HALOGENATED PERSISTENT ORGANIC POLLUTANTS IN HUMAN BLOOD PLASMA FROM SANMING, SOUTHEASTERN CHINA

Wu Qiugeng[1], Yang Limin[1] and Wang Qiuquan*[1,2]

[1] Department of Chemistry & the MOE Key Laboratory of Analytical Sciences, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China; email: qqwang@xmu.edu.cn
[2] State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen 361005, China

Abstract

Human plasma samples collected in January 2008 from 86 blood donors residing in Sanming, southeastern China, were analyzed for halogenated persistent organic pollutants (H-POPs) including organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs). The median values of HCB, $\sum_4$HCHs, $\sum_4$DDTs, $\sum_{10}$PCBs and $\sum_{15}$PBDEs were 31.6, 48.3, 1408, 12.4 and 2.5 ng/g lipid, respectively. Compared with the developed countries, such plasma H-POPs concentrations revealed relatively lower PCBs and PBDEs exposure levels, however, higher OCPs exposure levels in this general population in Sanming. The most frequently detected OCPs were p,p′-DDE and β-HCH, accounting for greater than 82% in DDTs and 66% in HCH isomers, respectively. PCB153, 180, 138, 163 and 118 were predominant congeners determined, contributing more than 93% of the $\sum_{10}$PCBs. Four out of the 86 plasma samples (accounted about 5%) was found measurable BDE209 concentration (2.9-3.6 ng/g lipid), indicating potential pollution of commercial Deca-BDE. Correlation between H-POPs exposure levels and individual information such as age, occupation and gender were analyzed. Some kind of OCPs and PCBs were observed to correlate positively to human age. Relatioship between the plasma H-POPs levels and those in the environmental media and dietary intake is being investigated in our laboratory.

Introduction

As the agricultural and industrial application of halogenated persistent organic pollutants (H-POPs) including organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs), they have become ubiquitous trace pollutants in various environmental compartments. Worldwide concerns about the impact of H-POPs on human health have been raised during the recent decade since H-POPs are apt to bioaccumulate and biomagnify in human tissues and cause toxic effects including teratogenicity, carcinogenicity, immunotoxicity, endocrine disruption and reproductive effects. Potential health risk investigations are essential because of the increasing usage of PBDEs and suspected emission of banned PCBs and OCPs. In China, however, assessments of the general population exposure to H-POPs, particularly to PBDEs, are still quite limited and mostly focused on southern coastal areas where manufacturing industry are greatly developed[1]. In this study, blood plasma samples of the residents from Sanming located in Fujian province southeastern China were collected. Examination of the concentrations and congener profiles in the blood plasma samples is expected to reflect the contamination status of this general population.

Materials and Methods

Sampling. Human blood plasma samples collection was approved by the Health Department of Fujian Province and assisted by Sanming municipal blood station. Urban area of Sanming is at longitude 26°13′, latitude 117°36′ and altitude 310 m above sea level, with 290,000 inhabitants and 76.8% forest coverage surrounding. In January 2008, a total of 86 volunteers aged from 19 to 54 were recruited. A survey containing race, sex, age, blood type, occupation and residence location as well as medical history was carried out for the volunteers (Figure 1). Before phlebotomy, infectious diseases (e.g. HIV, hepatitis B&C, syphilis etc.) were tested to ensure eligible blood. Cubital vein blood of 200-400 mL was drawn for each volunteer by phlebotomist into transfusion bag, which containing 28 mL anticoagulant solution (Citrate-phosphate-dextrose-adenine, CPDA). Chylemia must be eliminated by notifying the volunteers to avoid fatty food before donating blood. Plasma was separated by centrifugation (500 g for 30 min at 5°C) within 24 hours after sampling. Aliquots of 20 mL plasma were respectively stored in dark at -20 °C for further H-POPs analysis.

