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Concentration and Gas-particle Partitioning of Hexachlorobenzene in the Ambient Air Before and After the Beijing Olympic Games

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Abstract Systematic studies of hexachlorobenzene in the ambient air before and after the Beijing Olympic Games were carried out during July 2007 to March 2009. Air samples were collected around 20th monthly on the roof of a building near the Olympic center. The average concentration of hexachlorobenzene was 264 $pg \cdot m^{-3}$, which was higher in winter than other seasons. However, hexachlorobenzene concentration was decreased clearly in winter in 2008 compare with in 2007 due to the implementation of a series of "Green Olympic" policies. Gas-particle partitioning shows that the increase of hexachlorobenzene levels in winter time was mainly contributed by the high total suspended particulate from combustion processes such as coal-burning and traffic emission.

Keywords Hexachlorobenzene · Air · Gas-particle · Beijing Olympic Games

China has launched impressive green policies during the 2008 Beijing Olympics Games as previously promised. Wherein, the air quality of the city was more concerned than any times (Fu 2008). However, monitoring on air was mainly focused on SO_2, CO, O_3, NO_2, and PM_{10}, little was known about persistent organic pollutants (POPs) before and after the Beijing Olympic Games. As one of the 12 priority POPs, hexachlorobenzene has been observed all over the world in the atmosphere. The objective of the current work is to identify monthly concentration of hexachlorobenzene in the ambient air of Beijing between July 2007 and March 2009. Gas-particle (G/P) partition of hexachlorobenzene during this period was also investigated.

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Materials and Methods

The sampling site was located on the roof (39°59′N, 116°25′E; 39 m above ground level, and 82 m above sea level) of Sino-Japan Friendship Center for Environmental Protection, which is near the National Olympic Sports Center. Aerosol particles were sampled on three sequential days around 20th every month from July 2007 to March 2009. Sampling was performed by using a high volume air sampler (HV-1000F, SIBATA, Japan) at a flow rate of 700 $L \cdot min^{-1}$ with 24 hours of sampling intervals. Particulate matter was collected on a weighed quartz fiber filter (QFF) and organic trace gases were adsorbed on two polyurethane foam (PUF) plugs placed downstream of the filter in order to study the G/P distribution of hexachlorobenzene. Field blanks were obtained by placing QFF or PUF into the sampler head without sucking.

Samples were extracted by accelerated solvent extraction (ASE 300, Dionex, USA), which was performed with 1:1 methylene chloride/acetone at 100 °C. The extract obtained was then concentrated to approximate 1 mL, and it was further cleaned up with a Florisil solid phase extraction cartridge (1g, 6 mL, Supelco, USA), The elute was concentrated to around 1 mL under a centrifugal vacuum evaporator system (CVE3100, Eyala, Japan). 20 μL of deuterated phenanthrene, deuterated pyrene, and deuterated chrysene mixture standard solution (10 $ng \cdot \mu L^{-1}$) was added

to the solution as internal standard prior to transferring to a glass of microvial for GC injection.

The determination of hexachlorobenzene was performed on a Shimadzu GCMS-QP2010 equipped with a fused silica capillary DB-5MS column (30 m×0.25 mm i.d., film thickness: 0.25 μm) using electron ionization with selective ion monitoring mode. The injector, transfer line, and ion source temperature were 250°C, 260°C, and 230°C respectively. 2 μL of each sample was injected in the spilt mode with 1:14.1. Internal standards were used for quantification.

Results and Discussion

The method detection limit (MDL) for hexachlorobenzene was calculated based on the standard deviations of analytical results from seven parallel blank matrix samples spiked with low concentration of hexachlorobenzene standards. The analytical procedure of MDL was identical to that of sample analysis, including sample preparation. The MDL of hexachlorobenzene was 0.87 $pg{\cdot}m^{-3}$ and recoveries ranged from 60% to 95%. The MDL and recovery were sufficient to meet the data quality requirements for this study. Reported values were not recovery corrected but were blank corrected using the mean field blank value. Field blank values were less than 5% of sample amounts. The instrument efficiencies were estimated using quality control standards after every six samples run on the GC-MS. Peak were only integrated when the signal to noise ratio was higher than 3.

