-alkanes was performed with a GC/mass spectrometer (GC/MSD, Hewlett-Packard 6890 GC/5973 Mass Selective Detector) equipped with a HP-5MS fused silica column (30 m × 0.25 mm i.d., 0.25 μm film thickness). The temperature program for GC oven was the same as for GC analysis. The components were identified by the comparison of their GC retention times and mass spectra with those of references (authentic *n*-alkanes).

2.3. Compound-specific stable hydrogen isotope analysis

Hydrogen isotopic compositions of individual *n*-alkanes were determined by using GC/isotope ratio mass spectrometer (GC/IRMS, Hewlett-Packard 6890 GC/ Finnigan MAT Delta Plus XL IRMS). Conversion of *n*-alkanes to H_2 was performed at 1450℃ (Yamamoto and Kawamura, 2010). The GC was equipped with an on-column injector and DB-5MS fused silica capillary

column (30 m × 0.32 mm i.d., 0.25 μm film thickness). The GC oven temperature was programmed from 50 to 120℃ at 10℃/min, and to 310℃ at 4℃/min, and then held isothermally for 25 min. Helium was used as a carrier gas at a flow rate of 1.5 ml/min. One to two μl of samples were injected with an internal standard (C_{20} *n*-alkanoic acid methyl ester; $\delta D = -166.7 \pm 0.3$‰, Indiana University, USA). An example of a typical GC/ IRMS trace for the *n*-alkanes in the aerosol samples from Okinawa is shown in Fig. 2. The D/H ratios of *n*-alkanes are reported in the delta notation with respect to the Vienna Standard Mean Ocean Water (VSMOW) as follows:

$$\delta D \, (\text{‰}) = [(D/H)_{sample} / (D/H)_{VSMOW} - 1] \times 1000$$

Prior to the sample measurement, a standard mixture containing C_{16} to C_{30} *n*-alkanes was injected into the GC/IRMS to assess the condition of the machine. Analytical accuracy and precision of the standards was generally within ±5‰ and 4‰, respectively, when a minimum sample of 35 ng H was used. Most samples were analyzed in duplicate, and the mean values are reported.

3. Results and discussion

3.1. Origin of *n*-alkanes in the atmospheric aerosols from Okinawa, Japan

A series of C_{21} to C_{36} *n*-alkanes are detected as major hydrocarbons in the aerosols collected from Okinawa, Japan, with a predominance of C_{27}, C_{29} and C_{31} homologues (Fig. 3a). Short chain (C_{21} and C_{22}) *n*-alkanes
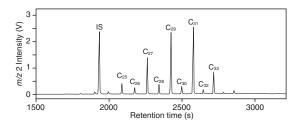
Fig. 2. A GC/IRMS trace of *m/z* 2 for *n*-alkanes from a marine aerosol sample (OKI102) collected at Cape Hedo, Okinawa, Japan. IS, internal standard (C_{20} *n*-alkanoic acid methyl ester).

show no odd/even carbon number predominance (Fig. 3a), indicating a large contribution from vehicular exhausts and fossil fuel (petroleum and coal) combustion residues. In contrast, long chain (C_{23}–C_{36}) n-alkanes exhibit an odd/even carbon number predominance ($CPI_{25-35} = 3.8 \pm 1.1$; Fig. 3a), suggesting contributions from both fossil fuel components and terrestrial higher plant waxes. Total concentrations of n-alkanes range from 1.7 to 9.0 ng m^{-3} (average 4.7 ng m^{-3}; Table 1), being similar to those reported for 2008 spring samples from the same site (Wang et al., 2009b).

Stable hydrogen isotopic compositions (δD) of the n-alkanes range from –201 to –115‰ (Fig. 3b; Table 1). The δD values of C_{22} to C_{24} n-alkanes show gradual decreases with an increase in the number of carbon atoms. The δD values of C_{26} to C_{32} even-carbon numbered n-alkanes (–178 to –115‰) are slightly enriched in deuterium compared with their odd-carbon

numbered homologues (Fig. 3b). A similar sawtooth pattern was previously reported in urban aerosols from Tokyo where the n-alkanes could also be derived from both terrestrial higher plants and fossil fuel combustion residues (Yamamoto and Kawamura, 2010). However, we cannot distinguish more detailed origins in the Okinawa aerosols from only the δD values because they are similar to both those of typical fossil fuel sources (mainly coal and petroleum; –234 to –61‰; Li et al., 2001; Xiong et al., 2005; Tuo et al., 2006) and to those of contemporary higher plant leaf waxes in Far East Asia (–185 to –145‰; Chikaraishi and Naraoka, 2007) (Fig. 3b).

