PARTICLE-BOUND DECHLORANE PLUS IN THE ATMOSPHERE OF HARBIN, CHINA

MA Wan-Li [1], LI Yi-Fan [2, 1], QI Hong [1], SUN De-Zhi [1], LIU Li-Yan [1]

[1]International Joint Research Centre for Persistent Toxic Substances (IJRC-PTS), State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, China; [2]Science and Technology Branch, Environment Canada, Toronto, Ontario M3H5T4, Canada

Abstract

Seventeen air samples were collected using a high-volume air sampler during May to August, 2008 in Harbin, China for measuring Dechlorane plus (DP) concentrations in air. Both particulate and gaseous phase air were collected, however only particulate phase DP was detected. The average total concentrations of DP (syn plus anti) was 0.35 ± 0.21 pg m^{-3}, which is lower than that of the Great Lakes region. The anti-DP was consistently greater than that of the syn isomer. The average fractional abundance (f_{syn}) was very close to the technical DP composition according other studies in the Great Lakes region, which indicates that there may be some new sources in this study region and further research is needed to better understand the behavior of DP in China. As we know, this study is the first attempt to measure exact atmospheric DP concentrations in China.

1. Introduction

Dechlorane plus ($C_{18}H_{12}Cl_{12}$, DP) is one of organic halogenated flame retardants (HFR), which is used to resist spread of fire. Dechlorane plus is a ubiquitous chemical in the environment due to its heavy application, such as electrical wires and cables, computer connectors, and plastic roofing materials[1]. DP has been used as a commercial chemical for more than forty years. However, only a few existing data on DP concentration in various environmental media have been presented, mainly focusing on North America, especially in the Great Lakes region. Recently, DP has been detected in air[2,3], sediment[4,5], indoor dust[6], tree bark[7], and biotas[1,8], which suggested their persistent and bioaccumulation in food webs.

In 2008, there was a paper published the results of DP in air samples in 97 Chinese urban and rural sites by using polyurethane foam (PUF) based passive air sampler (PAS), which was the first work to measure DP concentrations in atmosphere outsides the American continent[9]. The results indicated that mean air concentrations of DP in China from mid july to mid October, 2005 was 15.6 ± 15.1 pg m^{-3} in urban centers and 3.5 ± 5.6 pg m^{-3} in rural areas. These DP levels were likely attributable to local sources rather than trans-boundary influences.

In this study, 17 air samples were collected by using active sampler during May to August, 2008 at Harbin, one site of the Chinese Air Active Sampling Program (CAAS). The goal of this study is to provide the atmospheric level of DP and isomeric composition in a typical urban city air of China.

2. Materials and Methods

2.1 Sampling Information

Located at northeast of China, Harbin is the capital city of Heilongjiang province, China. Harbin is an old industrialized city, with population 3.84 million and urban area of 4272 km^2. The annual mean temperature is 3.6 °C and annual average rainfall is 523.3 mm.

Air samples were collected using a high-volume air sampler (~1 m height) with a rate of ~0.8 m^3/min on a building in the campus of Harbin Institute of Technology, Harbin, China. Sampling volumes were approximately 1151 m^3. Overall, 17 samples were collected with 24h every week during May to August, 2008. Air was drawn through a glass fiber filter (GFF, 20 cm × 25 cm) to collect particles and then through a cartridge containing two polyurethane foam

(PUF) plugs (length 5.0 cm, diameter 9.5 cm) to collect compounds presenting in vapor phase. Prior to sampling, GFFs were baked at 450 °C for 7 h to remove any organic contaminants, and PUF plugs were Soxhlet extracted for 24 h with acetone and for another 24 h with hexane. PUF plugs were dried into a vacuum desiccator and placed in a pre-washed glass flask sealed with Teflon cap until sampling. After sampling, loaded GFFs were wrapped with pre-baked aluminum foils, PUF plugs were placed in acetone rinsed glass flasks and then transported to the International Joint Research Center for Persistent Toxic Substances (IJRC-PTS) laboratory in HIT, where they were stored frozen (at -20 °C) until required for extraction.