Hexachlorobenzene is highly persistent in the environment. The global picture of hexachlorobenzene emissions was provided, but potential sources of hexachlorobenzene in developing countries are still not clear (Bailey 2001). In fact, hexachlorobenzene concentrations in the atmosphere are very uniform. The average ambient hexachlorobenzene concentrations in the atmosphere of northern hemisphere was 55 $pg{\cdot}m^{-3}$ (Barber et al. 2005). However, the average concentration of hexachlorobenzene in our study was 264 $pg{\cdot}m^{-3}$. It was comparable or slightly higher than recent reported values on the same city (Li et al. 2009). Although hexachlorobenzene has never been registered as a pesticide in China, it can be released as a byproduct of chlorination processes such as pesticide production. As there were no distinct current hexachlorobenzene sources, wind dispersion together with volatilization and subsequent redeposition by precipitation of chemicals containing hexachlorobenzene should contribute to the hexachlorobenzene in the ambient air of Beijing.

The temporal distribution of hexachlorobenzene in the ambient air before and after the Beijing Olympic Games is shown in Fig. 1. The concentration of hexachlorobenzene in ambient air of Beijing was in the range of 47.3–1470 $pg{\cdot}m^{-3}$ during July 2007 to March 2009. The highest concentration appeared in December 2007 while the lowest dose detected in May 2008. According to the charts illustrated in Figure 1, hexachlorobenzene concentration in the

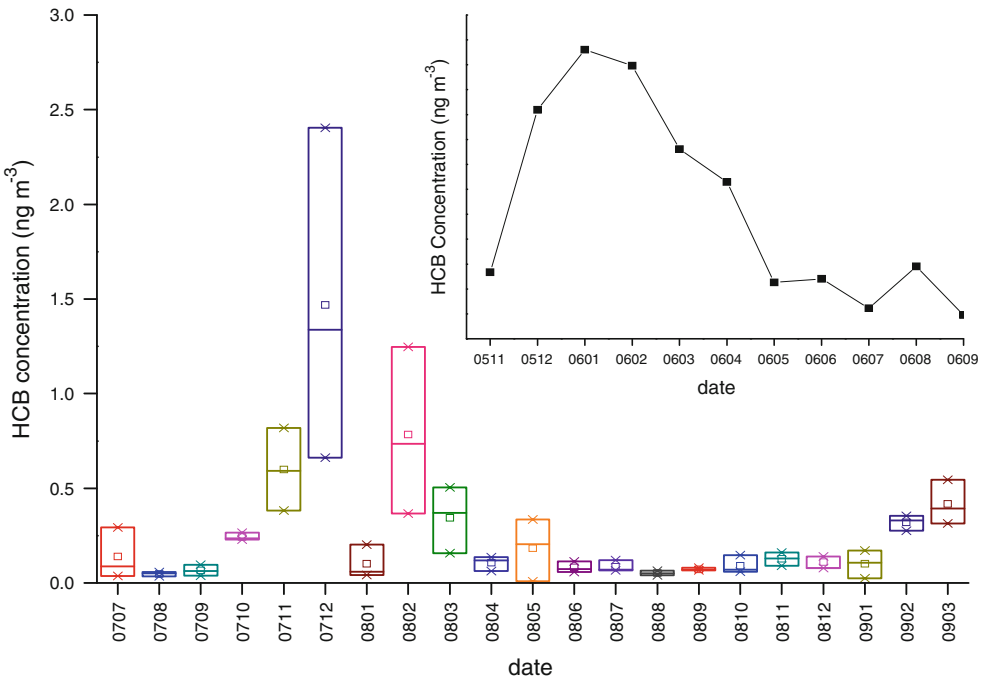

Fig. 1 Concentration of hexachlorobenzene in the ambient air of Beijing during July 2007 to March 2009

Table 1 Average temperature (°C) and calculated TSP* ($\mu g \cdot m^{-3}$) during the sampling dates

Date	0707	0708	0709	0710	0711	0712	0801	0802	0803	0804	0805
Temperature	32.0	37.5	24.2	17.6	8.2	7.6	0.72	12.0	14.4	18.6	29.6
TSP	270	293	117	411	329	411	155	520	589	201	513
Date	0806	0807	0808	0809	0810	0811	0812	0901	0902	0903	–
Temperature	28.2	36.7	30.4	19.7	16.9	14.4	4.3	2.6	5.6	21.2	–
TSP	232	273	195	14	148	131	215	276	249	621	–

