

Correlations of PCBs, DIOXIN, and PBDE with TSH in Children's Blood in Areas of Computer E-waste Recycling*

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Abstract

Objective To study correlations of polychlorinated biphenyls (PCBs), DIOXIN, and polybrominated diphenyl ethers (PBDE) with thyroid stimulating hormone(TSH) in children, and assess the impact on children's health.

Methods Three hundred and sixty nine children aged from 6 to 8, including 195 from Luqiao, the computer E-waste recycling area, and 174 from Longyou, the control area, were selected for this investigation to elucidate the correlation of PCBs, DIOXIN, and PBDE with TSH in children's blood samples. The children had a physical examination and their blood levels of PCBs, DIOXIN, PBDE, and TSH were detected after sample collection.

Results In the E-waste recycling area, the contents of PCBs, PBDE, DIOXIN, and TSH in the blood samples of children were $484.00 \pm 84.86 \text{ ng} \cdot \text{g}^{-1}$ lipid weight, $664.28 \pm 262.38 \text{ ng} \cdot \text{g}^{-1}$ lipid weight, $26.00 \pm 19.58 \text{ ng} \cdot \text{g}^{-1}$ lipid weight and $1.88 \pm 0.42 \text{ } \mu\text{IU/mL}$ (serum) respectively, while in the control area, the PCBs, PBDE, DIOXIN, and TSH contents were $255.38 \pm 95 \text{ ng} \cdot \text{g}^{-1}$ lipid weight, $375.81 \pm 262.43 \text{ ng} \cdot \text{g}^{-1}$ lipid weight, $39.64 \pm 31.86 \text{ ng} \cdot \text{g}^{-1}$ lipid weight, and $3.31 \pm 1.04 \text{ } \mu\text{IU/mL}$ respectively.

Conclusion The health status of children in the control area are better than that in the contaminated area. Among children who are exposed to persistent organic pollutants, the pollutant content increases significantly in their serum, and the distribution of TSH levels in their bodies are also affected.

Key words: PCBs; DIOXIN; PBDE; TSH; E-waste; Children's blood samples

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INTRODUCTION

It has been reported that about 80% of computer E-wastes are exported to Asia, and 90% of these exports have been shipped to China^[1]. In the process of recycling or disposing these E-wastes, they will release into the environment large amounts of persistent organic pollutants (POPs), such as PAHs, PCBs, PBDE, and DIOXIN. Persistent Organic Pollutants (POPs) are stable and accumulated within living organisms and can migrate with the atmosphere. PCBs are difficult to degrade in the environment and have a long

half-life. In addition, they can relocate in various ways and through different channels and then cause a wide range of pollution. Furthermore, PCBs are highly fat-soluble and can induce high accumulation of toxicity in human and animal bodies. Children may be especially sensitive to hormone disruption from chemicals including PCBs and PBDE^[2]. Increasing evidences have demonstrated that PBDE as well as PCBs have thyroid disrupting activity, neurotoxicity and reproductive toxicity, etc^[1]. Environmental chemicals may interfere with thyroid homeostasis through coupling effects of the multiple mechanisms; and at the receptor level, they may bind to transport

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proteins via cellular uptake pathways or by modifying the metabolism of TSH^[3]. The primary objective of our study is to explore how PCBs, DIOXIN and PBDE affect TSH levels in selected children, and assess how they will affect children's health based on the sampled data.

MATERIALS AND METHODS

Study Subjects

Three hundred and sixty nine children were selected as the samples of the survey, which adopted Luqiao as the area of E-waste recycling^[9] Longyou as the control area. The enrolled children met with the following conditions: ① being aged from six to eight; ② living in the investigated district for over five years (including five years); ③ being free from thyroid diseases and without a history of taking thyroid medication.

Physical Examination

After inquiring children's age, gender, diet, previous health status, their parents' name, and other relevant circumstances, 66 children were selected to receive physical examination including height, weight, acne, skin pigmentation, and mentality development etc.

Sample Collection

Fasting peripheral blood of 10 mL was collected early in the morning from each subject for TSH detection. As the blood samples were not enough for other detections, more children of the same age, sex and period of residence were selected, and 7 portions of blood samples (blood samples from 3-4 children were mixed as 1 portion) were collected for PCBs, DIOXIN, and PBDE detection.

