High level of PCDD/Fs in Duck Egg Sampling in the Vicinity of an Oxidative Zinc Recovery Plant

Ching Chang Lee [1, 2*], Hsiu Ling Chen[3], Jeng Fang Huang[4], Chai Ching Lin[5], Tsung Yi Lin[6], Shuen Rong Lee[4]

[1]Department of Environmental and Occupational Health, Medical College, National Cheng Kung University, Tainan, Taiwan
[2]Research Center of Environmental Trace Toxic substances, Medical College, National Cheng Kung University, Tainan, Taiwan
[3]Department of Industrial Safety & Health, Hung Kuang University, Taichung, Taiwan
[4]Ilan Branch, Livestock Research Institute, Council of Agriculture, 28-1 Jehsin Village, Wuchieh, Ilan, Taiwan
[5]Institute of Biotechnology, National Ilan University, Ilan, Taiwan
[6]Council of Agriculture, Executive Yuan, Taipei, Taiwan

Introduction

Due to the environmental persistence and potential for bioaccumulation in biota, PCDD/Fs may be transferred through air, soil, water, sediment, biota and finally into human body. The food chain is widely recognized as the most important pathway for the human exposure to PCDD/Fs. A study in Taiwan has shown that the PCDD/Fs level in eggs was 0.904 pg WHO-TEQ/g fat, that was smaller than the concentration in muscle meat of fish and fishery products, milk and fat. In addition, egg consumption contribute 7% of PCDD/Fs to daily TEQ intake in Taiwanese (Hsu et al., 2007). Lovett et al. (Lovett et al., 1998) have indicated that consumption of eggs from the sites close to the incinerators would constitute a substantial proportion of recommended daily intakes for PCDD/Fs and PCBs. Moreover, a notable PCDD/Fs level in duck egg was measured in central Taiwan from the study of the food market basket survey in 2004, which were higher than the maximum PCDD/Fs level of hen egg and egg products set at 3 pg WHO-TEQ/g fat by Scientific Committee on Food (SCF) of the European Commission (EU, 2001). The transportation of agricultural (Ma et al., 2002) and livestock products around Taiwan is common. The study therefore aims to evaluate the PCDD/Fs levels in duck eggs around Taiwan. Furthermore, the study also wants to verify the cause of the contaminated scenario is an unexpected accident or a stationary polluted source. The results will provide for searching the source of the PCDD/Fs pollution and controlling PCDD/Fs contamination in food.

Materials and Methods

Duck's egg collection PCDD/F levels were analyzed for a total of 55 duck egg samples in this study, of which 22 samples were collected in Hsien-His village and 3 collected in Shen Kang village, the two villages in Changhua County were considered polluted by dioxins. In addition, 5 samples in other towns of Changhua County and 25 samples in Taiwan nationwide were collected. First, a food market basket survey was conducted in Taiwan in 2004, and the duck eggs' data showed notably high PCDD/Fs levels in Changhua County. We further selected the duck eggs produced in several duck egg farms of Hsien-Hsi Village where situated in Changhua County (n=22). At the same time, a comprehensive study for assessing the PCDD/Fs levels in duck eggs was proceeded around Taiwan. All samples were randomly selected in traditional market, supermarkets and duck farms.

Sample Cleanups, HRGC/HRMS Analysis of PCDD/Fs, dioxin-like PCBs, and Fat Content Determination The isotope dilution high-resolution gas chromatography and high-resolution mass spectrometry (HRGC-HRMS) method was utilized to determine the levels of 17 PCDD/Fs congeners in ducks' eggs. Analytical procedures were adopted from USEPA Method 1613B (USEPA, 1994) and USEPA Method 1668A (USEPA, 1999) with minor modifications. For egg samples, each 50 g sample was homogenized in 150 mL ethanol/acetone/hexane (1/1/1, w/w) and added an internal standard mixture containing fifteen $^{13}C_{12}$-labeled PCDD/F and twelve $^{13}C_{12}$-labeled PCB standards as defined in USEPA Method 1613B (USEPA, 1994) and USEPA Method 1668A (USEPA, 1999). The homogenized sample was extracted with hexane (three times). Following these extraction procedures, a sub-sample (1/20 extracted solution) was used for lipid content determination by gravimeter. The sub- sample was evaporated at room temperature overnight and then the dry lipid was weighted. The other sample (19/20 extracted solution) was treated with concentrated sulfuric acid, followed by three solid-phase extraction clean-up procedures (acid silica, acid alumina, and Florisil □columns). When analytes were eluted

