

Seasonal changes in TC and WSOC and their ^{13}C isotope ratios in Northeast Asian aerosols: land surface–biosphere–atmosphere interactions

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Abstract In order to understand the relative importance of anthropogenic and biological sources of carbonaceous aerosols in Northeast Asia, we measured total carbon (TC) and water-soluble organic carbon (WSOC) and their stable carbon isotope ratios ($\delta^{13}\text{C}$) in total suspended particulates collected from Sapporo, northern Japan (43.07°N, 141.36°E) over a 1-year period (during 2 September 2009 and 5 October 2010). Temporal variations of TC showed a gradual decrease from mid-autumn to winter followed by a gradual increase to growing season with a peak in early summer. Both $\delta^{13}\text{C}_{\text{TC}}$ and $\delta^{13}\text{C}_{\text{WSOC}}$ showed very similar temporal trends with a gradual enrichment of ^{13}C from mid-autumn to winter followed by a depletion in the ^{13}C to early summer and thereafter it remained stable, except for few cases. Based on the results obtained together with the air mass trajectories, we found that biogenic emissions including biological particles (e.g., pollen) and secondary organic aerosol formation from biogenic volatile organic compounds are the important sources of carbonaceous aerosols in spring/summer whereas fungal spores from soil and biomass burning and enhanced fossil fuel combustion contribute significantly in autumn/winter and in winter, respectively, in Northeast Asia.

Keywords Carbonaceous aerosols · Stable carbon isotope ratios · Sources · Northeast Asia

1 Introduction

Aerosol loadings are commonly observed to be high in the East Asian atmosphere. Carbonaceous aerosols, particularly organics, represent a large (up to 90%) fraction of the submicron aerosols (Kanakidou et al. 2005). While elemental carbon (EC) emits from only fossil fuel combustion and biomass burning, organic aerosols (OA) are emitted directly from fossil fuel combustion, biomass burning, soil dust and biota and also produced in the atmosphere by photo-oxidation of gaseous precursors emitted from various sources including plants, biomass burning, and fossil fuel combustion (Robinson et al. 2007). Carbonaceous aerosols have serious impacts on the Earth's climate system directly by scattering and absorbing solar radiation and indirectly by acting as cloud condensation nuclei and cause adverse effects on human health (Ramanathan et al. 2001). East Asian aerosols are further transported long distances over the Pacific Ocean and thus impact the climate changes at regional to global scales.

Over the past two decades, the study of East Asian aerosols has received a great attention including large-scale field experiments such as ACE-Asia (Aerosol Characterization Experiments over East Asia and western Pacific region), EAREX 2005 (East Asian Regional Experiment 2005) etc. (Nakajima et al. 2007 and references therein). They provided invaluable information and suggested that fossil fuel combustion followed by biomass burning and soil dust are the major sources of atmospheric aerosols including OA in this region. However, on the contrary, global models predict that biomass burning emissions and

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SOA formation from biogenic volatile organic compounds (BVOCs) are the two major sources of OA (Kanakidou et al. 2005). The relative importance of such sources has not been understood yet in East Asia.

Stable carbon isotope ratios ($\delta^{13}\text{C}$) of total carbon (TC) and organic compounds are very useful for investigating the sources and long-range atmospheric transport of organic aerosols (Pavuluri et al. 2011 and references therein). Here, we report the TC and water-soluble organic carbon (WSOC) contents and their $\delta^{13}\text{C}$ measured in atmospheric aerosols (TSP) collected from Sapporo, northern Japan, an ideal site for studying the air masses delivered from Siberia, China and surrounding oceans, over a 1-year period. Based on seasonal variations in concentrations and $\delta^{13}\text{C}$ of TC and WSOC together with the local meteorological data and backward air mass trajectories, we discuss the influence of biological activity on atmospheric loading of carbonaceous aerosols over Northeast Asia.

2 Materials and methods

2.1 Aerosol sampling

Site description and details of aerosol (TSP) sampling are provided elsewhere (Pavuluri et al. 2013). Briefly, Sapporo is located in the western part of the Hokkaido Island, northern Japan (43.07N, 141.36E). The input of organics into the Sapporo atmosphere is expected to be small from local emissions and hence, the source regions and composition of carbonaceous aerosols in Sapporo are mainly controlled by the East Asian monsoon. Aerosol sampling ($n = 21$) was performed on the rooftop (~ 20 m AGL) of the Institute of Low Temperature Science building, Hokkaido University, Sapporo during 2 September 2009 and 5 October 2010 using a pre-combusted quartz fiber filter and high volume air sampler. Each sample was collected for ~ 2 consecutive weeks to obtain sufficient amount of carbon for ^{14}C analyses at organic molecular levels, another objective of this research, and placed in a pre-combusted glass jar with a Teflon-lined screw cap and stored in dark cold room at -20 °C prior to analysis.

