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Contamination Status of Hexachlorobenzene (HCB) in Sandstorm Depositions from Beijing and the Origination Region

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Abstract In China, sandstorms play an important role in the long-range atmospheric transport and deposition of hexachlorobenzene (HCB). Concentrations of HCB in sandstorm depositions sampled from Beijing and the origination region were measured to reveal HCB levels during atmospheric transport. The results suggested a constant level of HCB during atmospheric transport. The values were close to environmental background values indicating that no potential source of HCB existed along the transport route. A tendency for HCB levels in Beijing to increase from north to east was also observed, which was probably due to the influence of wind speed and industrial zone distribution.

Keywords Contamination · Deposition · Hexachlorobenzene · Sandstorm

Hexachlorobenzene (HCB) has been observed worldwide in air, water, and biota (D'Have et al. 2007). The physical–chemical properties of HCB such as semi-volatility, high stability, and hydrophobicity are favorable for its long-range transport and widespread distribution in nature. Due to bioaccumulation and persistence of HCB, as well as its potential toxicity, international organizations have introduced regulations to reduce or ban the use of HCB (Bailey 2001). Further information on the contamination status of HCB in the environment is still needed by legislators and scientists to identify the contribution of diffusive sources, and to better understand the environmental behavior and source–sink relationships of persistent organic pollutants (POPs).

Long-range atmospheric transport and deposition of pollutants are important aspects of the regional and global transport of these pollutants and of their impact on ecosystems. Of the studies which have focused on the atmospheric occurrence and long-range movement of pollutants such as HCB, only a few have investigated the transport of these pollutants by sandstorms (Weiss et al. 2000). Sandstorms can carry a great many particles and take place irregularly in northern China. For example, northern China experienced eleven sandstorms in 2006, and one storm covered approximately one-eighth of China and deposited about 330,000 tons of sand in Beijing (Han et al. 2007). This event motivated our research into whether sandstorms play an important role in the diffusion of POPs during long-range atmospheric transport and deposition.

Northeast China is one of the areas most affected by sandstorms. Beijing is located in northeast China and is one of the most densely populated cities in the world, with more than 15 million residents. Sandstorms have seriously contaminated Beijing's atmosphere and have had a direct influence on public health. Some of the particles transported by sandstorms can enter the human body via ingestion, inhalation, and dermal routes (D'Have et al. 2007). HCB is a ubiquitous environmental pollutant (D'Have et al. 2007), and carries a high probability of exposure. Nevertheless, few studies have been conducted on the contamination of sandstorm particles and the pollution status has not been well characterized. POPs especially those with environmental persistence such as HCB, can easily accumulate on particles, and eventually

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result in direct or indirect human exposure to these pollutants.

The present study was conducted as a preliminary investigation into the HCB contamination status of sand/dust deposited during a sandstorm and was carried out in order to evaluate the potential risk to human health and to assess eco-environmental safety. This approach was designed to provide information on the extent of HCB contamination in the deposited sandstorm particles in Beijing and in the region of Baotou, where the sandstorm originated, and to determine the spatial distribution of the particles, to identify the possible sources of pollution and to investigate possible factors affecting HCB contamination.

Materials and Methods

A serious sandstorm which developed from the Mongolian cyclone blew over Beijing on April 16, 2006 (Han et al. 2007). Samples of deposited particles were taken in Beijing and Baotou, which are about 600 km apart (Fig. 1). The first sampling region consisted of 10 urban sites in Beijing covering an area of 750 km^2. The climate, at the time, was dominated by temperate, semi-humid monsoon conditions, with daily temperatures ranging from 10 to 27°C. The second sampling region consisted of three sites in Baotou, Inner Mongolia. Baotou city was chosen as it was in the sandstorm's origination area. The climate in Baotou city was dominated by semi-arid, temperate, continental monsoon conditions, with daily temperatures ranging from 4 to 6°C. The spring season in Baotou is characterized by strong winds and dry weather. The deposition samples from both regions were ground, sieved through a 60 mesh, then transferred to pre-cleaned amber glass bottles and stored at 4°C until analysis.

A HCB standard solution (100 μg mL^{-1}) was purchased from the National Research Center for Certified Reference Materials of China. 2,4,5,6-Tetrachloro-*m*-xylene was purchased from Supelco (Bellefonte, PA, USA). The standards were further diluted to the desired concentration with isooctane and used as working standards. Florisil (60–100 mesh) was purchased from Supelco (Bellefonte, PA, USA) and was activated in a drying oven at 130°C for 16 h. Anhydrous sodium sulfate (Beijing Chemical Factory, China) was heated at 600°C for 12 h to destroy organic contaminants before use. All solvents used were of pesticide grade (J. T. Baker, USA).