from the Florisil® column, the sample was eluted by 40 mL dichloromethane for analyses of 17 PCDD/Fs in subsequent HRGC-HRMS analysis. Quality assurance/quality control (QA/QC) protocols were established, according to those defined in USEPA Method 1668A (USEPA, 1999), in the laboratory to ensure positive identification and measurement quality. The QA/QC protocols included MS Resolution, GC Resolution, calibration verification, ongoing precision and recovery, blank, internal standard recovery.

Prediction of Ambient air PCDD/Fs emission The ambient air PCDD/Fs emissions for each towns or villages around Taiwan were provided by Taiwan EPA that were used for considering the duck eggs the sampling areas. The emission quantities were calculated base on the environmental monitoring or the calculation with emission factor by the Taiwan EPA.

Statistical Methods PCDD/F concentrations are reported as pg WHO-TEQ/g fat. The Statistica software package (version 6.0; StatSoft, Inc., Tulsa, OK) was used for data management, and for Principal Component Analysis (PCA) and Factor Analysis.

Results and Discussion

Table 1 showed PCDD/Fs levels of duck eggs in three areas: (1) Hsien-Hsi and Shen Kang, Changhua County, (2) other towns in Changhua County, (3) others in Taiwan nationwide. The average highest PCDD/F level (6.457 pg WHO-TEQ/g fat) in duck eggs was collected from Hsien-Hsi and Shen Kang; and the following was in other towns in Changhua County (0.924 pg WHO-TEQ/g fat), and the lowest level was observed in other counties in Taiwan nationwide (0.446 pg WHO-TEQ/g fat). The results showed the higher level was found in Changhua County than those samples taken from other areas in Taiwan. The PCDD/F levels of duck eggs in Changhua County were shown in Fig. 1. The duck eggs taken from Changhua County showed that the highest PCDD/Fs were found in Hsien-Hsi (village A2), and the second was in Shen Kang (village A1) where there is a metal recovery plant situated there.

Table 2 showed the concentrations of 17 PCDD/Fs congeners in the duck eggs taken from Changhua County and others counties around Taiwan. The result showed 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD were the abundant contributions in egg samples. Furthermore, the samples were grouped into 4 categories: first in A1 (Shen Kang), second in A2 (Hsien-Hsi), third in B and other samples were fourth for C. Fig. 2 showed the profile of PCDD/Fs congener of duck eggs in four areas located near a polluted factory. High percentage of TeCDF, PeCDF and HxCDF, PeCDD, and HxCDD were found in those taken from Group A1 and A2 than those in group B and group C, whereas the notably high percentage of HpCDD, and OCDD were found in group B and group C. To identify the possible polluted sources for all monitored samples, 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 75.89% and factor 2 explained 15.85% of the total variance; both account for 91.74% of total variance (Fig. 3). The score plot showed that the samplings were clustered into 4 groups: Group 1 (village A1 and village A2), Group 2 (village A2), Group 3 (Village B1 and B2), and Group 4 (Village B5). 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 data might suggest that the similar PCDD/Fs pattern of duck egg were shown in village A1 and A2. Due to the further investigation had found an oxidative zinc recovery plant situated there, the present study might suggest that the PCDD/Fs emission of the oxidative zinc recovery plant may emit and deposit abundantly in village A1 and A2.

Fig. 4 showed the high correlation of PCDD/F levels between duck eggs and predicted air emission in each villages and towns of Changhua County ($n=29$, $R^2=0.590$, $p<0.05$).

