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Temporal trends of polychlorinated biphenyls in precipitation in Beijing, China

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ABSTRACT

Temporal trend of polychlorinated biphenyls (PCBs) was determined in precipitation and monthly depositional fluxes were calculated in Beijing for the first time from February 2009 to March 2011. Total PCBs concentrations ranged from 7.00 to 993 ng L^{-1} in dissolved phase and from 1.00 to 133 ng L^{-1} in particulate phase, with a two orders of magnitude variation. Concentrations of PCBs were dominated by dissolved phase, which accounted for 82.5% of the total PCBs in precipitation, implying PCBs enrichment in rainwater due to efficient scavenging of highly contaminated gas phase and nonfilterable submicron particles which easily adsorbed organic contaminants in urban atmosphere. Highest concentrations of PCBs were measured in snow, which were about two times higher than those in rainwater, demonstrating more efficient scavenging of PCBs by snow. The sum of bi-, tri- and tetrachlorinated congeners accounted for 70.5% of total PCBs in precipitation, suggesting that PCBs mainly come from the historical usage of domestic PCB product, e.g., trichlorobiphenyl. PCBs concentrations in both dissolved and particulate phases showed slow rate of decline, with a half-life of 16.9 years in precipitation, suggesting that the atmospheric concentrations of PCBs were decreasing slowly in Beijing. The wet deposition flux of ∑PCBs ranged from 0.240 to 6.55 μg m^{-2} $month^{-1}$ (mean: 1.41 μg m^{-2} $month^{-1}$), indicating a relatively high level of PCBs contamination in Beijing atmosphere.

1. Introduction

Polychlorinated biphenyls (PCBs) are a key group of persistent organic pollutants (POPs) (Lohmann et al., 2004), which were listed along with 9 organochlorine pesticides, PCDD and PCDF as serious threats to health and the environment by the Stockholm Convention for the first batch, because of their persistence, toxicity and bioaccumulation (Lallas, 2001). PCBs could be effectively removed from the atmosphere by precipitation (Offenberg and Baker, 1997; Van Ry et al., 2002) and deposit to the whole terrestrial and aquatic ecosystems (soil and surface waters), where PCBs were accumulated in those two environmental matrixes and also in all kinds of living beings through the food chain, creating threats to the human health and other living organisms (Jones and Voogt, 1999; Mullin et al., 1984; Zhang et al., 2008).

The cumulative global production of commercial PCBs was approximately 1.3×10^6 tons (Breivik et al., 2002), about 1.0×10^4 tons of PCBs made in China from 1965 to 1974, with 9.0×10^3 tons as trichlorobiphenyl and 1.0×10^3 tons as pentachlorobiphenyl (Xing et al., 2005). About 10% of this cumulative tonnage was employed as additives to paint, with the remainder being utilized in electrical and in carbon-free copy papers (Fu et al., 2003). In most cases, up to now, a downward trend of PCBs concentration has been observed evidently due to the effectiveness of restricted use and regulated storage and/or disposal of PCBs since 1970s (Mandalakis and Stephanou, 2004; Pearson et al., 1996; Simcik et al., 2000; Sun et al., 2006; Venier and Hites, 2010). Unfortunately, it seems that the current occurrence of PCBs in Asia have not been appreciably reduced over years (He and Balasubramanian, 2010). Furthermore, analysis of PCBs concentrations from the 1980s to 1990s in China had demonstrated an increasing trend all over the whole country, possibly due to the illegal dismantling, improper disposal of and leakage from PCBs container, chemical transfers, unwanted by-products of combustion of chlorine containing waster, certain chemical processes involving organochlorines, such as polyvinylchloride (PVC), and vehicle exhaust emission during the rapidly developing industrial

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and agricultural activities, municipal development (Fu et al., 2003; Huang et al., 2010; Li et al., 2010; Xing et al., 2005).

A considerable amount of work has been done to assess wet deposition of PCBs across terrestrial gradients in developed countries (Agrell et al., 2002; Backe et al., 2002; He and Balasubramanian, 2010; Mandalakis and Stephanou, 2004; Simcik et al., 2000; Sun et al., 2006; Teil et al., 2004), however, little work has been published in China. Most of the available literature regarding the environmental media in China pertained to sediment, water, air, organism and soil (Fu et al., 2003; Guocheng et al., 2010; Xing et al., 2005). As one of the biggest developing countries in the world, China has undergone rapid economic developing during the past three decades, resulting in various environmental concerns (Fu et al., 2003; Huang et al., 2010; Li et al., 2010). Furthermore, the study of PCBs contamination is an important approach to the risk assessment, due to their toxic effects on humans and wildlife (Guocheng et al., 2010). Therefore, as an indicator of the effectiveness of the Stockholm Convention, it is necessary to focus on the amount and distributing of PCBs in the precipitation in China in an attempt to get a comprehensive understanding of the transportation of PCBs, especially the temporal and spatial variation of PCBs.

