



Simultaneous observation of seasonal variations of beryllium-7 and typical POPs in near-surface atmospheric aerosols in Guangzhou, China

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ABSTRACT

Near-surface atmospheric aerosol samples were collected at the sampling frequency of 2–3 d per week for one year from August 2006 to August 2007 at a low latitude station in Tianhe District, Guangzhou, Guangdong Province of southern China. The samples were analyzed for cosmogenic nuclide ⁷Be and persistent organic pollutants, i.e. organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs). The annual average ⁷Be concentration was 2.59 mBq m⁻³, with the maximum occurred in May (8.45 mBq m⁻³) and minimum in late August and early September (0.07 mBq m⁻³). Winter and spring were the seasons in which the ⁷Be concentrations were high while summer and autumn were the lower ⁷Be seasons. Spring peaks in ⁷Be in the near-surface atmospheric aerosols may have associated with the “spring leak maximum” episode. The annual average Σ OCPs concentration was 345.6 pg m⁻³, Σ_{33} PCBs 317.6 pg m⁻³, and Σ_{31} PBDEs 609.0 pg m⁻³. The variation trends in the time-series of ⁷Be, OCPs, PCBs, and PBDEs in near-surface atmospheric aerosol showed both common features and differences. Significant correlations ($R^2 = 0.957$ and 0.811 , respectively, $p = 0.01$) were observed between the monthly average ⁷Be concentrations and those of Σ PCBs and Σ PBDEs in summer, autumn, and early winter. The difference between the seasonal variation features of OCPs and PCBs (and PBDEs) could be attributed to the different source functions and physical–chemical properties which could control the behaviors of these compounds in air–aerosol partitions as well as atmospheric transport.

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1. Introduction

Beryllium-7 (⁷Be) is a natural radionuclide originated by interaction of cosmic rays with nitrogen and oxygen in the stratosphere and upper troposphere. The seasonal and longitudinal changes in ⁷Be atmospheric production rate can be neglected. It changes with altitude and latitude but in a relatively stable way (Kulan et al., 2006). When ⁷Be is formed, it quickly binds with atmospheric aerosols (Lal et al., 1958). In the top upper troposphere, its production rate is two-fold higher than that in near-surface. The half-life of ⁷Be is 53.3 d and the residence time in the troposphere is about 35 d (Bleichrodt, 1978; Dutkiewicz and Husain, 1985). ⁷Be can be transported from stratosphere, which serves as the source for

⁷Be production and accumulation, into the troposphere via air exchanges between the stratosphere and troposphere or through the Brewer–Dobson circulation on a global scale (Feely et al., 1989; Holton et al., 1995; Zanis et al., 1999; Liu et al., 2001).

There are over 70 observatory stations carry out long-term monitoring of ⁷Be concentration in the atmosphere. The average concentration of ⁷Be in atmospheric aerosols observed at stations with altitude >700 m are reported as 3.54 mBq m⁻³, while the average concentration at low altitude was 1.84 mBq m⁻³ with the global mean concentration of ⁷Be in atmospheric aerosols as 2.45 mBq m⁻³ (Koch et al., 1996). With advantage of short half-life and easy determination, ⁷Be has been widely used as a tracer in atmosphere science (Lin et al., 2003; Zheng et al., 2005, 2008; Wan et al., 2006; Narazaki and Fujitaka, 2009; Ayub et al., 2009; Ali et al., 2010). Most studies on application of ⁷Be as a tracer in atmosphere were restricted in aerosol itself, such as estimation of the mean residence time of aerosols (Lee et al., 2004; Cho et al., 2007; Papastefanou, 2006, 2009). A few researches were involved in relations of ozone and some pollutants in the atmosphere such as

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nitrate, sulfate, and mercury (Savoie et al., 1989; Koch et al., 1996; Igarashi et al., 1998; Lamborg et al., 2000; Garimella et al., 2003). So far there is no report available on simultaneous study on ^7Be and persistent organic pollutants (POPs) in the atmospheric aerosols. Such a study could further explore ^7Be as a geochemical tracer and provide a different perspective on the global fate of POPs.

POPs are toxic with lipophile and semi-volatile properties and can be long-range transported through the atmosphere, posing potential threat to human health and ecosystem. Located in the East Asia monsoon zone, the Pearl River Delta region in South China is a fast developing industrial area both as a POPs pollution source area and a receiving area for POPs pollutant input from other regions via long-range atmosphere transport (Fu et al., 2003).

China is located in eastern Asian monsoon domain; variations in meteorological fields associated with the monsoon can influence transport, deposition, and chemical reactions of aerosols over eastern China (Zhang et al., 2010). In an attempt to explore the possibility of application of the cosmogenic nuclide ^7Be as a geochemical tracer for long-range transport of aerosols and pollutants in the atmosphere, and to help identify the sources of POPs in aerosols in the Pearl River Delta region during different seasonal wind periods, Guangzhou, a well developed economic and industrial city in the Pearl River Delta area, was chosen as the investigation site in this study. Near-surface atmospheric aerosols were collected at the sampling frequency of 2–3 d per week for one year and the concentrations, compositions, and temporal distributions of ^7Be and some typical POPs compounds such as organic chlorinated pesticides (OCPs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ether (PBDEs) in the aerosol samples were simultaneously analyzed, so as to provide base-line data for application of ^7Be as a geochemical tracer.