It should be noted that since the sampling time is long (~ 2 weeks), the negative (volatilization of semi-volatile organics from the particles) sampling artifacts should be more significant rather than positive (adsorption of gas phase organics onto the filter) sampling artifacts and thus the reported concentrations may be underestimated. However, based on the comparability of the concentration ratios of lower molecular weight (≤ 4 rings) polycyclic aromatic hydrocarbons (PAHs) to higher molecular weight (≥ 5 rings) PAHs for different seasons (Pavuluri et al. 2013), we

consider that the evaporative loss of the organics is minimal.

2.2 Chemical analysis

TC and WSOC contents and their ^{13}C isotope ratios ($\delta^{13}\text{C}_{\text{TC}}$ and $\delta^{13}\text{C}_{\text{WSOC}}$, respectively) are determined using an elemental analyzer (EA) (Carlo Erba NA 1500) and an isotope ratio mass spectrometer (irMS) (Finnigan MAT Delta Plus), respectively (Pavuluri et al. 2011). An aliquot of filter sample (1.8 cm in diameter disc \times 3) was extracted for WSOC with ~ 15 mL Milli Q water under ultrasonication for 20 min and filtrated with a syringe filter (GL Sciences Chromatodisc Type A, 0.45 μm). The pH of extracts adjusted to 8–9 with ~ 0.5 mL of 0.05 M KOH, and concentrated to dryness using a rotary evaporator under vacuum and then re-dissolved in 200 μL Milli Q water. An aliquot of filter sample (1.0 cm diameter disc for TC and 50 μL of water extract, a subsample of the 200 μL re-dissolved extract, adsorbed onto ~ 20 mg of pre-combusted Chromosorb for WSOC) was placed in a pre-cleaned tin cup and introduced into the EA and then oxidized in a combustion column packed with CuO at 1020 °C. The resulting CO_2 gas was measured with a thermal conductivity detector in the EA and transferred to irMS via an interface (ConFlo II) for $^{13}\text{C}/^{12}\text{C}$ measurement. The $\delta^{13}\text{C}$ values relative to Pee Dee Belemnite (PDB) are calculated using the equation:

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

The analytical uncertainties (i.e., relative standard deviation) in a single set of duplicate analyses of filter samples were within 4% for TC, 3.4% for WSOC, 0.1‰ for $\delta^{13}\text{C}_{\text{TC}}$ and 0.36‰ for $\delta^{13}\text{C}_{\text{WSOC}}$. Aerosol samples were not decarbonated prior to the measurements because we assume that Sapporo aerosols may contain negligible amount of CaCO_3 and its $\delta^{13}\text{C}$ (around 0‰) (Kawamura and Yasui 2005) may not affect the $\delta^{13}\text{C}$ of TC and WSOC. In fact, Ca^{2+} concentrations were found to be low (range 0.14–1.56 $\mu\text{g} \cdot \text{m}^{-3}$; average 0.51 $\mu\text{g} \cdot \text{m}^{-3}$) in these samples that further supports our assumption.

We also measured WSOC using a total organic carbon (TOC)/total nitrogen (TN) analyzer (Shimadzu TOC-Vcsh) by extracting an aliquot of filter disc (1.4 cm in diameter) with 15 mL organic free Milli Q water (18.3 M Ω) under ultrasonication for 20 min. The analytical error in duplicate analyses was within 9% (Pavuluri et al. 2013). Concentrations of WSOC measured by the EA and the TOC/TN analyser were comparable, except for 3 samples that are considered as the outliers ($1.25 \times$ Inter quartile distance) in the data obtained from the TOC/TN analyser. The

difference in concentrations of WSOC measured by two methods is insignificant ($a = 1.16 \pm 0.14$; $b = 0.97 \pm 0.14$; $r^2 = 0.76$), indicating that our technique is free from any significant analytical errors including isotopic fractionation.

