DISTRIBUTION OF AMBIENT AIR AND SERUM PCDD/FS EXPOSURE OF WORKERS IN ELECTRIC ARC FURNACE (EAF), SECONDARY ALUMINUM, AND COPPER SMELTING INDUSTRIES

Hsiu Ling Chen[3], Tung Seng Shih[2], Ching Chang Lee[1*]

[1] Department of Environmental and Occupational Health, Medical College, National Cheng Kung University, Tainan, Taiwan
[2] Institute of Occupational Safety and Health, Council of Labor Affairs, Taipei, Taiwan
[3] Institute of Occupational Safety and Hazard Prevention, Hung Kuang University, Taichung, Taiwan, Taichung, Taiwan

Introduction

Many countries have compiled inventories of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/F) emission sources that identify iron and steel smelters and other metallurgical processes as major contributors. Secondary copper and aluminum smelters primarily utilize recover copper from scrap and dross. The materials may contain organic impurities, such as plastic and organic chloride chemicals, and PCDD/Fs, which are formed during the smelting process. In Taiwan, secondary copper smelters account for over 39% of total PCDD/F emissions, municipal waste incinerators for 23.7%, electric arc furnaces and cement kilns for more than 10%.[1,2] The study therefore aims to compare the congener pattern of serum PCDD/F levels of the workers and ambient air concentrations in EAF, secondary copper smelters, and secondary aluminum smelters. To characterize PCDD/Fs emission patterns from the three types industries, the environmental monitoring of PCDD/Fs levels was conducted in different manufacturing process in field from the three industries individually.

Material and methods

For biological monitoring, serum samples of workers were recruited separately from different departments of an EAF plant, 2 secondary copper smelters, and 2 secondary aluminum smelters in Taiwan. After signing a consent form and the day after completing an overnight fast, each study participant provided 60 mL of venous blood. In EAF plant, a large amount of smoke was released into the work environment when the cover of the electric arc furnace was opened so that steel-making materials could be added. Two ambient air samples from the work environment were collected for PCDD/F analysis, one from near the furnace (Electric Arc Furnace Department) and the other inside the Casting Department. The similar sampling locations near furnace were also selected in secondary copper smelting furnace and aluminum smelting furnace. The sampling time was set as 48 hours. The sampling and analysis method for ambient PCDD/F level, the compendium method TO-9A (second edition, EPA/625/R-96/010b). Seventeen 2,3,7,8-substituted PCDD/Fs were measured in human blood samples and ambient samples, using isotope dilution high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS).

Results and Discussion

Table 1 showed that 134 workers were recruited in this study. Table 2 showed the congener pattern of serum PCDDD/F levels among the three metallurgical industries. The significant difference was found on 10 congeners of 2,3,7,8-substituted chloride PCDF and on 1,2,3,4,7,8-HxCDD and OCDD among the three industries. The highest serum PCDD/Fs level was observed in aluminum recovery smelter (21.94 pg WHO-TEQ/g lipid), and the followed is in copper smelter (21.48), finally for those in EAF plant (18.79) although it doesn't reach significant different. In Taiwan, serum

PCDD/F levels in metallurgical workers were higher than those in residents living near municipal waste incinerators.[3] In our earlier study has shown that OCDD, 1,2,3,4,6,7,8-HpCDD, OCDF, and 1,2,3,4,6,7,8-HpCDF was predominant in residents living in the vicinity of municipal waste incinerator, [4] which was different from the present study. For ambient samples, the highest ambient PCDD/Fs level was observed in copper recovery industry (12.415 pg WHO-TEQ/Nm^3), and the followed was in aluminum recovery industry (7.160), finally for those in EAF industry (1.811) (Table 3). Previous study in Taiwan has shown that the mean PCDD/F concentration in the stack gases of EAFs and secondary aluminum smelter are 0.28 and 3.3 ng I-TEQ/Nm^3.[5] The author also indicated the mean PCDD/F concentration in ambient air of industrial area was 0.15 ng I-TEQ/Nm^3, and 0.088 ng I-TEQ/Nm^3 in residential area.[6] The present result proved the metallurgical emission of PCDD/Fs in Taiwan was a remarkable problem, especial for secondary copper and aluminum smelters. Figure 1 presented the score plot from PCA, which factor 1 explained 74.0% of the total variance, while factor 2 explained 16.5% of total variance and both account for 90.5% of total variance. The score plot performed that the samplings were clustered into 3 groups, that is, Group 1 (aluminum smelters), Group 2 (copper smelters), Group 3 (aluminum smelter and EAF). The profiles of serum samples were added for further analyzing (Figure 2). The data is similar to Buekens reported that the 2,3,7,8 chlorine-substituted congener pattern from aluminum smelters was very different from copper smelter and municipal waste incinerator.[7] The score plot performed that the samplings were clustered into 3 groups, that is, Group 1 (all serum sample regardless of they collected in any kind of three metallurgical industries), Group 2 (air samples in copper smelters), Group 3 (air samples in aluminum smelters). Comparing the serum samples and ambient samples, the congener profile were consistent in serum sample, and the ambient sample also stable in copper smelters, but not for those collected in aluminum smelters and EAF. The reasons might be due to the feeding materials and furnace temperature[4], and it needs to be clarify in the future study.