The specific components of PCBs, DIOXIN, and PBDE tested in blood samples are shown in Table 1.

Laboratory Analysis

Sample preparation and purification^[10] Analytic Methods: Dioxins/ PCBs / PBDEs & lipid analysis and quality control are described in EPA Method 1613B (USEPA, 1997), 1668A (USEPA, 1999), and 1614 (USEPA, 2007). Quantification was performed by using an isotope dilution method. Thyrotropin (TSH IRMA PCS) was provided by the National Atomic Energy of China.

Table 1. PCBs, DIOXIN, and PBDE Measuring Index

Classification	Measuring Index
PCBs	PCB28 PCB52 PCB101 PCB138 PCB153 PCB180
	PCB77 PCB81 PCB105 PCB114 PCB118 PCB123
	PCB126 PCB156 PCB157 PCB167 PCB169 PCB189
DILXIN	2378-TeCDF 12378-PeCDF 23478-Pecdf OCDF
	123478-HxCDF 123678-HxCDF 123689-HpCDF
	123789-HxCDF 1234678-HpCDF 1234789-HpCDF
	2378-TeCDD 12378-PeCDD 123478-HxCDD OCDD
	123678-HxCDD 123789-HxCDD 1234678-HpCDD
PBDE	BDE-8 BDE-11 BDE-12/13 BDE-15 BDE-28 BDE-47
	BDE-99 BDE-100 BDE-116 BDE-118 BDE-119
	BDE-138 BDE-153 BDE-154 BDE-183

① Dioxins
Gas chromatography(GC) conditions: separate column: DB-5MS 60 m×0.25 mm×0.1 μm; constant pressure: 170 kPa; sample entrance: 300 °C, splitless mode. Temperature program: 100 °C maintaining for 0.5 minutes, 20 °C/ min heating to 200 °C, 1 °C / min heating to 215 °C maintaining for 7 min, 4 °C /min heating to 300 °C maintaining for 3 min.
Mass spectrometer (MS) conditions: source temperature: 300 °C; electron energy: 36.0; Trap electric current: 600 μA, detection mode: SIR; selected ion monitoring, resolution> 10 000, defined 10% as trough. Quantitative method: the relative response factor; quality reference standards: PFK; quantitative methods: isotope internal standard method (The lowest limit is 0.1 pg/g).

② Polychlorinated biphenyls (PCBs) analysis
Gas chromatography(GC) conditions: separate column: DB-5MS 60 m×0.25 mm×0.1 μm; constant pressure: 150 kPa; sample entrance: 280 °C, splitless mode. Injection volume: 1 μL. Temperature program: 80 °C maintaining for 2min, 8 °C /min heating to 150 °C, 4 °C / min heating to 300 °C and maintaining for 2 min.
Mass spectrometer (MS) conditions: ion source temperature: 260 °C; electron energy: 36.0 ev; Trap electric current: 600 μA; detection mode: selected ion monitoring (SIR), resolution> 10000 (defined 10% as trough, PFK as reference material); quantitative methods: isotope internal standard method (The lowest limit is 0.05 pg/g).

③ Polybrominated diphenyl ethers (PBDEs) analysis
Gas chromatography(GC) conditions: separate column: VF-5HT 30 m×0.25 mm×0.1 μm; constant pressure: 70 kPa; sample entrance: 320 °C, splitless mode. Injection volume: 1 μL. Temperature program: 100 °C keeping for 1min, 2 °C / min heating to 140 °C, 4 °C/min heating to 220 °C, 8 °C / min heating to 330 °C.
Mass spectrometer (MS) conditions: ion source temperature 300 °C; electron energy: 36.0; Trap

electric current: 600 μ A; detection mode: SIR selected ion monitoring, resolution> 10 000, defined 10% as trough. Quantitative method: the relative response factor; quality reference standards: PFK; quantitative methods: isotope internal standard method (The lowest limit is 0.05 pg/g).

Data Analysis

The values which were below the detection limit of the analytical method were assigned as half value of the detection limit. The basic data analyses such as sum, average and standard deviation were done by using excel, and then all data were analyzed with SPSS16.0. Data in groups were analyzed by linear regression, and meanwhile, thyrotropin indexes were packed as well. The average values were obtained by combining PCBs, dioxin, and PBDE; correlation analyses were conducted to check data between groups, and *t*-test was used to find whether there were significant differences.