3 Results and discussion

Concentrations of TC and WSOC ranged from 2.32 to $8.37 \mu\text{g} \cdot \text{m}^{-3}$ and $0.52\text{--}1.72 \mu\text{g} \cdot \text{m}^{-3}$, with an average of 5.10 ± 1.37 and $1.01 \pm 0.26 \mu\text{g} \cdot \text{m}^{-3}$, respectively, during the campaign, while $\delta^{13}\text{C}_{\text{TC}}$ and $\delta^{13}\text{C}_{\text{WSOC}}$ were -25.6% to -23.1% (average $-24.8\% \pm 0.68\%$) and -26.7% to -21.2% ($-24.2\% \pm 1.59\%$), respectively. Their temporal variations are shown in Fig. 1. The temporal variations of TC showed a gradual decrease from mid-autumn to winter with minimum in February followed by a gradual increase to growing season with a peak in early summer (Fig. 1a). Similarly, WSOC showed a decreasing trend from mid to late autumn and then an increasing trend from early to late spring, although the variations are not significant in autumn, winter and summer (Fig. 1a). On the other hand, both $\delta^{13}\text{C}_{\text{TC}}$ and $\delta^{13}\text{C}_{\text{WSOC}}$ showed very similar temporal trends with a gradual enrichment of ^{13}C from mid-autumn to winter with a peak in February followed a gradual

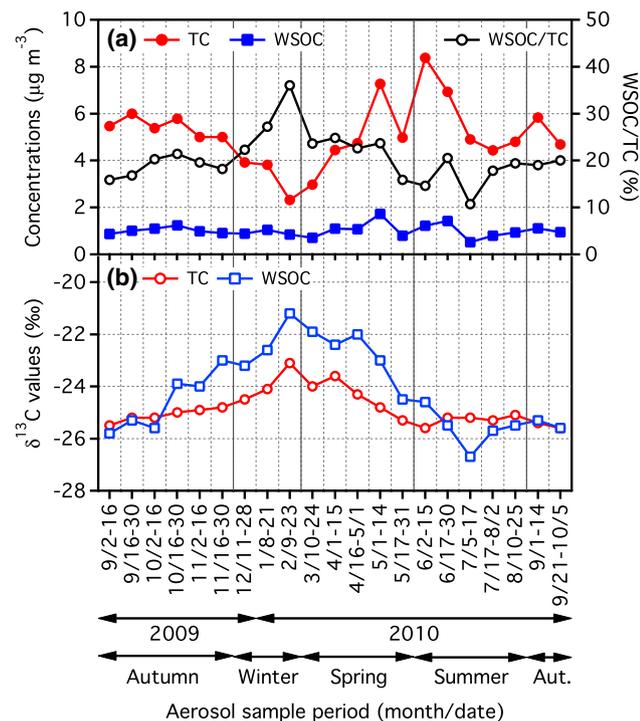


Fig. 1 Temporal variations of concentrations of total carbon (TC) and water-soluble organic carbon (WSOC), mass ratios of WSOC/TC, and stable carbon isotope ratios ($\delta^{13}\text{C}$) of TC and WSOC in aerosols (TSP) from Sapporo, northern Japan during the campaign

depletion in the ^{13}C to early summer and it remained stable thereafter, except for few cases (Fig. 1b).

In contrast, TSP masses that ranged from 13.5 to $73.8 \mu\text{g} \cdot \text{m}^{-3}$ (average $30.0 \pm 12.7 \mu\text{g} \cdot \text{m}^{-3}$) did stay low during winter and then suddenly peaked in early April, and such high loading of the TSP in spring has been interpreted for an enhanced contribution of Asian dusts (Pavuluri et al. 2013). In fact, the EC did not show any clear trend but somewhat similar to that of TSP, whereas the organic carbon (OC) showed a very similar temporal trend (see Fig. 3a from Pavuluri et al. 2013) to that of TC (Fig. 1a). Therefore, it is apparent that the seasonal variations of carbonaceous aerosols were driven by the variations of OC that should have been mainly derived from other (biospheric) sources rather than those (anthropogenic) of EC. It is likely because the biological emissions are increased from winter to growing season followed by a decrease toward autumn (Guenther 1997) and thus SOA formation from BVOCs is increased on local to regional scale with the increasing ambient temperature.

