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# East Asia monsoon's influence on seasonal changes of beryllium-7 and typical POPs in near-surface atmospheric aerosols in mid-latitude city Qingdao, China

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## HIGHLIGHTS

- $^{7}$Be in near-surface atmospheric aerosols was measured weekly for one year in Qingdao.
- The maximum and minimum levels of $^{7}$Be occurred in September and May, respectively.
- HCHs, DDTs, and PCBs followed a trend of being lower in summer and higher in winter.
- OCPs exhibited positive correlations with $^{7}$Be during a period of 10 months.
- Seasonal oscillations in $^{7}$Be concentration and POP/$^{7}$Be ratio were observed.

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## ABSTRACT

Near-surface atmospheric aerosols were collected at sampling frequency of 3 d per week for one year from August 2009 to July 2010 in Laoshan District, Qingdao, located in the mid-latitude coastal region of East Asia monsoon region. The samples were analyzed for cosmogenic nuclide beryllium-7 ($^{7}$Be), organochlorine pesticides (OCPs), and polychlorinated biphenyls (PCBs). The annual average $^{7}$Be concentration was 6.83 ± 0.40 mBq m$^{-3}$, with the variation range from 1.52 to 14.58 mBq m$^{-3}$. The maximum and minimum levels were observed in September and May, respectively. Autumn and spring were the seasons with high $^{7}$Be concentrations and summer was the lowest $^{7}$Be season. Enhanced wet precipitation may have caused lower $^{7}$Be observed in summer when southeasterlies were prevailing. Higher $^{7}$Be concentrations in autumn 2009 were caused by the abnormal atmospheric circulation. Concentrations of HCHs, DDTs, and PCBs followed a trend of being lower in summer and higher in winter. Higher chlorinated PCB isomers were predominant in winter and lower chlorinated PCB isomers were predominant in summer. ∑OCPs generally showed positive correlations with $^{7}$Be but were interrupted by the "spring leak maximum" episode for $^{7}$Be in the atmosphere in April when the stratosphere–troposphere exchange was enhanced, and in December when abnormally high HCHs were observed. No significant correlation was found between $^{7}$Be and PCBs except for PCB28. Seasonal oscillations in $^{7}$Be and the ratios of POP/$^{7}$Be were observed.



## 1. Introduction

Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) are two well-known groups of persistent organic pollutants, which are potentially carcinogenic, mutagenic, and have endocrine-disrupting impacts on human endocrine system. China is a large producer and consumer of pesticides and PCBs. Although production and usage of these products have been officially banned in China since 1980s, their residues have remained in the environmental media to a certain extent (Ren et al., 2007; Cai et al., 2008) and can be subjected to long-range atmospheric transport due to their properties of volatility and persistence in the environment (Wania and Mackay, 1996).

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Due to the irregularity in geographical distribution of emission sources and changeable meteorological condition, the distribution of pollutants in local areas on a short-term time scale often shows a randomness feature both in time and in space. Thus we need a reference or tracer as an index of meteorological condition and atmospheric circulation for study on the POPs' behavior in atmosphere. The tracer should have no sources from land and its geographic distribution in troposphere is mainly governed by atmospheric circulation. Here we proposed to use cosmogenic nuclide berylium-7 ($^7$Be) as a reference to study the pattern of POPs atmospheric aerosols in East Asian monsoon climate system (EAMCS).

Beryllium-7, a short-lived cosmogenic radionuclide with a half-life of 53.3 days, is produced in the stratosphere and upper troposphere as a product of the spallation reaction of oxygen and nitrogen nuclei by cosmic rays (Brost et al., 1991). After formation it quickly binds with atmospheric aerosols (Doering and Akber, 2008). Enhanced exchange of air masses between the stratosphere and troposphere may cause increasing of the tropospheric concentration of $^7$Be. It was found that $^7$Be concentrations followed a pattern similar to that of the fallout fission products (Todorovic et al., 2005) which may enter the stratosphere during nuclear weapons tests or accidents of nuclear power plants.