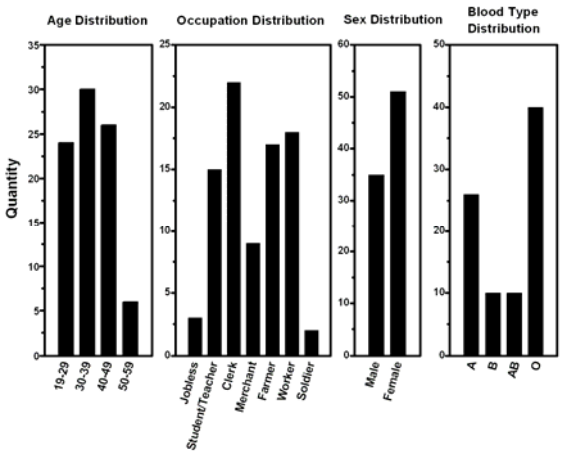

Figure 1: Statistical information of blood donors inhabiting in Sanming urban area, who have same Han nationality and are in good healthy condition

Sample Pretreatment and Analysis. A detailed description of sample pretreatment for plasma H-POPs analysis has been published elsewhere[2]. Briefly, $^{13}C_6$-HCB, D_6-α-HCH, $^{13}C_{12}$-PCB-77, 101, 141, 178 and $^{13}C_{12}$-BDE-77, 126, 209 as internal standards were spiked into 5 g sample prior to analysis. Plasma were denaturalized by hydrochloric acid and isopropanol, and extracted three times with hexane/methyl t-butyl ether (1:1). The extracts were then treated by concentrated sulfuric acid and cleaned up by silica/sulfuric acid column (silica/sulfuric acid 2:1 by weight). Procedural blanks were performed in parallel for every batch using anticoagulant solution from transfusion bags. Thirty four H-POPs including 9 OCPs (HCB, α, β, γ, δ-HCH, p,p′-DDT, o,p′-DDT, p,p′-DDE, p,p′-DDD), 10 PCBs (PCB-28, 52, 101, 105, 118, 138, 153, 163, 180 and 209) and 15 PBDEs (BDE-17, 28, 47, 49, 66, 71, 85, 99, 100, 138, 153,154,183,190 and 209) were analyzed using a GC-MS QP2010 equipped with electron capture negative ionization (ECNI) source[3].

Results and Discussion

OCPs in the plasma samples. The plasma concentrations of HCB, $\sum_4$HCHs and $\sum_4$DDTs (DDT and its metabolites) were in the range of 3.8-59.2, 10.4-89.5 and 1021-1794 ng/g lipid with median values of 31.6, 48.3 and 1408 ng/g lipid, respectively. The most frequently detected OCPs were p,p′-DDE and β-HCH, which accounted for greater than 82% and 66% among DDTs and HCH isomers, respectively. Comparison of the lipid normalized OCPs levels in the plasma or serum or adipose between Sanming and other area in the world are listed in Table 1. The levels of HCB and HCHs determined were close to those in other countries, however, the DDTs level in the plasma samples of the residents in Sanming was one order of magnitude higher than other developed countries and similar to those of Haojiang, Guangdong province China, indicating that comprehensive use of technical DDT in the area during the last decades. Greatly exceeded concentration of p,p′-DDE (855-1533

ng/g lipid; median value, 1203 ng/g lipid) than that of p,p′-DDT (98-390 ng/g lipid; median value 182 ng/g lipid) indicates indirect or historical exposure of DDT pesticide[4]. Relatively low ratio (greater than 5.4, median value 10.3) of p,p′-DDE/p,p′-DDT obtained in this study implied possible new source due to current use of dicofol containing DDT impurities.

PCBs in the plasma samples. The concentrations of $\sum_{10}$PCBs determined ranged from 2.4 to 34.6 ng/g lipid with median values of 12.4 ng/g lipid. PCB153, 180, 138, 163 and 118 were predominant congeners, contributing more than 93% of the $\sum_{10}$PCBs. The PCBs determined were mostly hexachlorinated congeners indicating higher chlorinated substituted products were used before. Unexpectedly, PCBs found in this study was approximately 10 times lower than those found in the developed countries, which may be ascribed to the less-polluted PCBs in this area.