In Fig. 4, we plot the δD values of the n-alkanes against CPI values to estimate relative contribution from fossil fuels and terrestrial higher plant waxes. The δD values of the C_{23} and C_{25} n-alkanes show a positive correlation with the CPI values (r^2 = 0.44 to 0.66), suggesting a combined contribution from terrestrial higher plant waxes and fossil fuel hydrocarbons. In contrast, the δD of the C_{22} and C_{24} n-alkanes show no relation with CPI values (r^2 = ～0.04; Fig. 4). These n-alkanes are found most abundantly in fossil fuels (Rogge et al., 1993) but are generally absent in terrestrial higher plant waxes (Eglinton and Hamilton, 1967). Thus, the lack of relation suggests that the even-chain components are mainly derived from fossil fuel combustion residues.

On the other hand, the δD values of the C_{26} to C_{33} n-alkanes show a weak negative correlation with the CPI values (r^2 = 0.09 to 0.32) except for the C_{31} and C_{33} n-alkanes (Fig. 4). Although the relation is not statistically significant for the C_{26}, C_{27}, C_{29}, C_{30} and C_{32} n-alkanes, such a trend suggests that these hydrocarbons have a mixed origin from terrestrial higher plants and fossil fuel combustion residues. In contrast, the δD values of the C_{31} and C_{33} n-alkanes show no relation with the CPI values (r^2 = ～0.04; Fig. 4). Because these n-alkanes are major constituents of plant waxes (Eglinton and Hamilton, 1967), this lack of relation should be interpreted to mean that they are unlikely to be contributed from fossil fuel combustion residues.
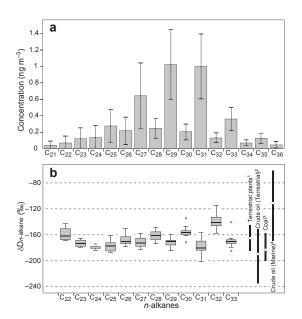

Fig. 3. Chain-length distributions of n-alkanes in aerosol samples from Okinawa, Japan, (a) and box plots of their δD values (b). Each box shows the median (black line), the interquartile range (box), and the min and max values that are not outliers (whiskers), and outliers (open circles). The δD ranges of n-alkanes (C_{21-36}) in terrestrial higher plant and typical fossil fuel sources are also shown in the right hand side of the lower column [[1]Chikaraishi and Naraoka (2007); [2]Xiong et al., (2005); [3]Tuo et al., (2006); [4]Li et al. (2001)].

Table 1. Concentrations and stable hyrogen (δD) isotope compositions of individual *n*-alkanes, CPI in the atmospheric aerosols from Okinawa, Japan

