EXPOSURE ASSESSMENT OF POLYCHLORINATED DIBENZO-*P*-DIOXINS AND DIBENZOFURANS FOR THE WORKERS OF ZINC OXIDE RECYCLING (WAELZ PROCESS) PLANT

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Introduction

High PCDD/Fs level in duck egg samples from central Taiwan were measured and a large zinc oxide recycling (Waelz process) plant with 13% emission of PCDD/Fs in Taiwan was found near those duck farms. The Waelz process is a classic technique for recycling zinc in the fly ash from electric arc furnace smelters. The fly ash is heavily contaminated with PCDD/Fs, and as a result of the treatment of fly ash, the PCDD/Fs are released on the flue gas[1-3]. It is highly likely that many workers in the plant are exposed to high levels of PCDD/Fs. This study therefore aimed to assess the distribution of serum PCDD/F levels and the congener patterns of workers according to their corresponding occupational exposure. The outcomes of these investigations should make recommendations possible for proactive occupational preventive programs in the plant.

Materials and Methods

Subject Selection and Serum Collection Thirty-eight workers were recruited from different departments of this zinc oxide recycling plant in Taiwan. We assigned them by job title to two groups: high-exposure (workers who working in department of raw materials feeding, raw materials storage, product packing, manufacturing line supervision or manufacturing line technician, cleaner), and low-exposure (workers who working in departments of slag collection, fly ash granulated area, equipment maintenance, production line inspector, manager, officer, laboratory stuff). After signing a consent form and the day after completing an overnight fast, each study participant provided 80 mL of venous blood. Blood samples were drawn into chemically cleaned tubes containing no anti-coagulants, and serum samples, obtained after centrifugation, were stored at –70°C until PCDD/F analysis.

Serum Sample Cleanups and HRGC/HRMS Analysis of PCDD/Fs Seventeen 2,3,7,8-substituted PCDD/Fs were measured in serum samples, using isotope dilution HRGC/HRMS. Each serum sample was spiked with a mixture containing fifteen $^{13}C_{12}$-PCDD and PCDF standards as defined in USEPA Method 1613. Serum samples were enriched and fractionated by C18, SCX, silica, and highly selective adsorbent magnesium-silica gel cartridges (Florisil) before analysis. Each analytical run consisted of a method blank, a quality control, and seven unknown samples for quality assurance and quality control. The detection limit of 2,3,7,8-TCDD for the analysis was 0.03 pg/column-injection or 0.007 pg/ML-serum. All PCDD/Fs were adjusted to the lipid content analyzed from the corresponding samples and were reported as pg WHO-TEQ/g lipid.

Sampling of Ambient Air in the Working Environment Two gas and particle-bound PCDD/Fs were collected at a flow rate of 0.225±10% m^3/min with PS-1 samplers consisting of a quartz fiber filter (QFF) backup by a polyurethane foam (PUF) cartridge at raw materials storage and product packing areas. The PS-1 samplers were calibrated by orifice calibrator in the beginning and the end of each sampling period and showed no variation in the air flow over the sampling period. The sampling time was set as 48 hours.

Ambient Air Sample Cleanups and HRGC/HRMS Analysis of PCDD/Fs Sample preparation was done according to the method TO-9A developed by USEPA. QFF and PUF sample were separately spiked with a cocktail of $^{13}C_{12}$-labeled PCDD/Fs and extracted for 24 h with toluene by Soxhlet extractor. The extracted sample was washed with H_2SO_4 and then extracted with hexane. Sample cleanup was accomplished with acidic silica-gel, alumina and activated carbon column. $^{13}C_{12}$-labeled PCDD/Fs recovery standards were spiked before analysis. The quantification of PCDD/Fs was performed with HRGC/HRMS with a DB-5MS column (60 m, 0.25mm i.d. 0.25 μm film thickness). Seventeen 2,3,7,8-substituted congeners were quantified. The peaks

were quantified when the criteria were met: (1) isotope ratio within ±15% of theoretical values, (2) signal/noise ratio ≥2.5. Recoveries of $^{13}C_{12}$-labeled PCDD/Fs internal standards in samples ranged from 40 to 130%.

Interviewer-administered Questionnaire Information obtained from the questionnaire included personal characteristics (sex, age, height, weight, neighborhood geography, etc), life style (alcohol intake and tobacco usage), occupational history (working histories related to Waelz process, job titles, working period, and usage of personal protective equipments, etc).

Results and Discussion

Table 1 showed the demographic characteristics and work years of the high and low exposure workers. Thirty-five (92%) of the workers were men and three was woman (8%). No significant differences of age, BMI, lipid content and work years were found between high and low exposure groups.