Acknowledgment

We are greatly in debt to our colleagues at the National Cheng Kung University, Tainan, Taiwan, for sampling and analytical assistance. This study was supported by grants from the Council of Labor Affairs in Taiwan.

Table 1 Demographic distribution of the workers in 3 metallurgical industries

Plant	Al	Cu	EAF	P value[#]
N Rows	43	46	45	
Age[†]	41.6 (26.0-59.0)	37.2 (22.3-55.7)	38.9 (23.4-49.7)	0.058
Body fat (%)[†]	24.2 (6.2-40.6)	22.0 (10.7-36.1)	21.1 (10.5-32.5)	**0.011***
BMI[†]	24.8 (17.7-33.3)	25.3 (16.2-40.8)	23.5 (18.8-32.1)	0.052
work period[†]	10.4 (2.5-22.0)	8.8 (0.1-55.7)	10.1 (1.0-49.7)	0.073

[†]: mean (minium-maximun), [‡]: Number (% of total subjects), [#]:analyzed by Kruskal-Wallis test

Table 2 Congener pattern of average serum PCDD/Fs levels (pg WHO-TEQ/g lipid) among 3 metallurgical industries

	Al	Cu	EAF	P value
2,3,7,8-TCDF	0.16	0.12	0.15	**0.007***
1,2,3,7,8-PeCDF	0.07	0.12	0.07	**0.0002***

2,3,4,7,8-PeCDF	10.21	8.61	7.47	**0.013***
1,2,3,4,7,8-HxCDF	0.87	1.18	0.58	**<0.0001****
1,2,3,6,7,8-HxCDF	0.95	1.26	0.64	**<0.0001****
2,3,4,6,7,8-HxCDF	0.27	0.57	0.19	**<0.0001****
1,2,3,7,8,9-HxCDF	0.04	0.09	0.14	**<0.0001****
1,2,3,4,6,7,8-HpCDF	0.17	0.31	0.21	**<0.0001****
1,2,3,4,7,8,9-HpCDF	0.01	0.02	0.01	**<0.0001****
OCDF	0.00	0.00	0.00	**<0.0001****
2,3,7,8-TCDD	2.08	2.01	2.40	0.072
1,2,3,7,8-PeCDD	4.98	5.26	4.63	0.404
1,2,3,4,7,8-HxCDD	0.22	0.31	0.25	**0.036***
1,2,3,6,7,8-HxCDD	1.37	1.09	1.50	0.123
1,2,3,7,8,9-HxCDD	0.31	0.34	0.30	0.535
1,2,3,4,6,7,8-HpCDD	0.20	0.18	0.23	0.233
OCDD	0.03	0.02	0.03	**0.025***
17 PCDD/Fs	21.94	21.48	18.79	0.232

*: p value< 0.05, **: p value < 0.0001

Table 3 Congener pattern of average PCDD/Fs levels (pg WHO-TEQ/Nm^3) in ambient air among 3 metallurgical industries

	Al	**Cu**	**EAF**
2,3,7,8-TCDF	0.293	0.226	0.359
1,2,3,7,8-PeCDF	0.161	0.201	0.040
2,3,4,7,8-PeCDF	3.393	5.019	0.545
1,2,3,4,7,8-HxCDF	0.608	1.033	0.247
1,2,3,6,7,8-HxCDF	0.497	0.970	0.103
2,3,4,6,7,8-HxCDF	0.725	1.624	0.123
1,2,3,7,8,9-HxCDF	0.316	0.486	0.009
1,2,3,4,6,7,8-HpCDF	0.137	0.440	0.029
1,2,3,4,7,8,9-HpCDF	0.030	0.057	0.005
OCDF	0.001	0.003	0.000
2,3,7,8-TCDD	0.204	0.265	0.060
1,2,3,7,8-PeCDD	0.589	1.254	0.163
1,2,3,4,7,8-HxCDD	0.048	0.177	0.017
1,2,3,6,7,8-HxCDD	0.072	0.283	0.037
1,2,3,7,8,9-HxCDD	0.056	0.212	0.053
1,2,3,4,6,7,8-HpCDD	0.028	0.155	0.019
OCDD	0.000	0.002	0.001
PCDD/Fs	7.160	12.415	1.811