PBDEs in the plasma samples. The total concentrations of the fifteen PBDEs found in all the plasma samples varied from 1.0 to 4.3 ng/g lipid with median value of 2.5 ng/g lipid. The exposure levels in Sanming population was similar to those of non-occupational population in Europe, such as the UK (4.7ng/g lipid)[4], Sweden (2.4ng/g lipid)[5], while 70 times lower than levels of residents from Haojiang in Guangdong province, southern China[1]. This obvious difference can be explained that there is an e-waste dismantling site nearby Haojiang and the residents consumed more polluted fishes. BDE209, the predominant congener in the deca-BDE commercial product, was banned to use in European Union, but still used widely in China. Measurable BDE209 concentration was found in four out of the 86 plasma samples (accounted about 5%) in the range of 2.9-3.6 ng/g lipid. This result suggested that slight pollution of BDE209 may have occurred in the general population which is needed continuous attention.

Correlation of exposure levels with population statistical factors. Considering the complicated influencing factors on H-POPs bioaccumulation in human body, single statistical information such as age, occupation and gender were analyzed for correlation with H-POPs exposure levels. Only the factor of individual age, however, was found correlated significantly with several kinds of H-POPs concentration. Linear regression analysis between H-POPs concentration and individuals' age were presented in Figure 2. The results showed that HCB, p,p′-DDE and $\sum_{10}$PCBs correlated significantly with age, while $\sum_{4}$HCHs and $\sum_{15}$PBDEs correlated weakly with age. Preliminary conclusion could be drawn that age is an important

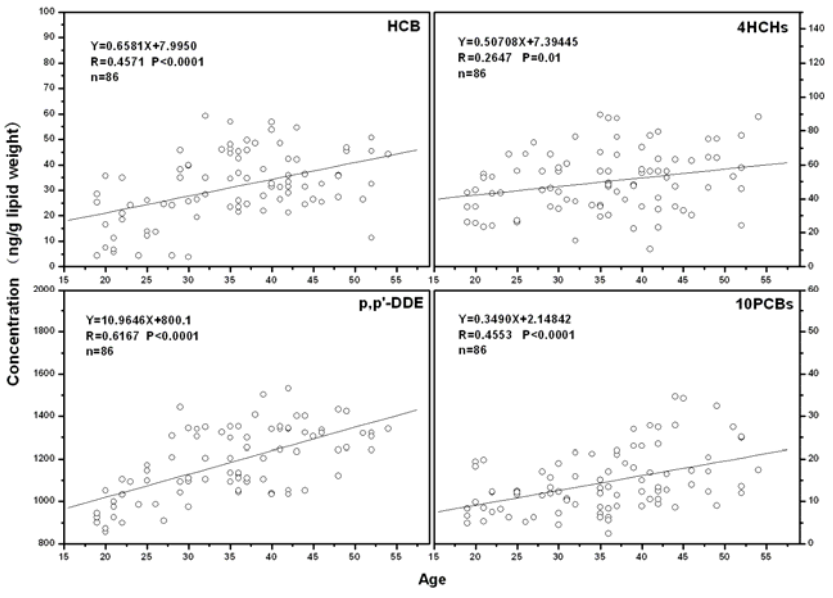

Figure 2: Selected H-POPs concentration (ng/g lipid weight) plotted against individual age

factor, but maybe not the only one, influencing the accumulation of H-POPs in human body. Further studies of H-POPs exposure levels in various environmental media are necessary to understand the exposure routes more clearly.

Acknowledgements

This study was supported financially by the National 863 Project of China (No.2006AA06Z404) and the National Basic Research Program of China (No.2009CB421605). We thank Sanming municipal central blood station and the Health Department of Fujian Province for samples collection assistance. The loan of the Shimadzu GC-MS QP2010 was much appreciated.

