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Mass and isotopic concentrations of water-insoluble refractory carbon in total suspended particulates at Mt. Waliguan Observatory (China)

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ABSTRACT

Mass concentration and isotopic values $\delta^{13}C$ and ^{14}C are presented for the water-insoluble refractory carbon (WIRC) component of total suspended particulates (TSP), collected weekly during 2003, as well as from October 2005 to May 2006 at the WMO-GAW Mt. Waliguan (WLG) site. The overall average WIRC mass concentration was $(1183 \pm 120)\,\text{ng/m}^3$ ($n = 79$), while seasonal averages were 2081 ± 1707 (spring), 454 ± 205 (summer), 650 ± 411 (autumn), and 1019 ± 703 (winter) ng/m^3. Seasonal variations in WIRC mass concentrations were consistent with black carbon measurements from an aethalometer, although WIRC concentrations were typically higher, especially in winter and spring. The $\delta^{13}C$ PDB value (-25.3 ± 0.8)‰ determined for WIRC suggests that its sources are C_3 biomass or fossil fuel combustion. No seasonal change in $\delta^{13}C$ PDB was evident. The average percent Modern Carbon (pMC) for ^{14}C in WIRC for winter and spring was $(67.2 \pm 7.7)\%$ ($n = 29$). Lower pMC values were associated with air masses transported from the area east of WLG, while higher pMC values were associated with air masses from the Tibetan Plateau, southwest of WLG. Elevated pMC values with abnormally high mass concentrations of TSP and WIRC were measured during a dust storm event.

Introduction

Carbonaceous aerosols are usually separated into organic carbon (OC) and elemental carbon (EC) fractions using thermal oxidation techniques. OC, oxidized at temperatures lower than 400 °C, is directly emitted from its primary source, or composed of secondary organic aerosols (SOA) formed through condensation and particulate conversion of hydrocarbon gas phase oxidation products. OC is also one of the main components of fine particulate matter, with an aerodynamic radius less than 2.5 μm ($PM_{2.5}$). In contrast, EC is emitted during oxygen-deficient combustion of biomass or fossil fuels, and covers a continuum from charcoal (or char) to soot particles (Hedges et al., 2000). Its chemical and physical properties are relatively inert. Black carbon (BC) measured by optical instruments, such as an aethalometer, is comparable with EC in its thermal, optical, and chemical behavior.

Carbonaceous aerosols may also be differentiated into water soluble and insoluble types based on their water-solubilities at a given temperature and pressure. Water-soluble organic carbon (WSOC) constitutes a significant fraction of fine carbonaceous particulate matter, having complicated molecular compositions of oxidized and hygroscopic materials (Novakov & Penner, 1993). In contrast, water-insoluble carbon in aerosol particles is refractory, incorporating oxidized and hydrophobic materials like EC and water-insoluble organic carbon (WIOC). Large aromatics ($\geq C_9$), lignin, and cellulose are the main compounds of WIOC (Saxena & Hildemann, 1996).

Carbon isotope technology provides a simple but effective method for EC and OC source apportionment. Stable ^{13}C isotope ratios are characteristic of different aerosol sources, while radioactive ^{14}C concentrations can differentiate modern biogenic-derived versus fossil fuel-derived carbonaceous matters because

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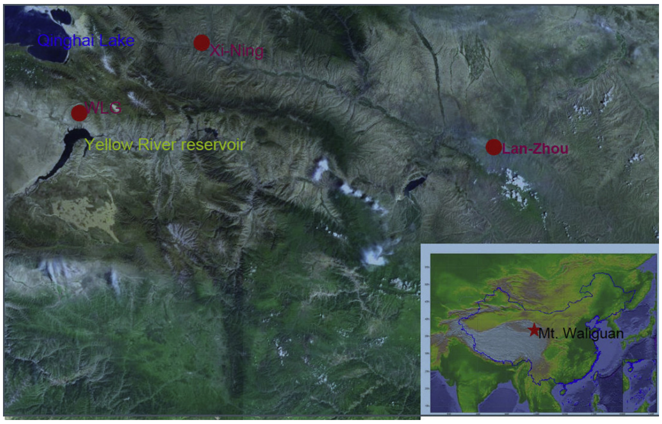

Fig. 1. Topographical map of Mt. Waliguan (WLG) showing the study site and surrounding regions.

^{14}C only exists in the contemporary biogenic-derived material (Currie, Klouda, & Cooper, 1980). Thus, ^{14}C measurements have vastly improved our understanding of $PM_{2.5}$ sources (e.g. Bench, Fallon, Schichtel, Malm, & McDade, 2007; Gustafsson et al., 2009; Heal et al., 2011; Sun, Hu, Guo, Liu, & Zhou, 2012; Szidat et al., 2004, 2006). In this study, we express ^{14}C in percent Modern Carbon (pMC).