Table 2 showed the difference of PCDD/Fs levels for each congener between high and low exposure groups of zinc oxide recycling (Waelz process) plant workers. Beside the 2,3,7,8-TCDF and OCDD, significantly higher levels of each congener, PCDDs, PCDFs, and total PCDD/Fs were found in the high exposure group than low exposure group ($P < 0.05$). The dominant congeners were 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD and this profile were consisted with the results of Chi et al[3]. The mean serum PCDD/Fs levels(34.5 pg WHO-TEQ/g lipid) in the high exposure workers of zinc oxide recycling (Waelz process) plant were higher than those in the electric arc furnace workers[4](24.0 pg WHO-TEQ/g lipid) and municipal waste incinerator maintenance workers[5](23.9 pg WHO-TEQ/g lipid) in Taiwan. In the preliminary walk survey, the high-exposure group was categorized according to their chances for exposure to PCDD/Fs in the working areas, and higher serum PCDD/F levels were found in the workers who have high probability to contact with raw materials, despite their having worn dust masks during the working period. Overall, the occupational PCDD/F exposure might be occurring inside the zinc oxide recycling (Waelz process) plant.

The ambient PCDD/Fs levels in the raw material storage and product packing area of zinc oxide recycling (Waelz process) plant were 3.16 and 1.39 pg WHO-TEQ_{DF}/Nm^3 respectively (Table 3). The dominant congeners in the ambient samples were also 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD and the same with the serum samples of workers.

Figure 1 and 2 showed the comparison of congener profile between ambient and serum PCDD/Fs (% of each congener to total PCDD/Fs and TEQ % of each congener to total PCDD/Fs). The percentage of tetra- to hexa- chlorinated dibenzo-*p*-dioxins and dibenzofurans in the ambient samples were similar with serum samples of high exposure group. Figure 3 and 4 showed that the serum PCDD/Fs levels of local ($N=29$, $R^2=0.375$, $P = 0.002$)and foreign ($N=9$, $R^2=0.510$, $P = 0.031$)workers were highly correlated with exposure index which integrated by job title, time-activity data, and seniority. It meant that the high exposure group was potentially exposed to higher concentration of PCDD/Fs emitted from zinc oxide recycling (Waelz process) plant. It is suggested that the transportation of fly ash and the packing of products should be modified to airtight in order to avoid the PCDD/Fs exposure of workers. The usage of suitable personal protective equipment was suggested to reduce the exposure of PCDD/Fs.

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Table 1 The demographic characteristics and work years of the workers (Wilcoxon Rank-Sums test)

	High exposure（n=18）	Low exposure（n=20）	P-value
Male/female	18/0	17/3	-
Age(year)	37.8(31-48)	36.3(30-65)	0.108
BMI	25.0(20.5-31.5)	24.2(19.1-34.2)	0.388
Lipid content(%)	22.2(11.4-28.8)	22.9(13.0-26.2)	0.953
Work years	4.6(2.0-8.0)	5.3(1.0-8.0)	0.363

*: P value＜0.05

Table 2 Difference of PCDD/Fs levels (pg WHO-TEQ/g lipid) for each congener of 38 workers of zinc oxide recycling (Waelz process) plant among high to low exposure groups (Wilcoxon Rank-Sums test)

	High exposure（n=18）	Low exposure（n=20）	P-value
2,3,7,8-TCDF	0.32	0.25	0.056
1,2,3,7,8-PeCDF	0.29	0.14	<0.001*
2,3,4,7,8-PeCDF	11.9	6.6	<0.001*
1,2,3,4,7,8-HxCDF	1.59	0.78	<0.001*
1,2,3,6,7,8-HxCDF	2.06	0.93	<0.001*
2,3,4,6,7,8-HxCDF	0.65	0.29	<0.001*
1,2,3,7,8,9-HxCDF	0.09	0.05	<0.001*
1,2,3,4,6,7,8-HpCDF	0.42	0.23	0.006*
1,2,3,4,7,8,9-HpCDF	0.02	0.01	<0.001*
OCDF	0.000	0.000	0.041*
2,3,7,8-TCDD	3.07	1.99	<0.001*
1,2,3,7,8-PeCDD	10.2	5.44	<0.001*
1,2,3,4,7,8-HxCDD	0.52	0.30	<0.001*
1,2,3,6,7,8-HxCDD	1.89	1.34	0.011*
1,2,3,7,8,9-HxCDD	1.03	0.50	<0.001*
1,2,3,4,6,7,8-HpCDD	0.43	0.30	0.004*
OCDD	0.03	0.04	0.260
PCDD/Fs	34.5	19.2	<0.001*
Mean(range)	26.4（6.8-66.0）		-

*: P value＜0.05

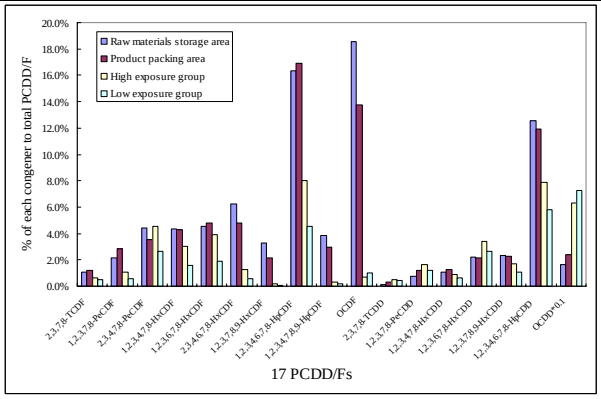

Figure 1 Comparison of congener profile between ambient and serum PCDD/Fs(% of each congener to total PCDD/Fs)