Sample	OKI081	OKI083	OKI084	OKI085	OKI086	OKI087	OKI088	OKI089	OKI090	OKI091	OKI092	OKI093	OKI094	OKI095	OKI096	OKI097	OKI098	OKI099	OKI100	OKI101	OKI102	OKI103	OKI104	OKI105
Start date	Oct 27, 2009	Nov 3, 2009	Nov 10, 2009	Nov 17, 2009	Nov 24, 2009	Dec 1, 2009	Dec 8, 2009	Dec 15, 2009	Dec 22, 2009	Dec 29, 2009	Jan 5, 2010	Jan 12, 2010	Jan 19, 2010	Jan 26, 2010	Feb 2, 2010	Feb 9, 2010	Feb 16, 2010	Feb 23, 2010	Mar 2, 1010	Mar. 9, 2010	Mar. 16, 2010	Mar. 23, 2010	Mar. 30, 2010	Apr. 6, 2010
[a]TSP ($\mu g\,m^{-3}$)	57.3	86.6	133.0	165.5	52.3	151.0	37.5	62.3	53.0	79.4	85.0	59.2	66.9	52.9	52.0	123.0	48.6	123.5	81.5	170.4	286.1	95.1	89.7	101.0
Concentration (ng m^{-3} air)																								
C_{21}	0.02	0.00	0.00	0.00	0.03	0.06	0.00	0.08	0.01	0.09	0.02	0.20	0.14	0.05	0.01	0.00	0.03	0.01	0.00	0.01	0.04	0.04	0.01	0.01
C_{22}	0.02	0.00	0.01	0.01	0.07	0.14	0.02	0.18	0.02	0.17	0.05	0.32	0.25	0.09	0.03	0.01	0.05	0.01	0.00	0.03	0.04	0.06	0.01	0.01
C_{23}	0.05	0.02	0.01	0.01	0.12	0.25	0.04	0.30	0.06	0.31	0.10	0.45	0.40	0.18	0.07	0.02	0.10	0.04	0.01	0.07	0.11	0.12	0.03	0.02
C_{24}	0.05	0.02	0.01	0.01	0.15	0.28	0.04	0.36	0.07	0.38	0.12	0.45	0.46	0.20	0.09	0.03	0.10	0.05	0.01	0.09	0.07	0.13	0.03	0.02
C_{25}	0.21	0.36	0.07	0.06	0.27	0.45	0.12	0.54	0.18	0.62	0.25	0.66	0.74	0.36	0.26	0.08	0.21	0.18	0.06	0.28	0.26	0.27	0.13	0.12
C_{26}	0.15	0.14	0.04	0.05	0.23	0.37	0.13	0.43	0.14	0.52	0.21	0.52	0.62	0.32	0.27	0.07	0.17	0.18	0.05	0.20	0.16	0.19	0.07	0.09
C_{27}	0.89	2.09	0.32	0.30	0.54	0.83	0.33	0.73	0.40	0.95	0.51	0.97	0.97	0.80	0.61	0.20	0.37	0.54	0.25	0.79	0.80	0.77	0.43	0.35
C_{28}	0.24	0.18	0.08	0.10	0.24	0.40	0.19	0.38	0.17	0.44	0.23	0.45	0.48	0.35	0.28	0.10	0.17	0.26	0.12	0.33	0.25	0.25	0.13	0.17
C_{29}	1.52	0.79	0.42	0.48	1.06	1.62	0.65	1.31	0.81	1.61	0.99	1.83	1.47	1.25	1.10	0.40	0.64	0.95	0.46	1.17	1.43	1.42	0.83	0.72
C_{30}	0.26	0.17	0.09	0.10	0.19	0.32	0.16	0.25	0.13	0.34	0.16	0.41	0.33	0.32	0.23	0.09	0.12	0.20	0.09	0.20	0.19	0.28	0.12	0.16
C_{31}	1.61	1.47	0.54	0.52	0.91	1.42	0.60	1.21	1.06	1.28	0.90	1.61	1.30	1.10	1.06	0.39	0.56	0.82	0.39	1.10	1.57	1.35	0.88	0.73
C_{32}	0.20	0.14	0.06	0.08	0.13	0.23	0.10	0.18	0.07	0.16	0.09	0.21	0.18	0.22	0.15	0.06	0.07	0.13	0.06	0.14	0.10	0.16	0.09	0.13
C_{33}	0.62	0.45	0.23	0.24	0.33	0.53	0.22	0.46	0.28	0.39	0.28	0.57	0.44	0.56	0.38	0.14	0.20	0.30	0.14	0.44	0.44	0.47	0.33	0.33
C_{34}	0.11	0.10	0.03	0.04	0.07	0.12	0.05	0.08	0.04	0.09	0.04	0.11	0.09	0.12	0.08	0.03	0.04	0.05	0.03	0.06	0.04	0.08	0.04	0.08
C_{35}	0.23	0.16	0.08	0.10	0.12	0.20	0.08	0.17	0.06	0.12	0.08	0.20	0.15	0.25	0.13	0.04	0.06	0.09	0.05	0.14	0.09	0.16	0.09	0.12
C_{36}	0.04	0.04	0.01	0.02	0.04	0.07	0.03	0.04	0.02	0.05	0.02	0.06	0.06	0.06	0.05	0.02	0.02	0.03	0.02	0.03	0.02	0.04	0.02	0.05
[b]CPI$_{25-35}$	4.9	7.0	5.0	4.3	3.2	2.9	2.9	2.6	4.4	2.6	3.5	2.7	2.4	2.8	3.1	3.3	3.1	3.2	3.7	3.8	5.7	4.0	5.5	3.5
δD (‰ vs. VSMOW)																								
C_{22}	nd	nd	nd	nd	nd	−169	nd	−143	nd	−158	nd	nd	−165	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
C_{23}	nd	nd	nd	nd	nd	−171	nd	−176	nd	−179	−165	−168	−177	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
C_{24}	nd	nd	nd	nd	−183	−174	nd	−178	nd	−182	−178	−179	−178	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
C_{25}	−168	nd	nd	nd	−178	−170	−176	−184	−185	−185	−181	−173	−186	−187	nd	nd	nd	−177	nd	−171	−160	−172	nd	nd
C_{26}	−170	nd	nd	nd	−166	−169	−149	−169	−178	−173	−177	−158	−170	−173	nd	nd	nd	−154	nd	−160	−173	−175	nd	nd
C_{27}	−180	nd	nd	nd	−177	−163	−174	−171	−182	−174	−174	−167	−170	−178	nd	nd	nd	−162	nd	−163	−182	−171	nd	−157
C_{28}	−161	nd	nd	nd	−170	−156	−160	−156	−169	−164	−172	−152	−152	−162	nd	nd	nd	−155	nd	−161	−173	−165	nd	−148
C_{29}	−170	nd	nd	nd	−174	−176	−179	−172	−183	−170	−169	−168	−166	−175	−165	nd	nd	−169	nd	−159	−184	−175	nd	−160
C_{30}	−161	nd	nd	nd	−159	−151	−147	−156	−154	−157	−160	−161	−153	−160	nd	nd	nd	−156	nd	−156	−171	−159	nd	−134
C_{31}	−167	nd	nd	nd	−183	−184	−185	−180	−201	−182	−182	−176	−177	−183	−168	nd	nd	−169	nd	−167	−194	−176	nd	−157
C_{32}	−146	nd	nd	nd	−138	−139	nd	−115	−148	−133	−158	nd	nd	nd	nd	nd	nd	−143	nd	−144	nd	nd	nd	−124
C_{33}	−165	nd	nd	nd	−172	−170	−168	−170	−184	−174	−173	−172	−167	−175	nd	nd	nd	−169	nd	−165	−179	−170	nd	−141

