SURVEY OF PERSISTENT ORGANOCHLORINE PESTICIDES IN HUMAN MILK FROM SHANGHAI, CHINA

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Abstract

The aim of our study was to obtain the daitery exposure of breast-fed infants to persistent organochlorine pesticides (OCPs) in Shanghai of China. The levels of OCPs in human milk, including Aldrin, Chlordane, Dieldrin, Endrin, Heptachlor, Hexachlorobenzene(HCB), Mriex, DDT, and hexachlorocyclohexane(HCH) were determined in 2 pooled human milk samples derived from 50 and 60 individual human milk samples respectively. The samples were collected in 2007 according to 4th WHO protocol. The range of concentration of OCPs in human milk was from 1.5 to1025.5 ng/g fat in urban and from 1.5 to 721.2 ng/g fat in rural. The estimated daily intake(EDI) of OCPs for breast –fed infants ranged from 0.0069 to 5.0250 ug kg^{-1} bw per day in urban and ranged from 0.0062 to 3.4329ug kg^{-1} bw per day, which were below the acceptable daily intake value of OCPs recommended by the Joint FAO/WHO Meeting on Pesticide Residues (JMPR) [1].

Introduction

Organochlorine pesticides (OCPs) are a group of chemicals, many of which persist in the environment. OCPs had been shown a wide variety of toxic actions in wildlife and humans. Furthermore, these compounds tend to resist degradation and bioaccumulate in the food-chain. On 23 May 2001，delegates from 115 countries countries and the European Commission had signed the Stockholm Convention on Persistent Organic that aims to eliminate or restrict the production and use of persistent organic pollutants (POPs). There were initially twelve distinct chemicals listed in three categories including OCPs such as Aldrin, Chlordane, Dieldrin, Endrin, Heptachlor, Hexachlorobenzene, Mriex, DDT. Other chemicals such as α-hexachlorocyclohexane,β-hexachlorocyclohexane and Lindane (gamma-hexachlorocyclohexane) that could pose similar hazardous threats to human health and the environment, were added by the Fourth Conference of Parties, May 2009. The Chinese government has undertaken to date in reducing the presence of (POPs) and has developed variety of monitoring for these chemicals especially biomonitoring with human milk. Now we have attempted a) to obtain the levels of organochlorine pollutants in human milk samples collected in Shanghai of China during 2007. b) to investigate whether significant alterations in levels of these contaminants have occurred since these pesticides were banned or restricted to use in china. c）to assess the health risk from OCPs for infants in Shanghai.

Merterials and methods

Donor selection and sample collection. The sampling was carried out in 2007. One urban site and two rural sites were selected for sampling in shanghai. 50 donors were selected in each urban area, and 30 donors were selected in each rural area. At least 50 ml of milk in total was collected from each mother. The samples were collected directly to the collecting jars pre-washed and were stored in the freezer at -20°C until analysis. Mothers provided the samples at the local contact places where collection can be supervised. The ages of mothers ranged from

18-35 with a mean of 25.6. From the questionnaires, there was no smoker and no one used DDT in the house. The number of vegetarian was too little to be considered.

Sample pooling and analyzing. The individual samples from urban areas were pooled into one pooled sample and individual samples from 2 rural areas were pooled into one pooled sample. As result, 2 pooled samples were created to biomonitor the burdens of OCPs in Shanghai. OCPs were analysis by gas chromatography-negative chemical ionization-mass spectrometry (GC-NCI-MS) in the selected ion monitoring mode with isotope dilution. About 20 ml pooled sample were dried in a freeze-dryer After spiking with $^{13}C_{12}$-labeled internal standard, samples were Soxhlet-extracted with a mixture of *n*-hexane and dichloromethane (1:1, 250 ml) for 24 h. Gravimetric lipid determination was performed after solvent evaporation. Most of lipid removal was achieved by automatic cleanup system of Gel Permeation Chromatography (GPC, J2 Scientific, USA). After the fractions containing OCPs were collected, the samples were concentrating to about 1ul. The identification and quantification was performed by a GC-NCI-MS (Shimadzu, Japan) with a VF5 -5MS capillary column (30 m x 0.10 mm i.d. x 0.25 um)(Varian,USA).

