SOURCE APPORTIONING AND MOLECULAR CHARACTERIZATION OF INCOMPLETE COMBUSTION PRODUCTS IN $PM_{1.1}$ AND PM_{10} AEROSOLS FROM RESIDENTIAL AREAS OF SUBURBAN TOKYO USING NATURALABUNDANCE RADIOCARBON

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Abstract

Incomplete combustion generates polycyclic aromatic hydrocarbons (PAHs) and black carbon (BC), two of the most important classes of pollutants to the atmospheric environment. Radiocarbon (^{14}C) is an ideal tracer to distinguish between fossil fuel (^{14}C-free) from modern biomass combustion sources (101 pMC of atmospheric $^{14}CO_2$ in 2004) of pyrogenic products. Our previous study revealed that ^{14}C content (in terms of percent modern carbon: pMC) of PAHs in PM_{10} aerosols from suburban Tokyo (45 and 33% pMC in summer and winter, respectively) is far exceeding the statistic-based expectations (~3%)[1]. For the same set of samples, we investigated ^{14}C content of BC and TOC and the temporal variations of molecular markers from biomass burning (e.g., levoglucosan: LG[2]). The ^{14}C-BC signals, 42 and 30% pMC in summer and winter aerosols, were significantly higher than those reported for the urban particulate matter from Washington DC (SRM1649a)[3] but almost identical to those of high molecular weight (MW≥226) PAHs in the same set of aerosol samples[1]. In addition, ^{14}C-TOC, 62% and 42% pMC in summer and winter, respectively, shows highest values compared with ^{14}C-PAHs and ^{14}C-BC results, suggesting higher contribution of plant activity in summer. However, it was significant low compared with modern carbon source from atmospheric $^{14}CO_2$.

Introduction

Atmospheric polycyclic aromatic hydrocarbons (PAHs) originate mostly from incomplete combustion of carbon-based fuels. Among atmospheric contaminants, PAHs account for most (35-82%) of the total mutagenic activity of ambient aerosols. Hence, reduction of air pollution by PAHs is essential for effective air quality control, which requires reliable source apportionment. Emitted from combustion sources, most of higher molecular weight PAHs with 5-6 aromatic rings are condensed/adsorbed onto airborne particles, whereas lower molecular weight species with 3-4 aromatic rings mostly exist in the vapor phase. BC is also one of atmospheric pollutants, originated from incomplete combustion. Recently it is focused as material associated with global warming due to decrease of solar albedo.

In this study, radiocarbon analysis was performed for PAHs, BC, and TOC associated with airborne particulate matter (APM) with diameter <10mm (PM_{10}) and <1.1mm ($PM_{1.1}$) collected from a residential area of suburban Tokyo, Japan to apportion sources of atmospheric PAHs and BC between biomass and fossil fuel combustions. This combined analysis of radiocarbon data from PAHs, BC, and TOC is first approach to assess the source and fate of these incomplete combusted products in the environment.

Materials and Methods

1.PAHs and BC preparations for AMS measurement

Each of the purified PAHs extracts was repeatedly injected onto a PCGC until sufficient quantity (>20µg) of compounds were obtained in each trap[4]. The PCGC system consisted of a Hewlett-Packard 6890 gas chromatograph equipped with a flame ionization detector (GC-FID), a Gerstel automated cooled injection system (CIS4), a zero-dead volume effluent splitter, and a Gerstel preparative fraction collector (PFC). The operational conditions for PCGC system were similar to those optimized for PAHs. PAHs were separated with a 60-m megabore (0.53 mm i.d.) fused silica column (SPB-5, SUPELCO; film thickness 0.5 µm). The PFC was programmed to open the "*trap window*" only when the target compound is eluting from the capillary column. The trapped compounds were recovered from the u-tubes with dichloromethane and transferred to a glass vial.

BC in PM_{10} aerosols was isolated by using widely used CTO375 method[5]. Preparation method for BC in our laboratory was developed using the urban particulate matter from Washington DC (SRM1649a)[3]. For BC isolation, organic carbon in aerosol samples was removed at 375°C, oxygen flow for 12 hours.

2. Graphitization of PAHs, BC, and TOC for AMS analysis

An aliquot of PAHs purified by PCGC were further cleaned on a SiO_2 column to remove any residual column bleed and then transferred to a precombusted quartz tube (25cm length, 9mm outer diameter). The solvent was evaporated under N_2 stream and CuO was added. The tube was evacuated to 10^{-6} Torr, flame sealed, and combusted at 850°C for 4-6hrs. Then CO_2 was reduced to make a graphite target for AMS analysis by using a specially designed micro-scale graphitization method in the case of <50 μgC[5]. BC and TOC were also treated with combustion to CO_2 and then reduction to graphite, similar to graphitization of PAHs. ^{14}C measurements of graphite targets were conducted at AMS facility(NIES-TERRA), the National Institute for Environmental Studies (NIES). All ^{14}C measurements are expressed as percent modern carbon(pMC)[6] with δ^{13}C correction for samples, the pMC values of the sample was calculated by a following equation:

$$pMC=\{(^{14}C/^{12}C)_{sample}/(0.749\times(^{14}C/^{12}C)_{HOX\ II})\}\times100 \qquad (1)$$

where the HOX II is a standard material with the known ^{14}C/^{12}C ratio.

Results and Discussion

^{14}C content (in terms of percent modern carbon: pMC) of PAHs in PM_{10} aerosols from suburban Tokyo (45 and 33% pMC in summer and winter, respectively) is far exceeding the statistic-based expectations (~3%)[1]. For the same set of samples, ^{14}C content of BC and TOC in summer and winter aerosols were 42 and 30% pMC in and 62% and 42% pMC, respectively. The ^{14}C-BC signals were significantly higher than those reported for the urban particulate matter from Washington DC (SRM1649a)[3] but almost identical to those of high molecular weight (MW≥226) PAHs in the same set of aerosol samples[1]. On the other hand, ^{14}C-TOC showed highest values compared with ^{14}C-PAHs and ^{14}C-BC results, suggesting higher contribution of plant activity in summer. However, it was significant low compared with modern carbon source from atmospheric $^{14}CO_2$. BC contents and BC/TOC ratio in PM_{10} aerosols were 0.85% and 0.075-0.084 in summer and 1.21% and 0.094 in winter. The ^{14}C-BC signals, 42 and 30% pM in summer and winter aerosols, were significantly higher than those reported for the urban particulate matter from Washington DC (SRM1649a)[5] but almost identical to those of high molecular weight (MW≥226) PAHs in the same set of aerosol samples[1]. This suggests that ^{14}C-BC approach can be a surrogate for PAHs specific ^{14}C analyses to monitor seasonal source variation of combustion-derived pyrogenic products.

In this study, the temporal variations of molecular markers from biomass burning (e.g., levoglucosan: LG[7]) is also investigated. LG was detected from all the samples analyzed. Its intense signals support the observation of the strong ^{14}C-signals of PAHs as well as BC, and indicate the utility of LG as a tracer for detecting emissions from vegetative combustions at higher time resolutions. Based on detailed comparison of temporal variations of LG and of PAHs molecular signatures, and their physico-chemical properties, however; LG based source discrimination was judged to be labile to antecedent rain events.

Our result of natural radiocarbon based source apportioning approach will provide a detailed insight into the sources and fate in the environment of these incomplete combustion products. In addition, the radiocarbon based source estimates were compared with statistical data to get an insight about combustion sources.

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