Notes: nd, not determined; [a]a total suspended particles; [b]CPI $= 0.5 \times [\Sigma(C_{23}-C_{35})\,\text{odd}\,/\,\Sigma(C_{22}-C_{34})\,\text{even}) + \Sigma(C_{23}-C_{35})\,\text{odd}\,/\,\Sigma(C_{24}-C_{36})\,\text{even}]$, where C is abundance of each *n*-alkane.

3.2. Transport of anthropogenic *n*-alkanes from the Asian continent

In Fig. 5, we present temporal variations of the concentrations of fossil fuel (anthropogenic; C_{22} and C_{24}) and terrestrial higher plant-derived (biogenic; C_{31} and C_{33}) *n*-alkanes, together with the abundance of anthropogenic *n*-alkanes relative to total (anthropogenic + biogenic) *n*-alkanes. The C_{29} *n*-alkane was not included in Fig. 5 because this source is influenced slightly by anthropogenic sources (see section 3.1). The concentrations of anthropogenic *n*-alkanes (0.01 to 0.8 ng m^{-3}) are generally lower than those of biogenic *n*-alkanes (0.5 to 2.2 ng m^{-3}); however, we found sharp increases in the relative abundance of anthropogenic *n*-alkanes in the OKI 086, 087, 089, 091, 093, 094, 095 and 098

samples (Solid arrows in Fig. 5).

In urban areas of inland China, the concentrations of fossil fuel-derived hydrocarbons are generally 3–30 times higher in winter than the rest of the year due to a large usage of coal for heating and an enhanced development of atmospheric inversion layers (Wang and Kawamura, 2005; Wang et al., 2006; Wang et al., 2009b). In contrast, the emission source strengths of pollutants in Japanese cities show a weak dependence on the season (Sato et al., 2008), and also the concentrations of fossil fuel-derived *n*-alkanes (14–36 ng m^{-3}; Tang et al., 2005) are much lower than those in Chinese cities (14–701 ng m^{-3}; Wang et al., 2006). The concentration of fossil fuel-derived *n*-alkanes in the aerosols from the remote site
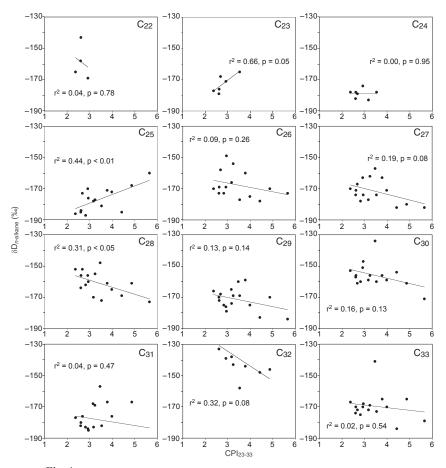
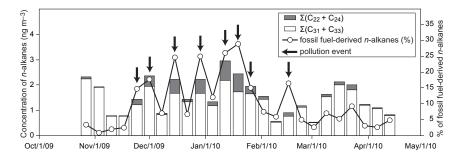**Fig. 4.** Cross plots of the δD of $C_{22} - C_{33}$ n-alkanes as a function of CPI values.

