

TRANSFORMATION PROCESSES, POSSIBLE SOURCES AND SINK OF PCDD/Fs IN A RESERVOIR IN NORTHERN TAIWAN

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Abstract

In this study, polychlorinated dibenzo-p-dioxin and dibenzofuran (PCDD/F) deposition was sampled at Feitsui Reservoir in northern Taiwan via traditional cylindrical vessels (atmosphere) and sediment trap (water body) from January to December 2008. The sampling results indicate that the PCDD/F deposition fluxes measured in atmosphere (1.37 to 19.3 pg-I-TEQ/m²-day) are significantly lower than that sampled in the water body (10.3 to 29.8 pg-I-TEQ/m²-day) at 20 m water depth. That may be attributed to the fact that the PCDD/F depositions collected in the water body are mostly provided by catchment erosion at down stream of the reservoir investigated. The results also indicated that around 26 to 46% PCDD/F input flux in the reservoir investigated was contributed by the atmospheric deposition. However, the contribution of atmospheric PCDD/F deposition reduced to 10% during the typhoon event. During the intensive typhoon events (September 2008), the PCDD/F deposition flux in water body at 70 m water depth (179 pg-I-TEQ/m²-day) was dramatically higher than that measured at 20 m water depth (21.1 pg-I-TEQ/m²-day). It is possible caused by the land slide taking place upstream of the reservoir during the typhoon period. Interestingly, the PCDD/F input flux from atmospheric deposition in the reservoir investigated increased to 57% during the Asian dust storm event.

Introduction

Major sources contributing to the load of PCDD/Fs to the environment include combustion processes, and reservoir sources such as the impurities of pesticide residue¹. Once emitted into the atmosphere, PCDD/Fs partition between the solid and vapor phases, undergo photochemical reactions and enter other environmental compartments via wet and dry deposition². Therefore, atmospheric transport and deposition is the main pathway moving PCDD/Fs from emission sources to the various environmental compartments³. Previous study⁴ demonstrated that significant fraction of dioxins accumulated in sediments originated from agrochemicals - especially pentachlorophenol (PCP) and chloronitrophen (CNP). Sediment is the ultimate sink for persistent pollutants, including PCDD/Fs. Vertical profiles of residues in dated sediment cores have been applied as historical records of pollution⁵. The high persistence of dioxin-like compounds causes the concentrations of these contaminants in soils and sediments to decrease very slowly. Few studies have reported historical profiles of contamination in sediment cores in reservoirs. Dating and time resolution are difficult. This study reports vertical profiles and depositional fluxes of a wide variety of PCDD/F compounds in a sediment core, collected from a young reservoir in northern Taiwan. The results provide a pollution history of PCDD/F compounds in the reservoir over last past two decades and are useful in elucidating temporal trends in atmospheric PCDD/F deposition. Additionally, the PCDD/F deposition flux collected in the water body of the reservoir investigated can help pointing out the possible under-estimation of the deposition flux recorded by the traditional cylindrical vessels (atmosphere).

Materials and Methods

The reservoir investigated, serving as the source of domestic water supply for the Taipei Metropolitan Area with a population over 5 million, started to operate in 1987 with the storage of 406 million m³. It is located in the upstream part of the Tanshui watershed, approximately 170 m above sea level. The main dam is located at the downstream of Peishih Creek, a tributary of Hsintien Creek (Fig. 1). The reservoir has a surface area of 10.24 km² and a mean depth of 40 m with the maximum depth of 113.5 m near the dam. The catchment area is 30 times the reservoir surface area. Reservoir construction started in mid-1979 and was completed for water storage in mid-1987. Most banks of this reservoir are the previous agricultural farms, primarily tea farms, which were flooded after the reservoir operation. Mean annual precipitation in this area is around 2,500 mm. The main geological substrates are interstratified with sandstone and shale formed after the Oligocene. To measure atmospheric PCDD/F deposition and obtain ambient air concentration of PCDD/Fs in northern Taiwan,

the sampling site was set up at the control center of the reservoir investigated. The long-term PCDD/F deposition (30 days) is collected with stainless cylindrical vessels (atmosphere) and sediment trap (water body) at the down stream of the reservoir investigated. The main apparatus cylindrical vessels are constructed of mirror polished stainless steel (D: 500 mm, H: 600 mm). Before sampling, about 10 L of de-ionized water was added to the vessel to cover the bottom surface. In addition, the PCDD/F deposition flux in water body was collected with sediment trap at 20 and 70 m water depth of the reservoir investigated. The PCDD/F concentration in surface water (0.5 m water depth) was also measured at same location. Ambient air samples for both vapor and solid phases of PCDD/Fs were collected using semi-volatile sampling trains (Shibata HV-700F). The HV-700F samplers are equipped with fiber glass filters for collecting all particle-bound compounds while PUF plugs are used for retaining the PCDD/F compounds in the vapor phase. The total volume of the air sampled was more than 1,200 m³ for a typical sampling duration of 7 days. The deposition and ambient air PCDD/F samples were taken from January 2008 to December 2008. In addition, a 32-cm sediment core was collected at a location near the down stream of the reservoir (Fig 1), where was the previous tea farms on terraces along riverbanks and was flooded after reservoir completion. Core collection was carried out directly by inserting plastic tubes into the bottom sediments by hand with caution in June 2008. The core was delivered to the laboratory within 2 hours and was sectioned immediately to slices with thickness of 1-2 cm. In our study, the sediment core at depth of 29-30 cm contained root debris showing yellowish color with the highest total organic carbon (TOC) content, which is distinguishable from the grayish sediments of the upper core. The bottom layer apparently is the old soil, which marked the reservoir filling. Therefore, the representative age of sediment core in different depths can be estimated (Table 1). For PCDD/Fs analysis, the dioxin-like congeners are analyzed with high resolution gas chromatography (HRGC)/high resolution mass spectrometer (HRMS) (Thermo DFS) equipped with a fused silica capillary column DB-5 MS (60m x 0.25 mm x 0.25µm, J&W).