Mt. Waliguan (36.287° N, 100.898° E; 3810 m AMSL; hereafter WLG) Observatory, one of 22 World Meteorological Organization-Global Atmosphere Watch (WMO-GAW) sites, is located on a remote mountaintop in the northeast region of the Tibetan Plateau. Fig. 1 shows the geographical and topographical context of WLG. The provincial capital cities, Lanzhou and Xining, are respectively about 270 and 90 km from WLG. It is important to explore sources of aerosol particles at this WMO-GAW site, since it is less influenced by anthropogenic pollution compared with most Asian sites. It has been demonstrated that aerosol particles at WLG mainly consist of WSOC, carbonate ($CaCO_3$), and NH_4SO_4 (Li, Tang, Xue, & Toom-Sauntry, 2000). Regional transport of air pollution from Lanzhou and Xining, as well as from east China contribute to BC levels at WLG, as reported by Tang et al. (1999). In addition, soil, crustal material, emissions from coal burning, vehicles, and industry are identified as primary sources of aerosols at WLG (Wen, Xu, Tang, Zhang, & Zhao, 2001). Biomass burning also is a significant primary source, as suggested by a correlation between BC with NO_3^-, K^+, NH_4^+, Ca^{2+}, and Mg^{2+} ions (Ma, Tang, Li, & Jacobson, 2003). Although particle size distributions suggest that air masses from west of WLG are dominant at this site, regional-scale transport from the northeast, including emissions from Xining and Lanzhou, frequently brings major anthropogenic pollutants with particle sizes in the Aitken mode ($21\ nm < d_p < 95\ nm$) and accumulation mode ($95\ nm < d_p < 570\ nm$) during summer (Kivekäs et al., 2009).

In this study, characteristics of carbon materials extracted from total suspended particulates (TSP) collected weekly at WLG are determined. TSP samples were collected over two periods: from December 25, 2002 to January 21, 2004; and from October 16, 2005 to May 17, 2006. Samples were measured for ^{10}Be and carbon isotopes, after ^{7}Be and ^{210}Pb were determined without damage to the original samples. Since samples were originally collected for ^{7}Be and ^{210}Pb analysis, a special procedure (see "Experimental" section), somewhat different from chemical-thermal oxidation techniques applied to aerosol particles collected on quartz filters, was used for extracting carbon in this study.

Experimental

Sample collection

TSP were collected using a high volume air sampler driven by Fuji-Electric Co (Japan) pumper (Model:VFC404p-5T), with a rectangular filter composed of three layers of 100% polypropylene web (Dynaweb DW7301L, 25.4 cm × 20.3 cm) (Lee et al., 2004). A flow rate of ca. 1.2 m^3/min was used. The sampling period was set to one week (168 h). Although the optimal size of particles is larger than 0.4 μm, our high volume sampling system collected TSP composed of differently sized particles, including pollen grains with sizes between 2.5 and 10.0 μm (Pavuluri, Kawamura, Uchida, Kondo, & Fu, 2013). For the first sample period, only three eighths of each filter was available for carbon extraction.

Sample pretreatments

A modified 3A (acid–alkali–acid) treatment was used to extract carbon, similar to the procedures used to extract BC from soil or marine sediments (e.g., Han et al., 2007; Khan et al., 2009) or from archived aerosol filter samples (Husain et al., 2008). The first acid treatment separates particles attached to the polypropylene fibers. This procedure involves soaking the filter in 6 M HCl solution at room temperature for 24 h, and then the extracted insoluble TSP materials are precipitated or floated, which are collected and washed to pH = 7.0 with deionized water before being dried. During the alkali treatment, these insoluble particles are soaked in 1 M NaOH solution at room temperature for 24 h. This removes humic-like substances from solids. The residues are collected by filtration, and washed to pH = 7.0 with deionized water prior to being dried for the last acid treatment. The final treatment eliminates any possible secondary carbonate produced in the first two treatments.

After these treatments, the dried residue is placed in a Vycors® combustion tube packed with pre-heated CuO and silver wire. The combustion tube is held under vacuum conditions with pressure around 1×10^{-3} hPa for 3 h, before being sealed by liquefied gas-oxygen flame welding. Thus, all volatile and semi-volatile organic substances are removed, leaving only stable recalcitrant carbonaceous matter. Although the attributes of this carbonaceous material are similar to BC chemically extracted from soil or marine sediments (e.g. Khan et al., 2009), we prefer to use the term water-insoluble refractory carbon (WIRC) because of the differences in its extraction method compared with traditional methods used for quartz or Teflon-filters.

Conversion to CO_2 and graphite target synthesis

The sealed tube of WIRC is combusted at 860 °C for 2 h in a muffle oven, and the carbon-containing gases evolving from the residue are converted to CO_2. The CO_2 is released into a cracker tube under vacuum conditions to determine the mass concentration of WIRC using CO_2 partial pressure measurements. The CO_2 is introduced to a dry ice ethanol-trap to eliminate water vapor, before it is cryogenically trapped using a liquid N_2 trap. The trapped CO_2 is divided into two parts: one is sealed in a tube for ^{13}C measurement, and the other is reintroduced into the dry ice ethanoland liquid N_2 traps 2–3 times to obtain more purified CO_2. This purified CO_2 is converted to graphite at 600 °C using zinc with iron, and a TiH_2 catalyst in excess hydrogen. This produces targets for ^{14}C analysis. Procedures for carbon separation, purification, and target synthesis are described in the literature (Ding et al., 2010; Shen et al., 1999).

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