* TSP was calculated from API (www.zhb.gov.cn and www.bjepb.gov.cn) and Yang et al (2002)

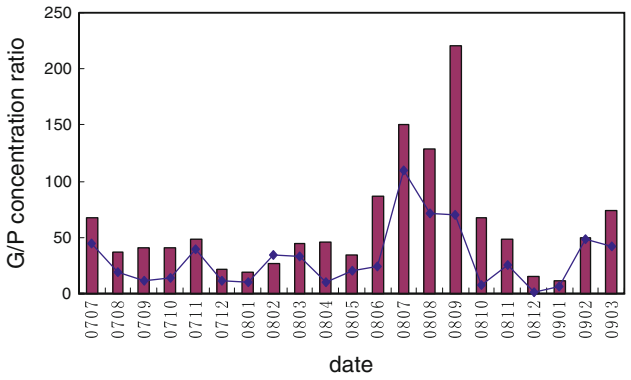

Fig. 2 Gas-particle concentration ratio (*bar*) and its standard deviation (*diamond*) of hexachlorobenzene in the ambient air of Beijing during July 2007 to March 2009

ambient air of Beijing was higher in winter (from November to the next year's March) than other seasons. Specifically, the average concentration of hexachlorobenzene in the ambient air of Beijing was 417.5 $pg \cdot m^{-3}$ in winter, 394.3 $pg \cdot m^{-3}$ in spring, 122.2 $pg \cdot m^{-3}$ in summer, and 95.4 $pg \cdot m^{-3}$ in autumn, respectively. This temporal trend was similar with our pervious studies (see Fig. 1, not reported) and literatures (Li et al. 2009; Liu et al. 2009). It is noteworthy to point out that, the space heating period in Beijing begins on the 15th from November to the next year's March, which was consistent with the temporal trend of hexachlorobenzene. As we known, air pollution of Beijing mainly resulting from vehicle exhaust and coal-burning. Nevertheless, with the implementation of green Olympic, many clean production policies and energy conservation & emission reduction technologies were carried out to reduce the emission of particulate matter and other pollutants. Fig. 1 illustrated the changes in hexachlorobenzene air concentrations before and after the Beijing Olympic Games. As we can see, hexachlorobenzene concentration was decreased clearly in December 2008 compared with December 2007.

The total suspended particulate (TSP) concentrations during the Olympic Games (Table 1) were evidently decreased, which were consistent with the hexachlorobenzene concentrations. However, by plotting the ratio of the gas-particle (G/P) partition (Fig. 2) it can be seen that hexachlorobenzene are basically detected in the gas phase with the average ratio of 60.

To study this G/P distribution, the partitioning coefficient (K_p, $m^3 \cdot \mu g^{-1}$) (Sauret et al. 2008) and the subcooled liquid vapor pressure P_L^0 (Pa) (Hinckley et al. 1990) were used as given in Eqs. (1) and (2).

$$K_p = \frac{[P]}{[G][\mathrm{TSP}]} \tag{1}$$

$$\log P_L^0 = 11.11 - \frac{3582}{T} \tag{2}$$

where [TSP] is the concentration of the total suspended particulate (TSP, $\mu g \cdot m^{-3}$), P and G are represent the compound concentrations ($pg \cdot m^{-3}$) in the particulate and gas phases, and T represents temperature (K).

According to the data in Table 1 and the two equations, the linear relation between $\log K_p$ and $\log P_L^0$ for hexachlorobenzene in Beijing air was calculated. Significant linear correlation was observed between the regression of $\log K_p$ and $\log P_L^0$ ($P < 0.01$). The slope value was −0.428, indicating hexachlorobenzene would not approach equilibrium between the particle and gaseous phase in the ambient air of Beijing. High TSP from coal-burning during the winter time and traffic emission may offset the established gas-particle equilibrium. Thus, the increase of hexachlorobenzene levels in winter time was mainly contributed by the high TSP instead of the regional use of chlorinated fungicides mentioned previously (Li et al. 2009). Coal-burning, waste incineration, as well as fuel combustion assumed to be the main sources of hexachlorobenzene in the ambient air of Beijing. Further investigation is needed to determine the emission inventories of hexachlorobenzene from different combustion sources in Beijing. The measured particulate fraction of hexachlorobenzene was compared with the predictions from Junge-Pankow model and K_{oa} absorption model. However, nothing could be drawn due to date deficiency.

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