Fig. 5. Temporal variations in the concentrations of fossil fuel (C_{22} and C_{24}) and terrestrial higher plant-derived (C_{31} and C_{33}) n-alkanes, together with relative abundance of fossil fuel-derived n-alkanes to total n-alkanes.

in Okinawa gradually increased from mid-November 2009 to February 2010 (Fig. 5), which can be consistently explained by enhanced emission and long-range transport of fossil fuel (coal) combustion residues from China during winter.

3.3. Stable hydrogen isotopic compositions of fossil fuel-derived n-alkanes in aerosols from Okinawa

The δD values of combustion-derived organic compounds generally depend on the type of fossil fuels and their combustion processes. For example, polycyclic

aromatic hydrocarbons (PAHs) derived from combustion of jet fuel are depleted in deuterium (by up to ～25‰) relative to those derived from combustion of gasoline, whereas PAHs derived from high-temperature combustion are depleted in deuterium (ca. 40‰) as compared to those derived from low temperature combustion (Sun et al., 2003). The fossil fuel-derived (C_{22} and C_{24}) *n*-alkanes in the aerosols from Okinawa (–183 to –161‰) exhibit significantly lower δD values (by ～95‰) than those from Tokyo (–78 ± 5‰; Yamamoto and Kawamura, 2010) and Sapporo (–122‰; Yamamoto and Kawamura, 2011), suggesting that they are likely produced from different fossil fuel sources and/or combustion processes.

As we discussed above, the atmospheric aerosols from Okinawa are probably affected by long-range transport of coal combustion residues from China (see section 3.2; Sato et al., 2008) in which the δD values of *n*-alkanes are clearly lower (by up to 140‰) than marine crude oil (Li et al., 2001; Xiong et al., 2005). Although we need to confirm that the *n*-alkanes in vehicle exhaust and coal combustion residues are isotopically stable in combustion processes, large variability (by up to 95‰) in the *n*-alkane δD values in the atmospheric aerosols within Japan suggests that the δD analysis of fossil fuel-derived *n*-alkanes in the atmospheric aerosols may provide detailed information on their sources and source regions in East Asia.

4. Summary and conclusions

Molecular compositions of *n*-alkanes and their stable hydrogen isotope ratios (δD) were investigated in atmospheric aerosols from Cape Hedo, Okinawa, Japan, to better understand the long-range transport of organic pollutants from the Asian continent. Considering the correlation between δD and CPI values, we suggest that at least C_{22} and C_{24} *n*-alkanes originate mainly from fossil fuel combustion residues. The concentrations of these *n*-alkanes significantly increased during mid-November 2009 to February 2010, which is consistent with the enhanced emission of coal burning aerosols in this season in China and which suggests

their long-range atmospheric transport to Okinawa. Moreover, the δD ratios of fossil fuel-derived *n*-alkanes from the Okinawa samples exhibit significantly lower values (by ～95‰) than those from Tokyo and Sapporo, suggesting that they originate from multiple sources in East Asia and are delivered by complex transport processes to Okinawa.

References

Bray E.E. and Evans E.D. (1961) Distribution of *n*-paraffins as a clue to recognition of source beds. *Geochim. Cosmochim. Acta* **22**, 2-15.

Chikaraishi Y. and Naraoka H. (2003) Compound-specific δD−δ^{13}C analyses of *n*-alkanes extracted from terrestrial and aquatic plants. *Phytochemistry* **63**, 361-371.

Chikaraishi Y. and Naraoka H. (2007) δ^{13}C and δD relationships among three *n*-alkyl compound classes (*n*-alkanoic acid, *n*-alkane and *n*-alkanol) of terrestrial higher plants. *Org. Geochem.* **38**, 198-215.