With the advantage of the short half-life and easy determination, $^7$Be has been widely used as a tracer in atmosphere science. $^7$Be has a life-time long enough to allow for long-distance transport (both horizontally and vertically), and on the other hand short enough to prevent long-term accumulation of the isotope in large reservoirs (Usoskin et al., 2009). Most studies on application of $^7$Be 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, 2009). A few researches were involved in relations with ozone (Graustein and Turekian, 1996), nitrate, sulfate, and trace metals (Savoie et al., 1989; Igarashi et al., 1998; Lamborg et al., 2000; Garimella et al., 2003; Ioannidou, 2011). So far few reports on simultaneous study on $^7$Be and persistent organic pollutants (POPs) in the atmospheric aerosols are available (Pan et al., 2011). Such a study could further explore $^7$Be as the geochemical tracer and provide a different perspective on the global fate of POPs.

China is located in East Asian monsoon climate system (EAMCS). Variations in meteorological fields associated with the monsoon can influence transport, deposition, and chemical reactions of aerosols over eastern China (Zhang et al., 2010). Therefore it is necessary to investigate atmospheric $^7$Be in EAMCS, especially at mid-latitude. The purpose of this study is to use the seasonal variation pattern of atmospheric $^7$Be as a reference for variation of atmospheric circulation so as to further explore the behaviors of POPs in aerosols in EAMCS during different seasons, and to provide base-line data for application of $^7$Be as a geochemical tracer for POPs in the atmosphere. Qingdao, in Shandong Peninsular in the East Asia monsoon region, was chosen as the investigation site in this study (Fig. 1).

## 2. Experimental methods

### 2.1. Sampling

The sampling site was located in Qingdao University, Laoshan District of Qingdao City, on the East coastal region of China (35°36′N, 119°30′E; 75 m above sea level (a.s.l.)). Qingdao is affected by the East Asian monsoon, characterized by dominant warm and wet southeasterlies in summer, and dry, cold northwesterlies in winter covering North and Northeast China, Korean Peninsular and Japan. The annual average temperature is 12.3 °C with the monthly average minimum temperature of −0.9 °C occurring in January and the monthly average maximum temperature of 25.3 °C in August. The annual average of rain precipitation is 680.5 mm, mainly focused from April to September during which the rain precipitation accounts for 92% of annual precipitation. During July and August, the average precipitation is 303.1 mm, accounting for 45% of the annual precipitation. In winter, the average precipitation is 34 mm, with the minimum of 9.8 mm occurring in December.

Near-surface atmospheric aerosol samples were collected from August 4th, 2009 to July 30th, 2010, at the frequency of generally three consecutive days weekly (one filter sample for each 24 h), using a large volume TSP (total suspended particles) sampler (KC-1000, Qingdao Laoshan Electronics Co, China) with a rectangular glass fiber filter film (GF: 200 mm × 250 mm, pore size of 0.4 μm, 47 mm diameter, Waterman. USA). Prior to sampling, GFs were baked at 450 °C for 6 h to remove any organic contaminant. Air samples were collected at 10 m above the ground with a constant flow rate of 1.04 $m^3$ $min^{-1}$. 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 GFs were wrapped with pre-baked aluminum foils and then transported to the laboratory and stored at −20 °C until extraction.

### 2.2. Analytical methods

#### 2.2.1. $^7$Be 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 mm × 52 mm. It was placed in a measuring vial, so that all filter papers had the same irradiation geometry to the germanium detector for $^7$Be measurements. The $^7$Be 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 $^7$Be was >43,200 s and the counting error was <7%.

Laboratory Sourceless Calibration Software (LabSOCS, http://www.canbera.com/products/839. asp) was used in establishment of the counting efficiency curve and treatment of $^7$Be counting data obtained from gamma-ray spectrometry measurement for atmospheric aerosol samples, and calculation of the $^7$Be 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 $^7$Be 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 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). PCB28, 52, 101, 118, 138, 153, and 180 (IUPAC No. system) mixed standard were from Accustandards, 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