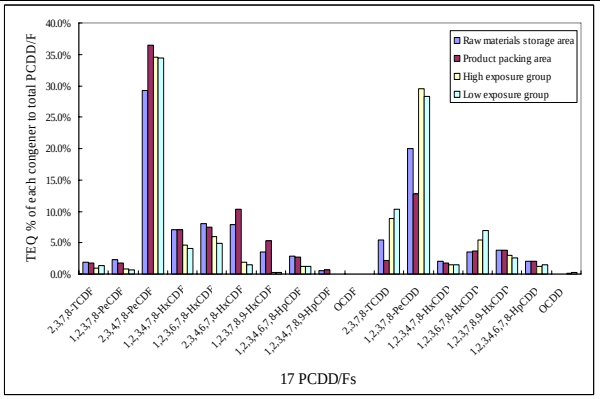

Figure 2 Comparison of congener profile between ambient and serum PCDD/Fs(TEQ % of each congener to total PCDD/Fs)

Table 3 The ambient PCDD/Fs levels (pg WHO-TEQ/Nm^3) in the raw material storage and product packing area of zinc oxide recycling (Waelz process) plant

	Raw material storage area	product packing area
2,3,7,8-TCDF	0.0571	0.0269
1,2,3,7,8-PeCDF	0.0551	0.033
2,3,4,7,8-PeCDF	1.1529	0.4073
1,2,3,4,7,8-HxCDF	0.2255	0.0989
1,2,3,6,7,8-HxCDF	0.2369	0.1107
2,3,4,6,7,8-HxCDF	0.3252	0.11
1,2,3,7,8,9-HxCDF	0.1686	0.0489
1,2,3,4,6,7,8-HpCDF	0.0846	0.0389
1,2,3,4,7,8,9-HpCDF	0.0201	0.0068
OCDF	0.001	0.0003
Total PCDFs	2.327	0.8817
2,3,7,8-TCDD	0.0707	0.0753
1,2,3,7,8-PeCDD	0.4061	0.2772
1,2,3,4,7,8-HxCDD	0.0542	0.0291
1,2,3,6,7,8-HxCDD	0.1151	0.0489
1,2,3,7,8,9-HxCDD	0.1202	0.052
1,2,3,4,6,7,8-HpCDD	0.065	0.0275
OCDD	0.0008	0.0005
Total PCDDs	0.8321	0.51
Total PCDD/Fs	3.16	1.39

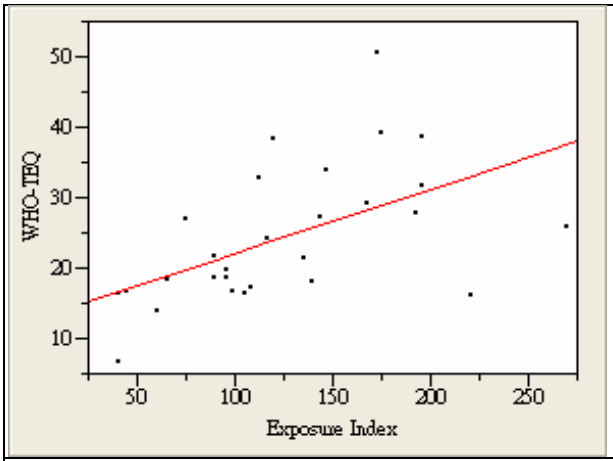

Figure 3 The correlation of serum PCDD/Fs levels of local workers and their exposure index which integrated by job title, time-activity data, and seniority (N=29, R^2=0.375, P＝0.002)

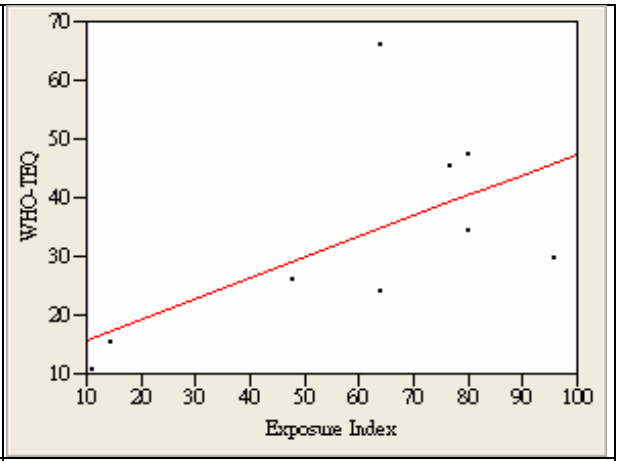

Figure 4 The correlation of serum PCDD/Fs levels of foreign workers and their exposure index which integrated by job title, time-activity data, and seniority (N=9, R^2=0.510, P＝0.031)