Collister J.W., Rieley G., Stern B., Eglinton G. and Fry B. (1994) Compound-specific δ^{13}C analyses of leaf lipids from plants with differing carbon dioxide metabolisms. *Org. Geochem.* **21**, 619-627.

Cooke W.F., Liousse C., Cachier H. and Feichter J.

(1999) Construction of a $1° \times 1°$ fossil fuel emission data set for carbonaceous aerosol and implementation and radiative impact in the ECHAM4 model. *J. Geophys. Res.* **104**, 22137-22162.

Eglinton G. and Hamilton R.J. (1963) The distribution of *n*-alkanes. *In* Swain, T., ed., *Chemical Plant Taxonomy*, Academic Press, 187-217.

Eglinton G. and Hamilton R.J. (1967) Leaf epicuticular waxes. *Science* **156**, 1322-1335.

Graedel T.E., Hawkins D.T. and Claxton L.D. (1986) *Atmospheric chemical compounds: sources, occurrence, and bioassay.* Academic Press, Orlando, Florida.

Kawamura K. and Kaplan I.R. (1991) Organic compounds in rainwater. *In* Hansen, L.D. and Eatough, D.J., eds., *Organic chemistry of the atmosphere*, CRC Press, Boca Raton, 233-284.

Kikuchi T., Suzuki N. and Saito H. (2010) Change in hydrogen isotope composition of *n*-alkanes, pristine, phytane, and aromatic hydrocarbons in Miocene siliceous mudstone with increasing maturity. *Org. Geochem.* **41**, 940-946.

Li M., Huang Y., Obermajer M., Jiang C., Snowdon L.R. and Fowler M.G. (2001) Hydrogen isotopic compositions of individual alkanes as a new approach to petroleum correlation: case studies from the Western Canada Sedimentary Basin. *Org. Geochem.* **32**, 1387-1399.

Mazurek M.A. and Simoneit B.R.T. (1984) Characterization of biogenic and petroleum-derived organic matter in aerosols over remote, rural and urban areas. *In* Keith, L.H., ed., *Identification and Analysis of Organic Pollutants in Air*, Ann Arbor Science, Butterworth Publishers, 353-370.

Murano K., Mukai H., Hatkeyama S., Jang E.S. and Uno I. (2000) Trans-boundary air pollution over remote islands in Japan: observed data and estimates from a numerical model. *Atmos. Environ.* **34**, 5139-5149.

Rogge W.F., Hildemann L.M., Mazurek M.A., Cass G.R. and Simoneit, B.R.T. (1993) Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. *Environ. Sci.*

Technol. **27**, 636-651.

Sato K., Tanaka Y., Li H., Ogawa S. and Hatakeyama S. (2007) Distributions and seasonal changes of organic aerosols at Cape Hedo, Okinawa: polycyclic aromatic hydrocarbons observed during 2005-2006. *Chikyukagaku (Geochemistry)* **41**, 145-153.

Sato K., Li H., Tanaka Y., Ogawa S., Iwasaki Y., Takami A. and Hatakeyama S. (2008) Long-range transport of particulate polycyclic aromatic hydrocarbons at Cape Hedo remote island site in the East China Sea between 2005 and 2008. *J. Atmos. Chem.* **61**, 243-257.

Schefuß E., Ratmeyer V., Stuut J.-B.W., Jansen J.H.F. and Sinninghe Damsté J.S. (2003) Carbon isotope analysis of *n*-alkanes in dust from the lower atmosphere over the central eastern Atlantic. *Geochim. Cosmochim. Acta* **67**, 1757-1767.

Schimidl C., Bauer H., Dattler A., Hitzenberger R., Weissenboeck G., Marr I.L. and Puxbaum H. (2008a) Chemical characterization of particle emissions from burning leaves. *Atmos. Environ.* **42**, 9070-9079.

Schimidl C., Marr I.L., Caseiro A., Kotianova P., Berner A., Bauer H., Kasper-Giebl A. and Puxbaum H. (2008b) Chemical characterization of fine particle emissions from wood stove combustion of common woods growing in mid-European Alpine regions. *Atmos. Environ.* **42**, 126-141.

Schimmelmann A. Sessions A.L. Boreham C.J. Edwards D.S. Logan G.A. and Summons R.E. (2004) D/H ratios in terrestrially sourced petroleum systems. *Org. Geochem.* **35**, 1169-1195.

Simoneit B.R.T. (1984) Organic matter of the troposphere－Ⅲ. Characterization and sources of petroleum and pyrogenic residues in aerosols over the western United States. *Atmos. Environ.* **18**, 51-67.