QA/QC. Limits of detection (LODs) were defined as three times the noise level. The LODs of α - HCH, β -HCH, γ -HCH and δ -HCH in human milk were 0.20, 3.00, 0.10 and 0.60 ng/gfat; LODs for op′ -DDE, pp′ -DDE , op′ -DDD , pp′ -DDD , op′ -DDT , pp′ -DDT were 3.00, 0.80, 3.00, 12.00, 10.00 and 4.00 ng/gfat ; The LODs for other OCPs were 0.01-4.00 ng/gfat. The recoveries of internal standard were all within the range of 74 to 127% . the laboratory performance was validated by successfully participating in inter-laboratory comparison studies of in OCPs milk powder (z-score of Heptachlor was -1.4) and fishoil (z-score of PP-DDE was 0.4; PP-DDD(TDE) was 0.2; Dieldrin was 1.1; Oxychlrodane was 0.4; Endrin was 0.3) organized by the FAPAS Proficiency Test in 2007 and 2008.

Results and Discussion

Organochlorine compounds were detected in the pooled human milk from Shanghai (Table 1). Typically，a wide range of concentrations for different OCPs were detected in the pooled human milk samples from 1.5 to1025.5 ng/g fat in urban and from 1.5 to 721.2 ng/g fat in rural. The most abundant contaminants were DDTs, HCHs and HCB, whereas other compounds such as chlordane related compounds, endrin, mirex, dieldrin, aldrin and heptachlor were present at relatively low levels.

The levels of total DDTs in breast milk declined 36% in Shanghai over a 4 year period and it was lower than the data reported in breast milk in 1998 from Beijing and in 2000 from Changsha[2,.3, 4]. The level of DDTs detected in the studied samples was generally lower than those reported from some developing countries, such as Mexico, Thailand and Tunisia[5,6,7]. In contrast, this level was higher than those reported from some developed countries, such as Sweden, Japan, Australia and United Kingdom[8.9.10,11].

The total concentrations of HCHs were second highest among OCPs (424.86ng/gfat in urban area of Shanghai, 321.00 ng/gfat in rural area of Shanghai). There are no significant difference found between the urban and rural area ($P>0.05$). The contaminants decreased dramatically compare to the average level of total HCHs 1590.00 ng/gfat in 2003 from Shanghai and it was lower than 2200.00 ng/gfat in2000 from Changsha and 1180.00 ng/gfat in 1998 from Beijing.

The concentration of HCB in human milk was 36.74 ng/g fat in urban area of Shanghai, and 22.55 ng/g fat in

urban area of Shanghai. The contaminant level of HCB which was reported in 2000 from Changsha was nearly 2 times than concentration of HCB in this study.

Table 1. Concentrations(ng/g fat) of OCPs in Human Milk from Chinese Shanghai

OCPs	urban	rural
Aldrin	ND	ND
trans-chlordane	ND	ND
cis-chlordane	ND	ND
oxychlordane	2.53	1.81
trans-nonachlor	2.70	1.80
dieldrin	ND	ND
op′ -DDE	ND	1.40
pp′ -DDE	978.85	675.8
op′ -DDD	ND	ND
pp′ -DDD	ND	5.90
op′ -DDT	ND	4.30
pp′ -DDT	32.65	32.30
Endrin	ND	ND
endrin ketone	ND	ND
Heptachlor	0.80	0.71
Trans-Heptachlor epoxides	ND	ND
HCB	36.74	22.55
α - HCH	2.15	2.00
β -HCH	397.41	313.10
ɣ -HCH	21.60	3.50
δ -HCH	3.70	2.40
Mirex	2.68	3.30

This study firstly reported the levels of chlordane (total), Heptachlor (total), mirex, endrin(total), aldrin and dieldrin in human milk from Shanghai in China. As shown in Table 1, chlordane (total), Heptachlor (total) and mirex were found in the human milk. Others were relative lower under the limited of detection.