2. Experimental methods

2.1. Sampling

The sampling site for aerosols was at Wushan, Tianhe District of Guangzhou City (23°08.25'N, 113°19'E; about 25 m above sea level). The annual average temperature is 22.6 °C with the monthly average minimum temperature of 13.7 °C occurring in January and the monthly average maximum temperature of 29.4 °C occurring in August. The rain precipitation is mainly focused in April–September during which the rain precipitation accounts for 92% of the total year's, with monthly average of 2050 mm.

From August 23, 2006 to August 8, 2007, near-surface atmospheric aerosol samples were collected at the frequency of 2–3 d per week using a large volume TSP (total suspended particles) sampler (KC-1000 with a constant flow rate of 1.04 m³ min⁻¹, Qingdao Laoshan Electronics Co, China) with a rectangular glass fiber filter film (GFF: 200 mm × 250 mm, pore size of 0.4 μm, 47 mm diameter, Waterman, USA). Prior to sampling, QFFs were baked at 450 °C for 6 h to remove any organic contaminant. Air was collected at 10 m above the ground.

The sampling duration was generally three consecutive days weekly (one filter sample for each 24 h). The integrated sampling volume of each sample was calculated automatically by the sampler from the real flow rate and sampling time. Immediately after collection, loaded QFFs were wrapped with pre-baked aluminum foils and then transported to the laboratory and stored at -20 °C until extraction. The three filter samples of each week were combined into one sample that was then divided into two for ^7Be and POPs (OCPs, PCB, and PBDEs) analysis respectively, in order to ensure that the two sub-samples were exactly under the same meteorological conditions during the same sampling duration. The

sampling for the 23rd, 24th, and 32nd week were missed, so that total 49 samples were collected during the one-year period.

2.2. Analytical methods

2.2.1. ^7Be analysis

The glass fiber filter sample was weighed, folded into a rectangle cube and then wrapped with aluminum foil with the bottom area of 64 cm × 52 cm. It was placed in a measuring vial, so that all filter papers had the same irradiation geometry to the germanium detector for ^7Be measurements. The ^7Be activity was measured by its 477.16 keV (the branching ratio: 10.5%) γ -ray using the high-resolution gamma-ray spectrometer measurement system (Canberra, US) with a BE5030 detector which has a range for γ -ray energy of 3 keV–3 MeV.

The measuring system is shielded with Canberra 747E lead chamber with the wall thickness of 10 cm. The detection efficiency was 50.93%. The spectrometer is operated by Genie 2000 software and DSA-1000 (Canberra, US) that allows automatic peak-search, calculation of peak area, reduction of background, self-absorption correction, decay correction, and interference correction. The counting time for ^7Be was >43,200 s and the counting error was <7%.

Laboratory Sourceless Calibration Software (LabSOCS, <http://www.canberra.com/products/839.asp>) was used in establishment of the counting efficiency curve and treatment of ^7Be counting data obtained from gamma-ray spectrometry measurement for atmospheric aerosol samples, and calculation of the ^7Be activity (Bq) which was corrected automatically by the software of the gamma-ray spectrometer for the sampling time, sampling time length, the time interval between sampling and measurement, and measurement time interval to calculate the ^7Be -specific activities (mBq m⁻³) in the atmospheric aerosol sample.

2.2.2. Analytical methods of POPs

2.2.2.1. Chemicals and standards. Organochlorine pesticide standards which contained α -, β -, γ -, δ -HCH, *p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT, *p,p'*-DDT, HCB, aldrin, dieldrin, trans-chlordane (TCs), cis-chlordane (CC), heptachlor, and heptachlor epoxide were purchased from ULTRA Scientific USA. The surrogate standards for OCPs were 2,4,5,6-tetrachloro-*m*-xylene (TMX) and PCB209 (Supelco Co., USA). PCB1, 5, 18, 31, 52, 44, 66, 101, 99, 87, 110, 151, 123, 118, 153, 141, 138, 187, 183, 180, 170, and 206 (IUPAC No. system) mixed standard and Aroclor 1242/1248/1254/1260 (1:1:1:1) mixed standard were from Accustandards, USA. BDE28, 47, 66, 85, 99, 100, 138, 153, and 154 (IUPAC No. system) mixed standard solution and BDE183 and BDE209 single standards were from Accustandards, USA. Recovery spikes PBDEs were ¹³C-PCB141 (Cambridge Isotope Laboratories, USA) and PCB209 (Accustandards, US). Internal standards for PBDEs were PCB24, 82, and 189 (Accustandards, USA) and ¹³C-PCB208 (Cambridge Isotope Laboratories, USA).

Hexane, acetone, dichloromethane, and anhydrous sodium sulfate (grade for pesticide residue analysis) were purchased from Fisher Company, USA. Silica (grain size: 0.038–0.063 mm), Alumina (grain size: 0.063–0.210 mm) were analytical grade obtained from Merck, Germany, which were baked at 450 °C for 6 h prior to use. Concentrated sulfuric acid (grade for pesticide residue analysis, 95%–98%) was purchased from Fluka Company of Germany. Anhydrous sodium sulfate (analysis grade, Xilong chemical factory of Guangdong, China) was baked for 4–5 h at 400 °C before use. The laboratory glassware was washed with acid and detergents, rinsed with distilled water and acetone, and then heated to 200 °C for 4 h prior to use.

2.2.2.2. Extraction and cleanup. The methods used for the extraction of POPs in aerosol samples followed Chen et al. (2006) and Liu

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