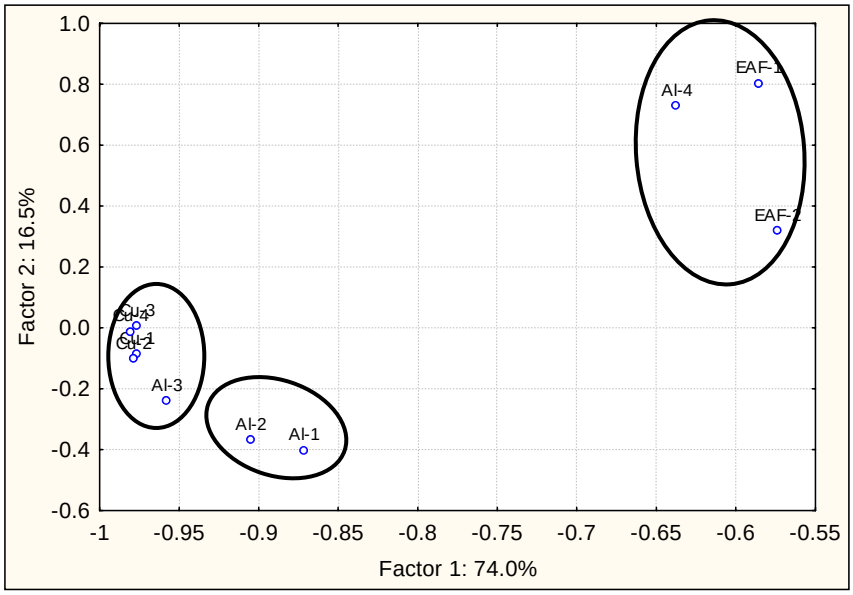

Fig 1 The score plot from PCA by using the mass fraction of PCDD/Fs congeners of the air samples

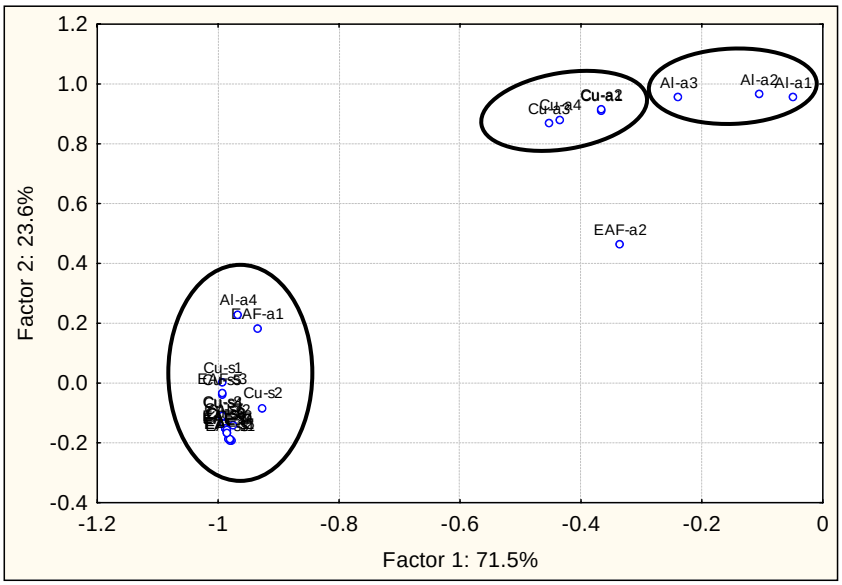

Fig 1-2 The score plot from PCA by using the mass fraction of PCDD/Fs congeners of the air and serum samples

References

1. Chen CM. *Chemosphere* 2004; 54: 1413-1420.

2. Chen SJ. *Atmospheric Environment* 2004; *38*: 3729–3732.

3. Chen HL. *Chemosphere* 2004; 54: 1421-1429.

4. Lee CC. *Chemosphere* 2005; 59: 1465-1474.

5. Lee WS. *J Air & Waste Manage associ* 2005**;** *55*: 219-226.

6. Lee WS. *Environ Sci Technol* 2004; *38*: 4937-4944.

7. Buekens A. *Chemosphere* 2000; *40*: 1021-1024.