The projects of this study are: 1) to quantify concentrations and assess temporal trends of PCBs in precipitation in Beijing from February 2009 to March 2011; 2) to analyze the role of snow on the concentrations of ∑PCBs in precipitation; 3) to discuss the dissolved/particulate partition behavior in precipitation; 4) to calculate the monthly depositional fluxes of total PCBs and deduce a consecutive yearly depositional flux to assess the PCBs pollution level in Beijing.

2. Experimental methods

2.1. Sampling site

Beijing is in a warm temperate zone and has a typical continental monsoon climate with four distinct seasons (Chan and Yao, 2008; Wenjie et al., 2010), which made Beijing a typical region of China to assess the temporal trends of POPs. Precipitation samples were collected on the rooftop of a building with a height ~9 m at our institute (39°54′ N, 116°14′ E) from February 2009 to March 2011 in Beijing, with a population of over 19 million by the end of 2009.

2.2. Extraction and cleanup

Sampling and analytical procedures were presented in details elsewhere (Mandalakis and Stephanou, 2004; Pearson et al., 1996) and summarized here. Precipitations were collected with stainless steel containers mounted 0.3 m above the roof from the onset to the end of rain/snow, divided into filter retained (particulate) phase and nonfilter retained (dissolved) phase with glass fiber filters (0.45 μm), and the dissolved phase volume was measured at the same time. Both phases were stored at −20 °C prior to extraction.

The filtrate was extracted with hexane (liquid–liquid extraction), and then the extract was dewatered with anhydrous sodium sulfate, concentrated to about 20 mL by rotary evaporation, treated with concentrated sulfuric acid until a clear and colorless hexane extracted was obtained, followed by washing 3 × 25 mL of 4% sodium sulfate aqueous solution to remove the water-soluble compounds (Offenberg and Baker, 1997; Poster and Baker, 1996). Subsequently, the organic layer was dewatered, concentrated to about 2 mL by rotary evaporation, transferred into a Kuderna-Danish apparatus, added the internal standards (CB-30 and CB-204) and evaporated to 0.4 mL under a gentle nitrogen steam.

The precipitation filters were triply ultrasonic extracted with hexane for 5 min, and the pooled extracts were treated with the same manner as the filtrate.

2.3. Gas chromatography and mass spectrometer (GC–MS) analysis

Samples were analyzed by gas chromatography (60 m × 0.25 mm i.d., 0.25 μm film thickness Zebron ZB-5MS column; Varian GC 3800) combined with mass spectrometer (Varian MS 2000) with purified helium as carrier gas. 1 μL of the sample was injected into the GC with split injection model. The temperature program was as follows: held 80 °C for 1 min; 80 °C–180 °C at 20 °C/min; 180 °C–280 °C at 3 °C/min; held 280 °C for 10 min. The mass spectrometer was operated under electron impact (EI) and selective ion monitoring (SIM) mode. The most abundant ions were selected for quantification, and one to four reference ions were used for confirmation of each analyte in SIM mode. PCBs congeners were furthermore identified based on relative retention times and quantified by the internal standard method according to Mullin et al. (Mullin et al., 1984). Congeners containing two through four chlorines were normalized to internal standard CB-30, and congeners containing five though seven chlorines were normalized to internal standard CB-204. Results reported as "∑PCBs" represent the summed contribution of 31 identified peaks representing 32 individual or co-eluting congeners: CB-8, 28, 52, 44, 49, 37, 74, 70, 66, 60, 101, 99, 87, 77, 82, 118, 114, 153, 105, 179, 138, 158, 126, 166 + 187, 183, 128, 156, 180, 169, 170, and 189.

2.4. Quality assurance/quality control (QA/QC)

Event-based sampling was introduced to avoid high field blanks, with cleaning of the sampler just prior to and immediately after an event with Milli-Q water (Offenberg and Baker, 1997). Quantitative PCBs standard solution containing all selected PCB congeners was spiked into sample media prior to analysis. The average recoveries of every congener were ranged 80–120% for both dissolved phase and particulate phase. Blanks containing field and analytical were examined for every 12 samples. The levels of PCBs in filers and Milli-Q water were very low and in most cases not detectable, therefore, no blank correction was performed. The instrumental detection limits ($S/N = 3$) of the selective PCBs ranged from 0.08 to 0.94 ng L^{-1}. Control calibration standards spiked with internal standards were measured regularly to check instrument performance and the linearity of calibration standards (>0.999) during analysis.

2.5. Statistical analysis

Pearson bivariate correlation matrix was performed to explore the effect of meteorological factors by using SPSS 17.0 for windows.

3. Results and discussion

3.1. PCBs in precipitation

Total PCBs concentrations measured in precipitation (dissolved plus particle phases) were listed in Table 1, along with sampling data on average wind speed, air temperature, rainfall and the percentage of PCBs in dissolved phase.

The total concentrations of PCBs ranged from 7.00 to 993 ng L^{-1} for dissolved phase and from 1.00 to 133 ng L^{-1} for particulate phase, respectively. Evidently, a significant variation between the lowest concentration and the highest concentration with about a magnitude of two orders in both dissolved phase and particulate