Simoneit B.R.T. (2006) Atmospheric transport of terrestrial organic matter to the sea. *In* Volkman, J.K., ed., *Hdb. Environ. Chem.* 2, Springer Berline, Heidelberg, 165-208.

Simoneit B.R.T. and Mazurek M.A. (1982) Organic matter of the troposphere－Ⅱ. Natural background of biogenic lipid matter in aerosols over the rural western United States. *Atmos. Environ.* **16**, 2139-2159.

Simoneit B.R.T., Chester R. and Eglinton G. (1977) Biogenic lipids in particulates from the lower atmosphere over the eastern Atlantic. *Nature* **267**, 682-685.

Simoneit B.R.T., Kobayashi M., Mochida M., Kawamura K., Lee M., Lim H.-J., Turpin B.J. and Komazaki Y. (2004) Composition and major sources of organic compounds of aerosol particulate matter sampled during the ACE-Asia campaign. *J. Geophys. Res.* **109**, D19S10, doi:10.1029/2004JD004598.

Standley L.J. and Simoneit B.R.T. (1987) Characterization of extractable plant wax, resin, and thermally matured components in smoke particles from prescribed burns. *Environ. Sci. Technol.* **21**, 163-169.

Streets D.G., Bond T.C., Lee T. and Jang C. (2004) On the future of carbonaceous aerosol emissions. *J. Geophys. Res.* **109**, D24212, doi:10.1029/2004JD004902.

Sun C., Cooper M. and Snape C.E. (2003) Use of compound-specific δ^{13}C and δD stable isotope measurements as an aid in the source apportionment of polyaromatic hydrocarbons. *Rapid Commun. Mass Spectrom.* **17**, 2611-2613.

Takami A., Miyoshi T., Shimono A., Kaneyasu N., Kato S., Kajii Y. and Hatakeyama S. (2007) Transport of anthropogenic aerosols from Asia and subsequent chemical transformation. *J. Geophys. Res* **112**, D22S31, doi:10.1029/2006JD008120.

Tang N., Hattori T., Taga R., Igarashi K., Yang X., Tamura K., Kakimoto H., Mixhukov V.F., Toriba A., Kuzu R. and Hayakawa K. (2005) Polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in urban air particulates and their relationship to emission sources in the Pan-Japan Sea countries. *Atmos. Envioron.* **39**, 5817-5826.

Tuo J., Zhang M., Wang X. and Zhang C. (2006) Hydrogen isotope ratios of aliphatic and diterpenoid hydrocarbons in coals and carbonaceous mudstones from the Liaohe Basin, China. *Org. Geochem.* **37**, 165-176.

Wang G. and Kawamura K. (2005) Molecular characteristics of urban organic aerosols from Nanjing: A case study of a mega-city in China. *Environ. Sci. Technol.* **39**, 7430-7438.

Wang G., Kawamura K., Lee S., Ho K. and Cao J. (2006) Molecular, seasonal, and spatial distributions of organic aerosols from fourteen Chinese cities. *Environ. Sci. Technol.* **40**, 4619-4625.

Wang G., Kawamura K. and Lee M. (2009a) Comparison of organic compositions in dust storm and normal aerosol samples collected at Gosan, Jeju Island, during spring 2005. *Atmos. Environ.* **43**, 219-227.

Wang G., Kawamura K., Xie M., Hu S., Gao S., Cao J., An Z. and Wang Z. (2009b) Size-distribution of *n*-alkanes, PAHs and hopanes and their sources in the urban, mountain and marine atmospheres over East Asia. *Atmos. Chem. Phys.* **9**, 8869-8882.

Xiong Y., Geng A., Pan C., Liu D. and Peng P. (2005) Characterization of the hydrogen isotopic composition of individual *n*-alkanes in terrestrial source rocks. *Appl. Geochem.* **20**, 455-464.

Yamamoto S. and Kawamura K. (2010) Compound-specific stable carbon and hydrogen isotopic compositions of *n*-alkanes in urban atmospheric aerosols from Tokyo. *Geochem. J.* **44**, 419-430.

Yamamoto S. and Kawamura K. (2011) Application of urea adduction technique to polluted urban aerosols for the determination of hydrogen isotopic composition of *n*-alkanes. *Intl. J. Environ. Anal. Chem.*, doi:10.1080/03067310903045505.