RESULTS

Health Status of the Children

After inquiring children’s age, gender, diet, previous health status, parents and other relevant circumstances, 66 children were selected to receive a physical examination which included height, weight, acne, skin pigmentation, and mentality development, etc. The ratio of boys to girls in Luqiao was 51.8:48.2 and it was 47.1:52.9 in Longyou. In Luqiao, the average height of children was 114 cm and the average weight was 21 kg, while in Longyou, children’s average height was 123 cm and the average weight was 24 kg. As shown in Table 1, in Luqiao, Item 5 (unresponsive, cold) had the highest incidence, which was present in 6.48% of the cases

and followed by Item 4 with the incidence rate of 3.70%. Compared with the children in Luqiao, the incidence of the symptoms that were detected in children in Longyou was marked lower except for Item 2 and 7 (Table 2). Persistent organic pollutants had certain impact on children's health, such as weight loss, skin and mucosal pigmentation, periorbital edema, gingival hyperplasia, and abnormal skull calcification^[4]. Moreover, children's health in Longyou is better than that in Luqiao.

Results of PCBs, DIOXIN, PBDEs, and TSH Detection

In the experiment, children's blood samples were analyzed for 18 groups of PCB congeners, 17 types of dioxin homologues, 15 varieties of polybrominated diphenyl ether homologue, and the total content of thyrotropin. The total content of PCBs in serum of the children in Luqiao was 484.00 \pm 84.86 ng/g on average while the figure in Longyou was 255.38 \pm 95.12 ng/g, which was as half as that in Luqiao. The total content of PBDEs was 664.28 \pm 262.38 ng/g in Luqiao, twice as much as that in Longyou (375.81 \pm 262.43 ng/g). The PBDE levels in the 2 areas were significantly different (*P*<0.05). The exposure level of DIOXIN in Luqiao (26.00 \pm 19.58 ng/g) was lower than that in Longyou (39.64 \pm 31.86 ng/g). In the later investigation, a smelter of waste aluminum was found nearby a primary school in Longyou, which directly caused pollution to the surrounding environment. The TSH content in Luqiao was 1.88 \pm 0.42 μ U/mL, which was significantly lower than that in Longyou (Table 3). Exposure to persistent organic pollutants would lead to the significant increase of concentration of pollutants in serum of children, affecting the distribution of thyroid hormone levels in the body.

Table 2. Children Prevalence Diseases Distribution

Areas	Luqiao		Longyou	
	<i>n</i>	<i>P</i> (%)	<i>n</i>	<i>P</i> (%)
acne, skin pigmentation, mucosal dark brown pigmentation	1	0.93	0	0.00
eyes blister, nose deformity, gingival hyperplasia, and small head circumference etc	3	2.78	4	3.25
pneumonia, bronchitis, allergic asthma	2	1.85	1	0.81
growth retardation, low muscle tone, spasm	4	3.70	2	1.63
unresponsive, cold	7	6.48	2	1.63
Clumsy	3	2.78	1	0.81
others	0	0.0	3	2.44

Note. The percentages were ratios of the number of children suffering from the symptoms to the number of total checkers in both areas.

Correlation Analysis

Correlation analysis was conducted between PCBs, DIOXIN, PBDE and TSH. The results showed that PCBs had a strong positive correlation with TSH, PBDE had a weak positive correlation with TSH, and there was a negative correlation between DIOXIN and TSH. Three pollutants in Longyou were positively correlated with TSH, and all greater than 0.6. The concentrations of PCBs, DIOXIN, and PBDE showed certain correlation with TSH. (Table 3, Figure 1, Figure 2).

Table 3. Results of TSH, PCBs, DIOXIN, and PBDEs in Children’s Venous Blood

Measuring Index (Unity)	Luqiao	Longyou
	Results <i>r</i>	Results <i>r</i>
ΣPCBs (ng g ⁻¹ Lipid Weight)	484.00±84.86 0.61	255.38±95.12 0.75
ΣDIOXIN (ng g ⁻¹ Lipid eight)	26.00±19.58 -0.15	39.64±31.86 0.64
ΣPBDE (ng g ⁻¹ Lipid eight)	664.28±262.38 0.39	375.81±262.43 0.78
TSH (μ IU/mL)	1.88±0.42	3.31±1.04