2.2. Extraction and Analysis

The GFF and PUF samples were extracted and analyzed separately. After spiked with surrogate (polychlorinated biphenyls 155, CB 155) (Accustandard Inc., New Haven, CT), GFF and PUF samples were extracted with 120 ml DCM, 550 ml acetone: hexane (1:1, v/v) for 24 h, respectively. Extracts volumes were reduced to 5 ml using a rotary evaporator, for GFFs the solvent was exchanged into hexane with the addition of 15 ml hexane and reduced to 5 ml too. Extracts were passed through a cleaning column containing 2g anhydrous sodium sulfate and 7g silica gel, then eluted with 70ml mixture of dichloromethane and Hexane (1:1, v/v). And then the eluant was rotary-evaporated again to 4 ml, solvent-exchanged into isooctane and then reduced to 1 ml under a gentler nitrogen gas flow.

Dechlorane plus has two stereoisomers, syn and anti, during its production. Analytical-grade solutions of the syn-DP and anti-DP isomers were purchased from Wellington Laboratories (Guelph, ON, Canada) and diluted in high-purity isooctane to four levels used as calibration standard solutions. DP was quantified by external standard calibration method. DP were analyzed using Agilent 6890 GC coupled with Agilent 5973N mass spectrometer detector (GC/MSD) equipped with a 30 m × 0.25 mm × 0.25 µm DB-5 MS capillary column (J&W Scientific, Folsom, CA) in selected ion monitoring (SIM) mode. The initial oven temperature was set at 90 °C for 0.5 min, ramped at 25 °C min^{-1} to 240 °C, and ramped at 2 °C min^{-1} to 260 °C, then ramped at 20 °C min^{-1} to 285°C, held for 5 min, at last ramped at 20 °C min^{-1} to 300 °C with 5 min hold time. The MS system was operated in methane negative chemical ionization (NCI) mode. The m/z 653.8 ion was used for quantification and m/z 651.8 ion was used for identification. Figure 1 presents the GC/MS chromatogram for the syn-DP and anti-DP isomers standards.

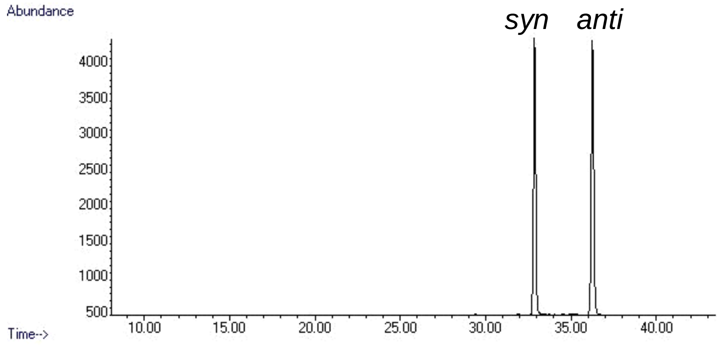

Fig. 1. Selected ion GC/MS chromatograms for syn-DP and anti-DP

2.3. Quality Assurance/Quality Control (QA/QC)

All data was subject to strict quality control procedures. When the GC retention time was matched those of the standards within 0.05 min, the compound was obtained. A field blank (prepared by loading a pre-cleaned PUF plug and GFF to the sampler for 1 min with no air drawing through) was got with each batch of four true air samples. Overall, for this study four field blanks and two laboratory blanks (solvent) were run, no DP isomer was detected in field and laboratory blanks. In this study, CB 155 was used as the surrogate for DP, because there are no difference between the recoveries of CB 155 and the DP isomers in our previous studies[9]. The average recovery efficiencies of CB 155 was 90 ± 12%, 89 ± 8% for PUF and GFF samples, respectively. The final sample concentrations were not surrogate recovery corrected.

3. Results and Discussion

3.1 Concentrations of Syn- and Anti-DP

In this study, both particulate and gaseous phase air were collected, but it was found that no DP was detected in any gaseous phase samples. As discussed in our previous, the log Koa for DP was estimated to be 14, which indicated that DP in air must be mainly associated with particle[9]. And in an early study, a similar result was also found that <1% of the atmospheric DP concentration was detected to be in gaseous phase air[2]. So in the following discussion, only particulate phase concentration was reported. Concentrations of syn- and anti-DP isomers in particulate phase were presented in Table 1. Both isomers were detected in all air samples with anti-DP consistently greater than that of the syn isomer. The total concentrations of DP (syn plus anti) ranged from 0.16 pg m^{-3} to 0.89 pg m^{-3}, with the average concentration being 0.35 ± 0.21 pg m^{-3} for the seventeen samples. The result was similar to the concentrations reported at Sleeping Bear Dunes and Eagle Harbor (0.8 pg m^{-3}) and lower than that of Chicago in 2005 to 2006 (2.4 ± 0.3 pg m^{-3}) and Sturgeon Point in 2004 (34 ± 24 pg m^{-3}), which are sites of Integrated Atmospheric Deposition Network in Great Lakes region[2,3]. In our previous study, mean DP concentration for urban and rural sites were 15.6 ±15.1 pg m^{-3} and 3.5 ± 5.6 pg m^{-3}, respectively in 2005[9]. Those results were one order magnitude higher than that presented in this study. Air sampling continuous in the same site, and more data will be available, which may explain why the air concentration of DP in the region is so low.