Sixteen of 25 PCDD/Fs level of ducks' egg were higher than the maximum PCDD/Fs level of hen egg and egg products (3 pg WHO-TEQ/g fat) by Scientific Committee on Food (SCF) of the European Commission. In addition, the levels of duck eggs taken from Hsien-Hsi and Shen Kang villages in the present study were significant higher than the chicken egg samples collected from other areas in Taiwan. The quick assessment of PCDD/Fs levels for duck eggs leads to the conclusion that the impact of this contamination is highly relevant and it's important in estimating the total body burden in someone favor to eat for such local contaminated eggs.

Acknowledgements

This study was financially supported by grants from Livestock Research Institute, Council of Agriculture, Executive Yuan, Taiwan.

References

1. Hsu, M. S., Hsu, K. Y., Wang, S. M., Chou, U., Chen, S. Y., Huang, N. C., Liao, C. Y., Yu, T. P. and Ling, Y. C., Chemosphere 2007.
2. Lovett, A. A., Foxall, C. D., Creaser, C. S. and Chewe, D., Chemosphere 1998.
3. Ma, H. W., Lai, Y. L. and Chan, C. C. Environment International 2002.

Table 1 PCDD/Fs levels (pg WHO- TEQ/g fat) of duck's eggs collected from Changhua County and other Counties around Taiwan

Locations / PCDD/Fs	Hsien-Hsi & Shen Kang in Changhua County	Others towns in Changhua County	Other counties around Taiwan
N=	25	5	25
Mean	6.457	0.924	0.446
Standard deviation	6.488	0.630	0.218
Min	0.312	0.510	0.211
Max	23.7	2.016	1.181
Higher than EU AL[†, ‡]	16 (64.0%)[‡]	0	0

[†]: EU AL—European Union Action Level: 3 pg WHO-TEQ/g fat
[‡]: N (% of 22 samples higher than the EU AL)

Table 2 Concentrations of 17 PCDD/Fs congeners of the duck eggs taken from Changhua County and Taiwan (pg WHO-TEQ/g fat)

	Changhua County							Taiwan
	A1	A2	B1	B2	B3	B4	B5	C
N=	22	3	1	1	1	1	1	25
2,3,7,8-TCDF	0.399	0.157	0.055	0.039	0.037	0.032	0.076	0.028
1,2,3,7,8-PeCDF	0.290	0.067	0.027	0.016	0.017	0.015	0.021	0.011
2,3,4,7,8-PeCDF	2.557	0.812	0.692	0.198	0.224	0.171	0.285	0.144
1,2,3,4,7,8-HxCDF	0.258	0.071	0.053	0.023	0.026	0.017	0.025	0.016
1,2,3,6,7,8-HxCDF	0.290	0.062	0.041	0.017	0.019	0.016	0.016	0.013
2,3,4,6,7,8-HxCDF	0.123	0.033	0.023	0.014	0.016	0.010	0.010	0.010
1,2,3,7,8,9-HxCDF	0.025	0.005	0.003	0.003	0.004	0.002	0.004	0.003
1,2,3,4,6,7,8-HpCDF	0.012	0.003	0.002	0.002	0.002	0.001	0.001	0.002
1,2,3,4,7,8,9-HpCDF	0.002	0.000	0.001	0.001	0.001	0.001	0.001	0.000
OCDF	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PCDFs	3.957	1.210	2.016	0.557	0.628	0.510	0.912	0.446
2,3,7,8-TCDD	0.591	0.226	0.097	0.054	0.069	0.051	0.125	0.048
1,2,3,7,8-PeCDD	2.121	0.662	0.778	0.138	0.163	0.148	0.298	0.125
1,2,3,4,7,8-HxCDD	0.096	0.034	0.069	0.008	0.014	0.009	0.014	0.008
1,2,3,6,7,8-HxCDD	0.174	0.064	0.154	0.027	0.021	0.024	0.017	0.022
1,2,3,7,8,9-HxCDD	0.077	0.023	0.014	0.008	0.013	0.009	0.013	0.009
1,2,3,4,6,7,8-HpCDD	0.018	0.009	0.007	0.011	0.003	0.004	0.005	0.008
OCDD	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.001
PCDDs	3.078	1.019	1.120	0.244	0.283	0.245	0.472	0.220