Five grams of each sample were weighed accurately and ground with anhydrous sodium sulfate into a free-flowing powder. The samples were extracted with 30 mL of hexane/acetone (1:1, v/v) by ultrasound for 4 min, and the extracts were then separated by centrifugation. This process was repeated three times. Before extraction, 2,4,5,6-tetrachloro-*m*-xylene was added as a surrogate standard. The extracts were cleaned using a chromatography column (30 cm × 10 mm i.d.) containing 4 g of activated florisil with 2 g anhydrous sodium sulfate. The column was pre-eluted with 40 mL hexane/diethyl ether (4:1, v/v) before loading the sample. The first fraction containing HCB was eluted using 60 mL hexane/diethyl ether (4:1, v/v). The solvent was evaporated to 100 μL in K.D. concentrator under a gentle N_2 stream.

Analysis of HCB was carried out using an Agilent 6890 gas chromatograph equipped with a micro-cell ^{63}Ni electron capture detector (μ-ECD). Separation was performed on a 30 m DB-5MS (30 m × 0.25 mm i.d., 0.25 μm film thickness) capillary column. The temperature of the injector and detector were 230°C and 305°C, respectively. The GC column was maintained at 100°C for 2 min, then ramped at 10°C min^{-1} to 160°C, further ramped at 4°C min^{-1} to 230°C, and finally ramped at 10°C min^{-1} to 280°C and held at this temperature for 10 min. The total run time was 40.5 min. Quantification of the samples was performed using an external standard.

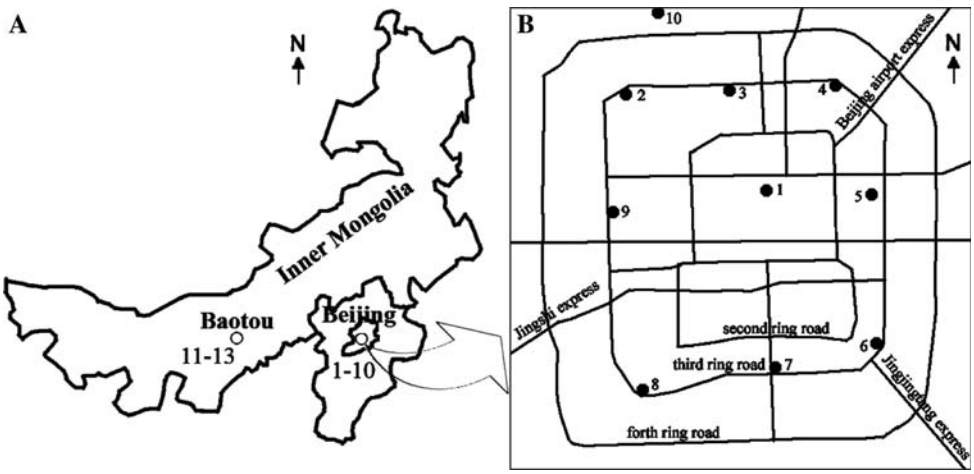

Fig. 1 Sampling sites of sandstorm deposition: (**A**) Sampling sites in Baotou and Beijing; (**B**) Detailed sampling sites in the urban area of Beijing

A laboratory blank was run to demonstrate freedom from interference and cross-contamination. In addition, a procedural blank was run in parallel for every set of six samples to check for interference and cross-contamination. The duplicate samples were analyzed in the laboratory along with regular samples, as another quality control tool to ensure the validity of the results. Instrument stability and relative response factor variance were measured by the analysis of calibration standard solutions during each sample batch.

Identification of HCB was confirmed, and concentrations were measured using an external quantification standard consisting of known amounts of the target compound. Two quality control criteria were used to ensure correct identification of the target compound: (a) The GC retention times matched those of the standard compounds within ±0.05 min. (b) The signal-to-noise ratio was greater than 3:1. The limit of detection (LOD) for HCB was defined by a signal-to-noise ratio greater than three times the average baseline variation. The residue concentrations in samples below detection limits were regarded as zero in the calculations of the sum and mean. The LOD for HCB was 0.6 ng g^{-1}. The matrix spike recovery of HCB was 85%. The recovery of the 2,4,5,6-tetrachloro-*m*-xylene surrogate in all samples was in the range 70–90%.

Results and Discussion

HCB was detected in all sandstorm deposition samples. HCB concentrations ranged from 1.1 to 14.6 ng g^{-1} (median: 4.4 ng g^{-1}, dry weight) in Beijing and 1.1–9.5 ng g^{-1} (median: 5.3 ng g^{-1}, dry weight) in Baotou (Fig. 2). The median concentrations of HCB in Beijing and in Baotou were similar, indicating a small difference in HCB concentrations during atmospheric transport. A general increase in HCB concentrations from north to east was also observed in the urban area of Beijing (Fig. 2B).

HCB was widely used in many countries as a cheap, broad-spectrum insecticide. Due to its widespread use, HCB has caused significant pollution in China (Wu et al. 1997). The best estimate of global HCB emissions from various sources are as follows: pesticide application –6,500 kg $year^{-1}$, manufacturing –9,500 kg $year^{-1}$, and combustion –7,000 kg $year^{-1}$ including 500 kg from biomass burning. This adds up to a total HCB emission of approximately 23,000 kg $year^{-1}$, with an estimated range of 12,000–92,000 kg $year^{-1}$ (Bailey 2001). Although the use of HCB as a herbicide has been prohibited, wastes derived from chlorine-related industries and combustion may be other possible sources of environmental HCB (Meijer et al. 2001).