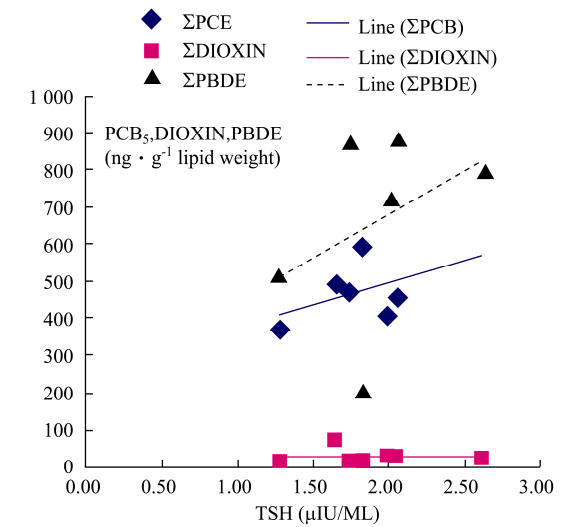


Figure 1. Correlations of PCBs, DIOXIN, PBDE with TSH in Luqiao.

The TSH level and the three kinds of pollutants had a positive correlation in Longyou, and the correlation coefficient of PCBs, DIOXIN, and PBDE were 0.753, 0.640, and 0.783, respectively. The correlation coefficients in Longyou were higher than in Luqiao. Especially, the DIOXIN exposure level was relatively higher, showing a strong positive correlation, but it revealed a weak negative correlation with TSH in Luqiao. The TSH level detected in Longyou was higher than that in Luqiao.

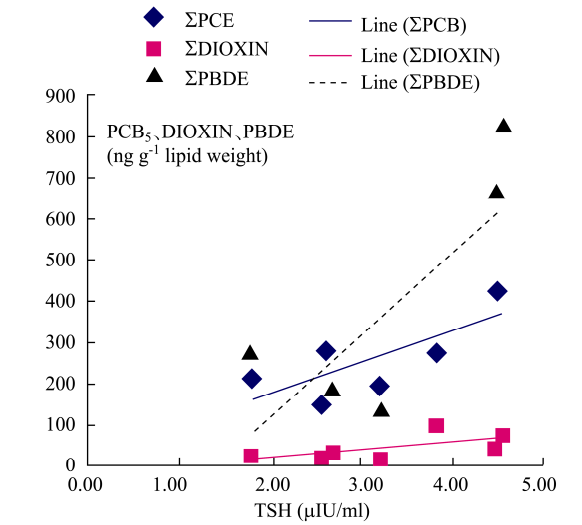


Figure 2. Correlations of PCBs, DIOXIN, PBDE with TSH in Longyou.

DISCUSSION

The results of our study have shown that the health status of children in the control area is better than that in the contaminated area. Due to exposure to the high concentrations of pollutants in the contaminated area, the level of pollutants in the children is high and affecting their normal distribution of TSH levels. The concentrations of PCBs, DIOXIN, and PBDE show correlation with TSH.

The Dutch researchers reported a study of women who were affected by PCBs and DIOXIN during their perinatal stage, demonstrating that it would lead to increase of the incidence of infectious and allergic diseases^[5] of their babies. Burns’ study focusing on a chemical factory in Russia showed that the boys who were eating local food or had breastfeeding from wet nurses who were employed in this factory had higher concentrations of DIOXIN and PCBs in serum than other boys^[6]. Japanese scholars reported that the decrease of T4 in the serum of 1-year-old children was linked with the PCB/TCDD concentrations of wet nurses’ breast milk during the first three months. However, in these studies, the TSH levels were still within the normal range, so no evidence was sufficient to prove that PCBs can cause defects or delays in neurobehavioral development of children in the future^[4].

In conclusion, PCBs, DIOXIN, and PBDE pose direct or indirect threats to human health. In addition, there is no doubt that these pollutions have endangered the environment and human survival, so some interventions must be taken^[7-8].

For example, strict management of the E-waste recycling area and reasonable disposition of the pollution sources are necessary. Moreover, direct skin contact with these pollutants shall be avoided, and people's awareness of these pollutants and knowledge of self-protection shall be enhanced.

This study represents a case, showing that higher concentrations of PCBs, DIOXIN, and PBDE in serum of children are caused by environmental pollution from recycling of waste household appliances and utilization of scrap aluminum.

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