

## THE OCCURENCE OF HBCD IN THE VICINITY OF A TYPICAL CHEMICAL INDUSTRIAL PARK

Bing DU, Jing GUO, Wenlong Yang, Liang DONG, Jinlin LIU, Ting ZHANG, Yeru HUANG

State Environmental Protection Key Laboratory of Dioxin Pollution Control, National Research Center for Environmental Analysis and Measurement, No.1 Yuhuinanlu, Chaoyang District, Beijing 100029, China

### Introduction

The compound 1,2,5,6,9,10-hexabromocyclododecane(HBCD,C<sub>12</sub>H<sub>18</sub>Br<sub>6</sub>) has been produced since the 1960s and is the third most heavily used brominated flame retardant in the world. Its major application has been in expanded (EPS),extruded (XPS),polystyrene foams, and many other polystyrene based consumer products for insulation and construction. The global production of HBCD almost doubled from 2001 (16700 tons) to 2011 (28000 tons).

Technical HBCD (*t*-HBCD), synthesized by bromine addition to 1,5,9-cyclododecatriene, is dominated by three diastereo-isomers:  $\alpha$ ,  $\beta$  and  $\gamma$ . The *t*-HBCD ultimately depends on the manufacturer, but the  $\gamma$ -isomer accounts for more than 70% of the total with the  $\alpha$ - and  $\beta$ - isomer contributing less than 10% in general, there are trace amounts of other diastereo-isomers ( $\delta$ - and  $\epsilon$ -) present in *t*-HBCD, HBCD was identified as POPs and PBTs due to its persistence, bioaccumulation ,toxicity and long-range transport potential by US EPA and UNECE-LRTAP. In 2014, HBCD was listed in the Annex A to the Stockholm Convention on Persistent Organic Pollutants. In Europe, the production of HBCD were stopped in 2003, however, no restrictive regulation is available till now on the production and usage of HBCD in China .Even though HBCD has been found widespread in the environment , knowledge are still limited on the exposure pathway of the process of HBCD production.

The aims of the present study were to investigate the occurrence of HBCD in a typical chemical industrial park in which a HBCD manufacturing plants was located in to assess the release of HBCD from the plant and to examine the levels and diastereo-isomer profile of HBCD in the environmental matrices.

### Materials and methods

#### Samples and Sampling

In brief, 120 samples in total including air, dust, sludge, sewage, surface water and bio-samples were collected from the plant, the industrial sewage treatment plant in the industrial park , and surrounding environment in August,2014.All samples were transferred immediately to the laboratory, and kept at -20°C until analysis .

#### Analytical procedure

The water sample were exacted by liquid to liquid extraction while the other samples were extracted by ASE after added <sup>13</sup>C labelled HBCD standard. The extracts were solvent exchanged to hexane and then cleaned up by a silica column. The elution were concentrated by rotary evaporation followed nitrogen blow-down to near dryness . finally, the exacts were solvent exchanged to menthol and spiked with deuterated  $\alpha$ -HBCD as injection standard.

### **Instrument Analysis**

The three diastereo-isomers of HBCD were quantified with HPLC/MS/MS ( Agilent 1260/ 6410 ). Chromatographic separation was performed on an Agilent corbax extend C-18 reverse Phase column(100mm × 3.0mm × 1.8 μ m),with a flow rate of 0.3 ml min<sup>-1</sup> and an injection volume of 5 μ L. The mobile phase consisted of acetonitrile and water with 2 mM ammonium acetate under a gradient elution program . The two (M-H)<sup>-</sup> → Br<sup>-</sup> transitions at m/z 640.8→ 80.9 and 640.8→ 79.9 were monitored for HBCD isomers. Quantification of HBCD was preformed using the isotope dilution method.

### **QA/QC**

The limit of detection was 2-2000 ng per sample. The sample would be diluted and reanalysis in the case of higher concentration. The batch blank, <sup>13</sup>C labelled standard recovery, ion ratio and RRT were also evaluated in this study.

### **Results and discussion:**

#### **HBCD from the manufacturing plant**

The results showed that the HBCD in cauldron bottom residues, dusts and dewatered sludge were at level as high as mg g<sup>-1</sup> and should be regard as hazard waste to disposal. There was a severe air pollution in the plant due to the semi-close manufacturing technique. In the plant office, the level of HBCD in air was as high as 224 ng m<sup>-3</sup> while the HBCD level in soil ranged from 0.175 to 1.75 mg g<sup>-1</sup>. The occupational HBCD exposures and environmental risks should be very high.

The HBCD in discharge from the plant were removed more than 99% after strong oxidation process with the initial concentration about 5800 ng L<sup>-1</sup>. The discharge were then processed by sewage treatment plant in the industrial plant and released to a river with the concentration about 107-157 ng L<sup>-1</sup>. The HBCD in the receiving water body were increased about 30% and the HBCD level of the receiving water and sediments were very high as ~30 ng L<sup>-1</sup> and 292-2960 ng g<sup>-1</sup> respectively. However, it still need more evidence to judge whether the investigating plant were the only source. The research on the HBCD trend analysis and other possible sources on the receiving water should be promoted in future.