In order to assess the infant health risk in Shanghai, the average daily intake of OCPs by infants was estimated. The calculation was based on the assumption of infant's daily milk consumption, 700mL and infant weight, 5kg[12]. The estimated daily intake of total DDT for breast feeding infants was 5.02 μg/kg body weight /day in urban area of Shanghai and 4.54 μg/kg body weight /day in rural area of Shanghai which were lower than the acceptable daily intake of 20.0 μg/kg body weight recommended by the Joint FAO/WHO Meeting on Pesticide Residues (JMPR) [1] . The estimated daily intake (EDI) of aldrin and dieldrin was both 0.0074μg/kg body weight /day in urban area of Shanghai and 0.0071μg/kg body weight /day in rural area of Shanghai which was below the acceptable daily intake of 0.1μg /kg body weight recommended by JMPR. EDI of chlordane (total), endrin (total)

and Heptachlor (total) didn't exceed the FAO/WHO acceptable daily intake. EDI of all of OCPs by μg kg^{-1} bw per day for breast –fed infants is shown in Table2.

Table2. EDI (μg kg^{-1} bw per day)of OCPs of infants in Shanghai in2007

OCPs	urban	rural	ADI (FAO/WHO)
aldrin	0.0074	0.0071	0.1
Σchlordane	0.0271	0.0186	-
dieldrin	0.0074	0.0071	0.1
ΣDDT	5.0250	3.4329	20.0
Σendrin	0.0167	0.0162	2.0
ΣHeptachlor	0.0069	0.0062	0.5
HCB	0.0013	0.1073	-
ΣHCH	0.0149	1.5280	-
mirex	0.0001	0.0157	-

The concentrations below LOD were treated as 1/2LOD fro calculation. ND, not detected.

"- " represents lack of value of ADI

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References

1. A REVIEW OF SELECTED PERSISTENT ORGANIC POLLUTANTS DDT-Aldrin-Dieldrin-Endrin-Chlordane Heptachlor-Hexachlorobenzene-Mïrex-Toxaphene Polychlorinated biphenyls Dioxins and Furans. http://www.who.int/ipcs/assessment/en/pcs_95_39_2004_05_13.pdf

2.Li Y.H., Guo C.Y., Wang G.Q., Yang Y. L., Zhu Y.P., Xu M.Z., Yuan H., Zhang G.Y., Gao S.S., Zhu X.Y., Zhao G.Y., Ruan S.Y., Yuan D., Wu L.M. *Journal of environmental &occupational medicine*.2003;181:185.

3.Yu H.F., Zhao X.D., Zhang X.M., Zhu Z.Q., Liu J.L. *Journal of environmental and health.*2001;352:354.

4.Cao H.J., Cao C.H., Hu X.H., Zhou X.D., Yang Y., Wang W.H., Yuan C.H., Liu J.Q., Fan D., Su A.X., Huang T. *Practical preventive medicine*. 2007;172:174.

5.Waliszewski S.M., Valencia Quintana R., Corona C.A., Herrero M., Sánchez K., Aguirre H.,Aldave I.A., Gomez Arroyo S., Villalobos Pietrini R. *Arch Environ Contam Toxicol.* 2009;685:690.

6. Stuetz W., Prapamontol T., Erhardt J.G., Classen H.G.. *Sci Total Environ.* 2001;53:60.

7.Ennaceur S.; Gandoura N.; Driss M. *Bull Environ Contam Toxicol.* 200;325:329.

8. Norén K, Meironyté D. *Chemosphere*. 2000;1111:1123.

9. Konishi Y, Kuwabara K, Hori S. *Arch Environ Contam Toxicol*. 2001;571:578.

10. Mueller JF, Harden F, Toms LM, Symons R, Fürst P. *Chemosphere.* 2008;712:720.

11.Kalantzi O.I., Martin F.L., Thomas G.O., Alcock R.E., Tang H.R., Drury S.C., Carmichael P.L.,Nicholson

J.K., Jones K.C. *Environ Health Perspect*. 2004;1085:1091.
12.Chan J.K, ,Xing G.H.,Xu Y, Liang Y, Chen L.X., Wu S.C., Wong C.K., Leung C.K., Wong M.H. *Environ Sci Technol*. 2007;7668:7674.