The physical–chemical properties of HCB, such as vapor pressure –0.0023 Pa, Kow –2.6 × 10^6, Koc –1.2 × 10^{-6}

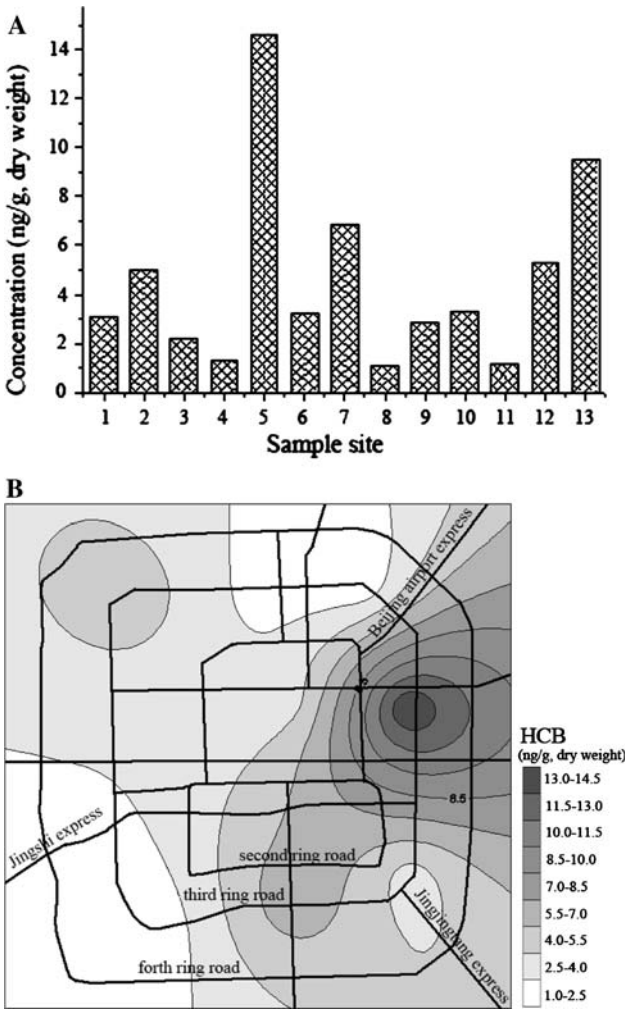

Fig. 2 HCB contamination status: (**A**) HCB in samples; (**B**) Contamination status of HCB in the urban area of Beijing

and BCF –2.5 × 10^6 are favorable for its long-range transport (Mackay et al. 1999). Beyer and other researchers have used the TaPL3 model (transport and persistent level III) to estimate the distance of HCB transport, and have calculated that the transport distance could reach 110,000 km in air (Beyer et al. 2000). Ockenden studied the worldwide distribution of HCB, and concluded that a high level of contamination occurred between north latitude 30° and 60° where the concentrations ranged from ND (not detected) to 5.1 ng g^{-1} dry weight (Ockenden et al. 1999). HCB concentrations were also found to be approximately 5.5 ng/g in soil in Belgium, Italy, Greece, and Romania (Covaci et al. 2002). The median HCB concentrations in the present study were similar to the levels found in these European countries which are located within north latitude 30°–60°, and close to that found in sediments from Shanghai, China (Nakata et al. 2005).

From the above observations, it can be concluded that the contamination status of HCB in sandstorm deposits

from Baotou and Beijing were similar, and the contamination values observed were close to background environmental values. These findings indicate that a potential source of HCB does not exist between Baotou and Beijing. This may be attributed to the banned use of HCB and the rigid regulations relating to HCB which have been in place for nearly 30 years.

Another interesting finding from the present study, concerned the higher concentration of HCB found at site 5 in east Beijing (14.6 ng g^{-1} dry weight, Fig. 2B). A trend in increased PCB concentrations from north to east was also observed in this study. In Beijing an increasing HCB concentration gradient from site 3 in the north to site 5 in the east was observed, with HCB levels from 2.2 to 14.6 (ng g^{-1} dry weight). A decreasing concentration gradient from site 2 in the north to site 8 in the south from 5.0 to 1.1 (ng/g dry weight) was also identified. Possible reasons for these findings are outlined below:

The contamination status of HCB in Beijing was possibly affected by wind speed. The sandstorm developed from a Mongolian cyclone on April 16, 2006 (Han et al. 2007). Wind-blown sand and floating dust extended to Beijing from northwest to southeast, and the wind speed was noted to be gentle. The huge sandstorm deposits amounted to approximately 20 g/m^2 spread over an area of almost 304,000 km^2 (Han et al. 2007). As HCB is a ubiquitous environmental pollutant, it could have been absorbed by airborne particles, transported slowly, and deposited in east Beijing resulting in a higher concentration in this area. Another reason which may explain the contamination status of HCB in Beijing may be the location of the industrial zone which is mainly in east Beijing. The HCB contamination status of the industrial zone was probably higher than that of any other site in the city. These reasons may explain the increased contamination status of HCB from north to east in the urban area of Beijing.

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