DISTRIBUTION OF AMBIENT AIR AND SERUM PCDD/F EXPOSURE OF ELECTRIC ARC FURNACE AND SECONDARY ALUMINUM AND COPPER SMELTERS

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Abstract

Iron and steel smelters and other metallurgical processes may generate organic impurities, such as plastic and organic chloride chemicals, polychlorinated dibenzo-*p*-dioxins, and polychlorinated dibenzofurans (PCDD/Fs) during the smelting process. We compared the congener patterns of serum PCDD/F levels of 134 workers and ambient air concentrations in electric arc furnaces (EAF), secondary copper smelters, and secondary aluminum smelters in Taiwan. The highest serum PCDD/F levels we found were 21.94 pg WHO-TEQ/g lipid in an aluminum recovery smelter worker, was 21.48 pg WHO-TEQ/g lipid in a copper smelter worker, and was 18.79 pg WHO-TEQ/g lipid in an EAF plant worker. These levels were higher than those in residents living within 5 km of municipal waste incinerators. For ambient samples, the highest ambient air PCDD/F levels we found were in the copper recovery industry (12.42 pg WHO-TEQ/Nm3), the aluminum recovery industry (7.16 pg WHO-TEQ/Nm3), and the EAF industry (1.81 pg WHO-TEQ/Nm3). Congener profiles were consistent in serum samples and in ambient air samples collected in copper smelters, but not in ambient air samples collected in aluminum smelters and EAF. Differing raw materials and diverse temperature, another concern may affect profiles.

Introduction

Many countries have compiled inventories of PCDD/F emission[1-2] sources that identify iron and steel smelters and other metallurgical processes as major contributors. Secondary copper and aluminum smelters are primarily used to recover copper and aluminum from scrap and dross. The materials may contain organic impurities, such as plastic and organic chloride chemicals, as well as polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (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 (EAF) and cement kilns for more than 10%[2-3]. The present study was conducted to monitor ambient air PCDD/F levels and serum levels of workers in aluminum, copper smelter and EAF. Finally, the significance of emission sources from the three kinds of industries was assessed using Principal Component Analysis (PCA) and Factor Analysis.

Materials and Methods

For biological monitoring, we took serum samples from workers recruited separately from different departments of an EAF plant (n = 45), 2 secondary copper smelters (n = 46), and 2 secondary aluminum smelters (n = 43) in Taiwan. 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. Similar sampling locations near the furnace were also selected in a secondary copper smelting furnace (n = 4) and an aluminum smelting furnace (n = 4). Seventeen 2,3,7,8-substituted PCDD/Fs were measured in human blood samples and ambient air samples using isotope dilution high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). Information obtained from the questionnaire included personal characteristics, life style, and the quantity of dietary intake for the previous 1 year based on a semi-quantitative food-frequency questionnaire.

Results and Discussion

134 workers recruited for this study. Their work experience ranged from a mean of 8.8 years to a mean of 10.4

years (Table 1).

A significant difference was found for 10 congeners of 2,3,7,8-substituted chloride PCDF and 1,2,3,4,7,8-HxCDD and OCDD in the three industries (Table 2). The highest serum PCDD/F level was in an aluminum recovery smelter (21.94 pg WHO-TEQ/g lipid), the second highest in a copper smelter (21.48 pg WHO-TEQ/g lipid), the lowest in an EAF plant (18.79 pg WHO-TEQ/g lipid) ($p>0.05$). In Taiwan, serum PCDD/F levels in metallurgical workers were higher than those in residents living within 5 km of municipal waste incinerators[4]. A considerably high percentage of OCDD, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, and 1,2,3,4,6,7,8-HpCDF were found in secondary copper smelter workers (Fig. 1).