#### **Levels and diastereo-isomer profile of HBCD in the industrial park and surrounding**

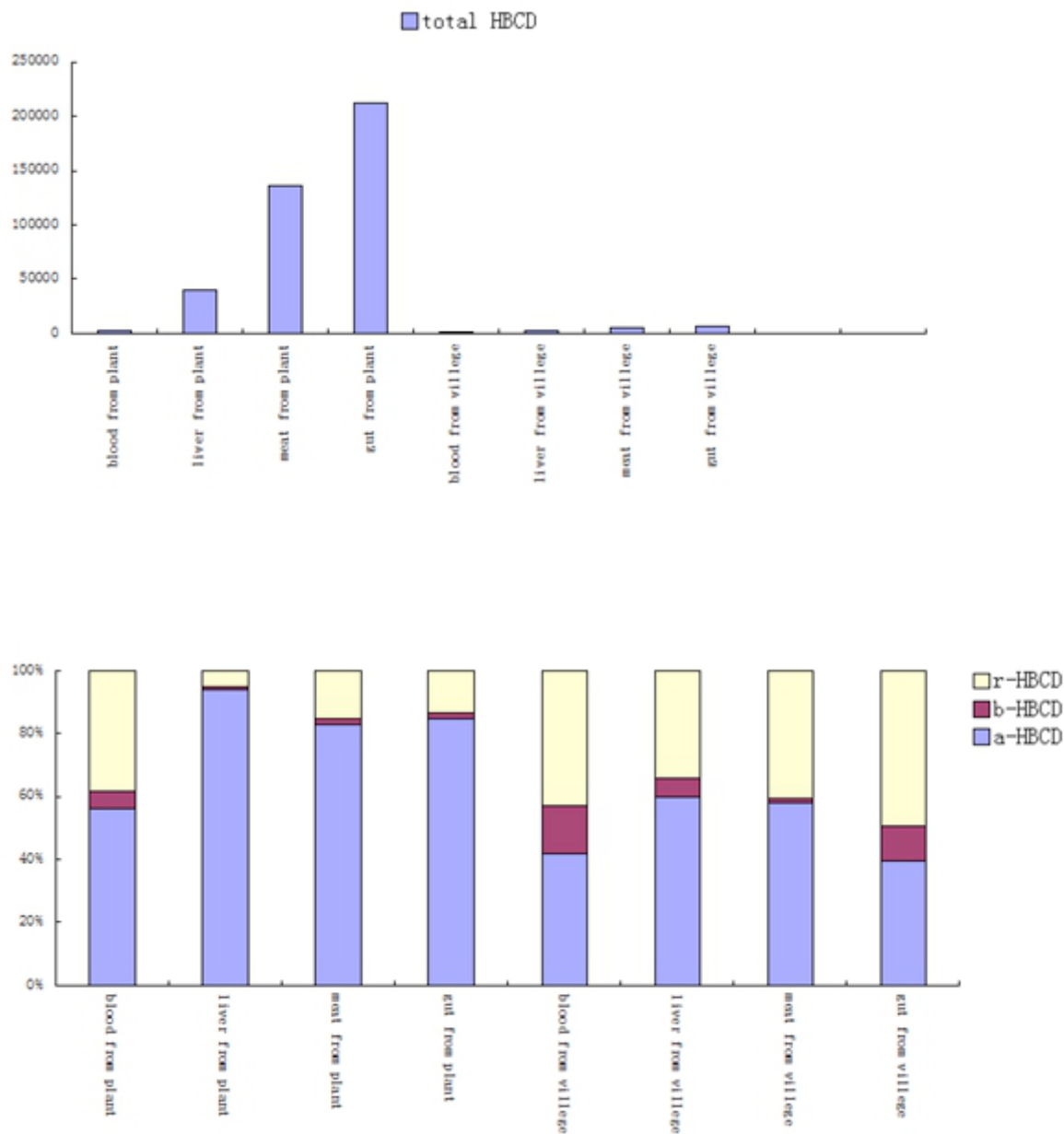
In the vicinity of industrial park , as results showed, the HBCD level in air and soils were even as high as those in the manufacture plant. The HBCD concentration in different organs of the duck was showed in figure 1 and figure 2. The total HBCD level in different organs from the manufacture plant were about 4-50 times than those in the duck from the village but the HBCD level proportion were similar. The HBCD proportion in meat, gut ,liver and blood were be about 0.64:1:0.19:0.01 from the plant while 1:0.79:0.35:0.09 from the village respectively. It might be implied that the oral ingestion was the most possible exposure way. However the HBCD diastereo-isomer profile were some different. Further research were needed to explore the factors influencing the HBCD diastereo-isomer profile in different environmental matrices and organism.

### **Acknowledgements:**

This research was financially supported by the National Key Fundamental Research Project (No. 2015CB453101) and National special fund for important instrument development (2011YQ 060084).

**References:**

1. Marvin, C. H., Tomy, G. T., Armitage, J. M., Arnot, J. A., McCarty, L., Covaci, A., and Palace, V. (2011), *Environmental Science & Technology* 45, 8613-8623.
2. XiaoJun,L.,SheJun,C., BiXian,M.,JiaMo, F.,(2010),*Science China-Chemistry*,961-973
3. G. Camp, B. G. G. A., Filippi, F., and D. D. (2011), in *Domesticated Plant Products*



**Figure 2 the HBCD diastereoisomer profile in different organs from different sites**