Further the decreasing trend in both $\delta^{13}\text{C}_{\text{TC}}$ and $\delta^{13}\text{C}_{\text{WSOC}}$ from late winter to early summer confirms the significant contribution from biogenic emissions because $\delta^{13}\text{C}$ values of unsaturated fatty acids emitted from higher plants should be depleted in ^{13}C as evidenced by $\delta^{13}\text{C}$ values (range -38.5% to -32.4%) of fatty acids from unburned C_3 vegetation (Ballentine et al. 1998). The steady state of $\delta^{13}\text{C}_{\text{TC}}$ and $\delta^{13}\text{C}_{\text{WSOC}}$ from early summer, except for one case of WSOC, to mid-autumn should have been controlled by significant atmospheric processing of organics through enhanced photochemical reactions under high solar radiation, which simultaneously cause the enrichment of ^{13}C in reactants and depletion of the ^{13}C in product compounds. The increasing trend in $\delta^{13}\text{C}_{\text{TC}}$ and $\delta^{13}\text{C}_{\text{WSOC}}$ from mid-autumn to late winter indicates the significant contribution of carbonaceous aerosols from biomass burning and fossil fuel combustion. The enrichment of ^{13}C occurs in the particles emitted from biomass burning and the $\delta^{13}\text{C}$ of the aerosol carbon derived from fossil fuel combustion is relatively higher than that derived from biospheric sources (Pavuluri et al. 2011 and references therein). In fact, the consumption of fossil fuels is much higher in winter than in other seasons for space heating in East Asia. Further the carbonaceous aerosol influenced by fungal activities in late autumn should have also enriched with ^{13}C .

Therefore, the carbonaceous aerosols in Sapporo should have significantly influenced by different sources in each season; biogenic emissions including biological particles (e.g., pollen) and SOA formation from BVOCs in spring/summer and fungal spores from soil and biomass burning in autumn/winter as well as enhanced fossil fuel combustion in winter. Further the enhanced mass ratios of

WSOC to TC in winter (Fig. 1a) indicates the significant contributions from biomass burning. Thus, the sources of Sapporo aerosols are highly associated with the biological activity throughout the year. These findings are in consistency with those derived from the measurements of percent modern carbon and organic molecular tracers in these samples (Pavuluri et al. 2013), which further confirms the importance of the biospheric sources to Sapporo aerosols.

Despite the fact that the growing season starts in May and extends into October when daily average ambient temperatures are $\geq 10^{\circ}\text{C}$ in Hokkaido (Toma et al. 2011), the concentrations of TC and WSOC start to increase in March and their $\delta^{13}\text{C}$ values start to decrease in the same month (Fig. 1). The average temperature in Sapporo was $\leq 10^{\circ}\text{C}$ from 11 November 2009 to 1 May 2010; hence local BVOC emission is insignificant until the end of April. Therefore, it is likely that the Sapporo aerosols should have significantly influenced by the long-range transported air masses rather than the local emissions. Ten-day backward air mass trajectories arriving in Sapporo at 500 m AGL computed for every 48 h during each sample period showed that the air masses mostly originated from Siberia and passed over northeastern Asian regions and the Sea of Japan during autumn, winter and spring, whereas from the East China Sea and/or western North Pacific passing over the coastal region and/or Honshu of Japan in summer and they mostly travelled at a height of less than 2000 m AGL in all seasons (Pavuluri et al. 2013). Hence, the advection of the air parcels from distant source regions to Sapporo should be significant during the campaign. Therefore, we interpret such seasonal changes in Sapporo aerosols to the air masses transported from distant source regions, although we do not preclude an impact from the local sources.

4 Conclusions

Seasonal variations of TC and WSOC and their $\delta^{13}\text{C}$ observed in Sapporo, northern Japan over a 1-year period during 2009 and 2010 showed that the TC decreased gradually from mid-autumn to winter and then increased to growing season with a peak in early summer. The seasonal trends of both $\delta^{13}\text{C}_{\text{TC}}$ and $\delta^{13}\text{C}_{\text{WSOC}}$ were similar and showed a gradual increase from mid-autumn to winter followed by a decrease to early summer, except for few cases. The results obtained from this study together with the air mass trajectories infer that the carbonaceous aerosols are mainly derived from biogenic emissions including

biological particles (e.g., pollen) and SOA formation from BVOCs in spring/summer and from fungal spores from soil and biomass burning in autumn/winter as well as from enhanced fossil fuel combustion in winter in Northeast Asia.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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