For ambient air samples, the highest ambient PCDD/F levels were in the copper recovery industry (12.42 pg WHO-TEQ/Nm3), the aluminum recovery industry (7.16 pg WHO-TEQ/Nm3), and the EAF industry (1.81 pg WHO-TEQ/Nm3) (Table 3). The present results prove that the metallurgical emission of PCDD/Fs in Taiwan is a serious problem, especially for secondary copper and aluminum smelters. 2,3,4,7,8-PeCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,7,8-PeCDD, and 1,2,3,4,7,8-HxCDF were also considerable contributors to toxic equivalency levels in secondary aluminum and copper smelters. To identify the possible pollution sources for all monitoring samples in the three metallurgical industries, we analyzed their PCDD/F congener profiles using PCA with the mass fraction of 2,3,7,8-congeners as the variables. Factor 1 explained 74.0% and factor 2 explained 16.5% of the total variance; both account for 90.5% of total variance (Fig. 2). The data points with similar congener profiles were closely located, while those with divergent patterns were separated according to the position of their corresponding coordinates with respect to the factor axis. The profiles of serum samples were added for further analysis (Figure 3). These data are similar to those of another study [5] reporting that the 2,3,7,8 chlorine-substituted congener patterns from aluminum smelters was very different from those of copper smelters and municipal waste incinerators. The ambient air samples were also stable within copper smelters, but not within aluminum smelters and EAF. The reasons might be differences in feeding materials and furnace temperatures, questions that need to be clarified by additional studies.

Acknowledgements

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References

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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
Sex ratio[‡]				0.056
Men	39 (90.7)	45 (97.8)	45 (100)	
Women	4 (9.3)	1 (2.2)	0	
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 Wilcoxon test

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

	Al	Cu	EAF	P value
N	43	46	45	
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 ambient PCDD/Fs levels (pg WHO-TEQ/Nm^3) in ambient air among 3 metallurgical industries

	Al	**Cu**	**EAF**
N	4	4	2
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

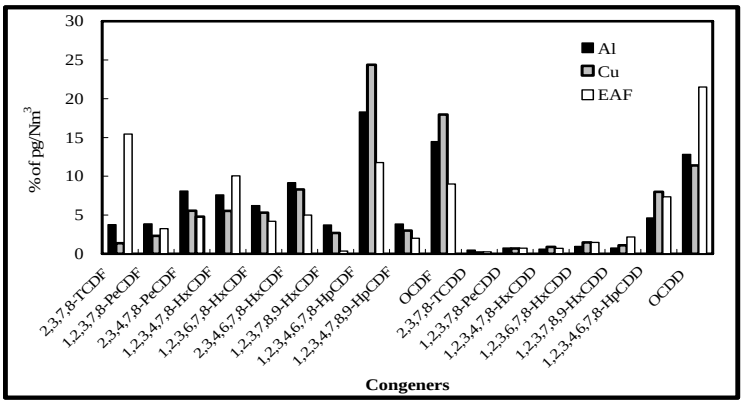

Fig 1 Distribution of PCDD/Fs levels for each congener (% of pg/g lipid) of workers' serum in the 3 metallurgical industries

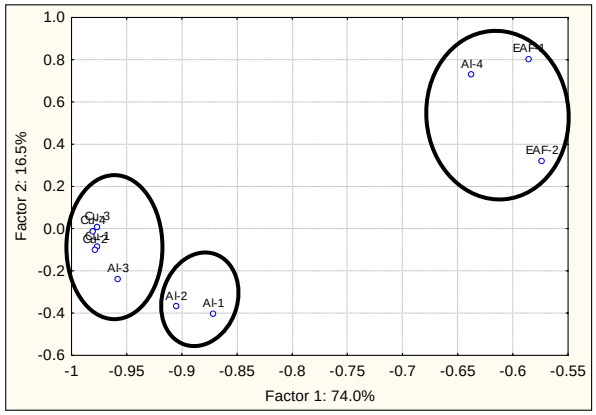

Fig 2 The score plot from PCA by using the mass fraction of 2, 3, 7, 8-congeners of the air samples as the variables

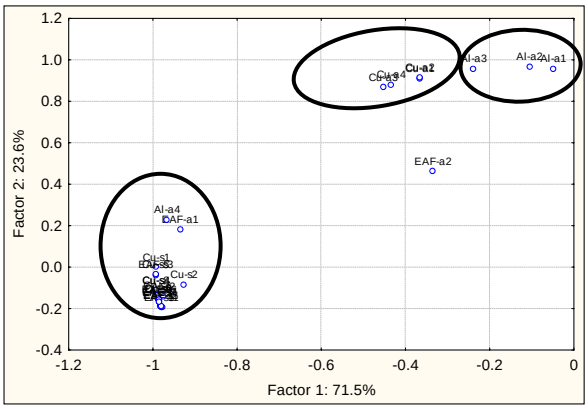

Fig 3 The score plot from PCA by using the mass fraction of 2, 3, 7, 8-congeners of the air and serum samples as the variables