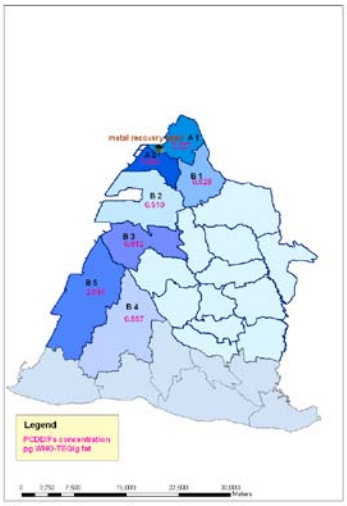

Fig 1 Map of the egg sample taken from Changhua County (A1, A2, B1-B5 were villages and towns in Changhua County)

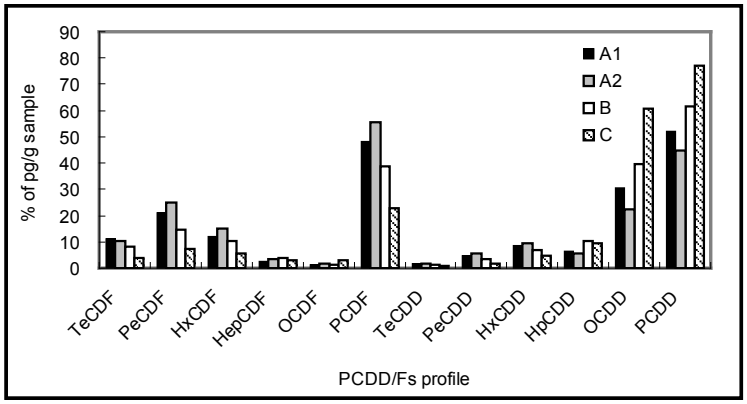

Fig 2 Profile of PCDD/Fs congener of duck's eggs in three areas situated near a polluted metal recovery plant. Area B include B1-B5, Area C include other counties in Taiwan nationwide.

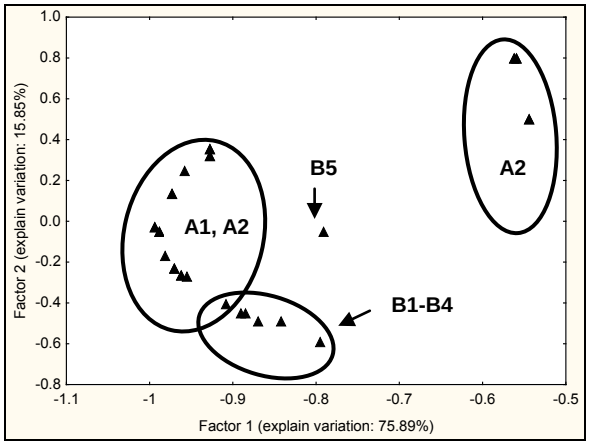

Fig 3 The score plot from PCA by using mass fraction of 2, 3, 7, 8-congeners of the duck egg samples as the variables

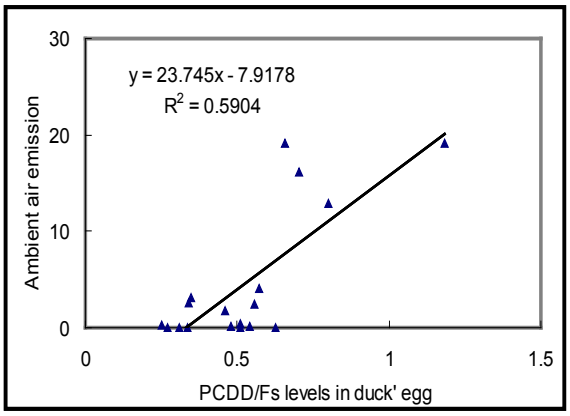

Fig 4 Correlation of PCDD/Fs levels in duck eggs and ambient air emission. X axis: PCDD/Fs levels in duck eggs (pg WHO-TEQ/g fat); Y axis: Annual PCDD/Fs levels in ambient air (g I-TEQ/year)