References

1. Bi, X. H.; Thomas, G. O.; Jones, K. C.; Qu, W. Y.; Sheng, G. Y.; Martin, F. L.; Fu, J. M., *Environ. Sci. Technol.* **2007,** *41*, (16), 5647-5653.
2. Hovander, L.; Athanasiadou, M.; Asplund, L.; Jensen, S.; Wehler, E. K., *J. Anal. Toxicol.* **2000,** *24*, (8), 696-703.
3. Zhao, Y. L.; Yang, L. M.; Wang, Q. Q., *J. Am. Soc. Mass Spectrom.* **2007,** *18*, (8), 1375-1386.
4. Thomas, G. O.; Wilkinson, M.; Hodson, S.; Jones, K. C., *Environ. Poll.* **2006**, *141*, (1), 30-41.
5. Thuresson, K.; Bergman, A.; Jakobsson, K., *Environ. Sci. Technol.* **2005,** *39*, (7), 1980-1986.
6. Van Oostdam, J. C.; Dewailly, E.; Gilman, A.; Hansen, J. C.; Odland, J. O.; Chashchin, V.; Berner, J.; Butler-Walker, J.; Lagerkvist, B. J.; Olafsdottir, K.; Soininen, L.; Bjerregard, P.; Klopov, V.; Weber, J. P., *Sci. Total Environ.* **2004,** *330*, (1-3), 55-70.
7. Johnson-Restrepo, B.; Kannan, K.; Rapaport, D. P.; Rodan, B. D., *Environ. Sci. Technol.* **2005,** *39*, (14), 5177-5182.
8. Dirtu, A. C.; Roberta, C.; Dragan, D.; Raluca, M.; Van Grieken, R.; Neels, H.; Covaci, A., *Environ. Int.* **2006,** *32*, (6), 797-803.
9. Kawashiro, Y.; Fukata, H.; Inoue, M. O.; Kubonoya, K.; Jotaki, T.; Takigami, H.; Sakai, S. I.; Mori, C., *Endocr. J.* **2008,** *55*, (6), 1071-1084.
10. Minh, T. B.; Watanabe, M.; Kajiwara, N.; Iwata, H.; Takahashi, S.; Subramanian, A.; Tanabe, S.; Watanabe, S.; Yamada, T.; Hata, J., *Arch. Environ. Contam. Toxicol.* **2005,** *51*, (2), 296-313.

Table 1. H-POPs concentrations in human tissues worldwide

Region	Year	type of sample	Concentration (ng/g lipid)					Ref.
			Median (range) of HCBs	Median (range) of ∑HCHs	Median (range) of ∑DDTs	Median (range) of ∑PCBs [b]	Median (range) of ∑PBDEs [c]	
North America [a]	2003-2004	adipose	22 (9.7-60)	15 (1.9-37)	308 (77-2051)	110 (18.9-816)	77.3 (17-9630)	[6, 7]
13 sites in the UK	2003	serum	11 (<4.8-72)	15 (<8.9-120)	100 (1.3-2600)	170 (4-670)	5.6 (0.63-420)	[4]
Iassy, Romania	2005	serum	30 (<2.0-107)	1114 (177-12180)	2420 （446-34930）	383 （45-4970）	1.04 [d]	[8]
Miyako, Japan	2005-2006	blood	7.8 (4.6-20)	28 (7.6-130)	230 (56-1400)	100 (24-200)	3.0 (1.8-17)	[9, 10]
Haojiang, China	2005	serum	31 (8.1-66)	39 (5.6-540)	2300 (380-5100)	63 (22-140)	170 (16-490)	[1]
Sanming, China	2008	plasma	31.6 (3.8-59.2)	48.3 (10.4-89.5)	1408 (1021-1794)	12.4 (2.4-34.6)	2.5 (1.0-4.3)	This study

(a) OCPs data came from population of Nunavik and Kitikmeot, Canada, while PCBs and PBDEs data came from New York, U.S.A.; (b) congener quantity of ∑PCBs determined from top to bottom was 52, 43, 14, 200, 43, 10, respectively; (c) congener quantity of ∑PBDEs determined from top to bottom was 11, 21, 6, 27, 14, 15, respectively; (d) a pooled sample was determined.