Table 1

Concentrations of syn- and snti-DP, and the values of *f*syn in air samples collected from May to August, 2008 in Harbin, China

Date	syn-DP	anti-DP	f_{syn}[a]	Date	syn-DP	anti-DP	f_{syn}
5/07	0.10	0.19	0.35	7/10	0.05	0.15	0.24
5/13	0.11	0.13	0.42	7/16	0.06	0.10	0.38
5/19	0.07	0.10	0.27	7/22	0.23	0.58	0.28
5/27	0.18	0.24	0.36	7/28	0.07	0.20	0.25
6/04	0.08	0.12	0.40	8/05	0.07	0.10	0.42
6/12	0.17	0.29	0.38	8/13	0.12	0.16	0.43
6/20	0.37	0.51	0.42	8/21	0.10	0.21	0.32
6/28	0.12	0.18	0.40	8/29	0.08	0.18	0.29
7/04	0.13	0.20	0.39				

[a] f_{syn} = concentration of syn-isomer divided by total of syn + anti concentrations for each sample

In this study, ambient air temperature and TSP were further investigated to find which parameter may influence the atmospheric concentration of DP in Harbin. The ambient air temperature and TSP ranged from 12 to 28 °C and 12 to 70 μg m^{-3}, respectively, during the sampling period. Unfortunately, no statistical correlation was found between ambient air temperature and DP concentrations. Actually, only particulate phase DP was detected in this study, which is not easily affected by ambient air temperature. When the DP concentration was plotted against TSP, a weak correlation ($R^2 = 0.12$) was obtained.

3.2 Syn- and Anti-DP Fractional Abundance

The f_{syn} values, defined as the concentration of syn-DP divided by the total DP, were presented in Table 1. The average f_{syn} value was 0.35 ± 0.6, which is very close to the technical value with DP product (0.35) [1]. This results is also consistent with our previous studies, as the mean f_{syn} value was 0.33 ± 0.10[9]. According to the studies in Great Lakes region, microbial degradation[5] and long range atmospheric transport[2] will result in change of the f_{syn} value, as the differences in the physical or chemical properties of the two stereoisomers. Unfortunately, little information on DP is obtained in China, so we supposed the f_{syn} value of DP used in China is 0.35 too. Our results suggest that the atmospheric DP is from recently used commercial products and there may be some sources in this study region. Further research is needed to better understand the fate of DP in China.

Acknowledgements

We would like to thank Jin-Min Shen of IJRC-PTS for his help of sample analysis. Financial support from Harbin Institute of Technology (HIT) is highly appreciated.

References

1. Tomy G.T., Pleskach K., Ismail N., Whittle D.M., Helm P.A., Sverko E., Zaruk D., Marvin C.H. *Environ Sci Technol* 2007; 41: 2249.
2. Hoh E., Zhu L., and Hites R.A. *Environ Sci Technol* 2006;40: 1184.
3. Venier M., Hites, R. A. *Environ Sci Technol* 2008;42: 4745.
4. Qiu X.H., Marvin C.H., and Hites R.A. *Environ Sci Technol* 2007;41: 6014.
5. Sverko E., Tomy G.T., Marvin C.H., Zaruk D., Reiner E., Helm P.A., Hill B., McCarry B.E. *Environ Sci Technol* 2008;42: 361.
6. Zhu J.P., Feng Y.L., and Shoeib M. *Environ Sci Technol* 2007;41: 7694.
7. Qiu X.H., Hites R.A. *Environ Sci Technol* 2008;42: 31.
8. Gauthier L.T., Letcher R.J. *Chemosphere* 2009;75: 115.
9. Ren N.Q., Sverko E., Li Y.F., Zhang Z., Harner T., Wang D.G., Wan X.N., McCarry B.E. *Environ Sci Technol* 2008 ;42: 6476.