Results and Discussion

Fig. 2 shows that the atmospheric PCDD/F concentration and deposition flux measured in the vicinity area of the reservoir investigated ranged from 4.90 to 39.0 fg-I-TEQ/m³ and 1.37 to 19.3 pg-I-TEQ/m²-day, respectively. The highest atmospheric PCDD/F (39.0 fg-I-TEQ/m³) and total suspended particle (128 µg/m³) concentration is measured at February 2008 during the Asian dust storm event. In the meantime, the atmospheric PCDD/F deposition flux also increased from 4.14 to 9.89 pg-I-TEQ/m²-day. In addition, the atmospheric PCDD/F deposition fluxes measured on winter are significantly higher than other seasons. Fig. 3 shows the PCDD/F deposition flux in the water body at down stream of the reservoir investigated. The results indicated that the PCDD/F deposition flux in the water body ranged from 10.3 to 29.8 pg-I-TEQ/m²-day and 9.13 to 179 pg-I-TEQ/m²-day measure at water depth of 20 and 70 m, respectively, and was significantly higher than the atmospheric PCDD/F deposition flux measured during same period. The temporal trend of the PCDD/F deposition flux in water body at 20 m water depth is quite similar with the atmospheric PCDD/F deposition flux. The significantly higher PCDD/F deposition flux in water body may be attributed to the catchment erosion at down stream of the reservoir investigated. On September 2008, the PCDD/F deposition flux in the water body at 70 m water depth was dramatically higher than that measured at 20 m water depth during the intensive typhoon events. We consider that the dramatic increase of PCDD/F deposition flux at 70 m water depth was caused by the land slide occurred at up stream of the reservoir during the intensive typhoon period. Based on the PCDD/F deposition flux measured in atmosphere and water body (20 m water depth), Fig 4 shows the contribution of PCDD/F input sources of the reservoir investigated during different periods. The results indicated that around 26 to 46% PCDD/F input flux in the reservoir investigated was contributed by the atmospheric deposition during normal periods. However, the contribution of atmospheric PCDD/F deposition increased to 57% and 66% during the Asian dust storm and Northeast monsoon episodes, respectively. During the typhoon event, the contribution of atmospheric PCDD/F deposition decreased to 10% due to the significant catchment erosion in the reservoir investigated. Fig 5 shows the distribution of PCDD/F homologue in ambient air, atmospheric deposition, surface water, deposition in water body and sediment core samples. The results indicated that the highest distribution of PCDFs (80%) was observed at vapor-phase ambient air sample. The increasing trend of PCDDs was also observed from the sample of atmosphere, water body to sediment. The reasons contributing to the increasing trend of PCDDs are twofold. The first reason is that the PCDDs are mostly distributed in solid phase in ambient air. Therefore, the suspended particles collected in atmospheric

deposition and water body would enhance the PCDD distribution. The second factor considered is the effect of catchment erosion in the reservoir investigated. The PCDD/F input sources in water body included atmospheric deposition and catchment erosion of the reservoir. Previous study⁶ indicated that the significantly higher distribution of PCDDs was observed in the soil samples. Fig 6 shows the vertical profiles of PCDD/Fs in a sediment core, collected from down stream of the reservoir investigated. During 1992 to 1995, several MWI had been operated, and the PCDD/F concentration of the sediment core increased from 0.798~1.80 ng-I-TEQ/kg (depth: 28-32 cm) to 2.86 ng-I-TEQ/kg (depth: 24-26 cm). In August 1997, the Taiwanese government set 1.0 ng-I-TEQ/Nm³ as the PCDD/F emission limit for existing large-scale MWIs, tightening it to 0.1 ng TEQ/Nm³ from August 2001. Hence, the PCDD/F concentration of the sediment core decreased from 3.09 ng-I-TEQ/kg in 1997 (depth: 16-18 cm) to 1.82 ng-I-TEQ/kg in 2002 (depth: 10-12 cm). That is related to the time of enforcement of the PCDD/F emission limit set by the Environmental Protection Administration (EPA) in Taiwan.

Acknowledgements

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References

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Table 1 Total organic carbon and water contents in sediment core at different depth in the reservoir investigated.

Depth	TOC content (%)	Water content (%)	Estimated age
0-2	1.20	71.4	2008
2-4	1.19	59.8	2006
4-6	1.00	56.9	2005
6-8	0.85	50.0	2004
8-10	1.11	52.7	2002
10-12	0.91	50.4	2001
12-14	1.20	54.5	2000
14-16	1.41	56.7	1998
16-18	1.24	55.7	1997
18-20	1.12	53.7	1996
20-22	1.17	42.2	1994
22-24	1.27	37.1	1993
24-26	1.55	39.2	1992
26-28	1.52	43.5	1990
28-29	1.62	41.1	1989
29-30	2.17	44.6	1987
30-32	1.99	33.9	-

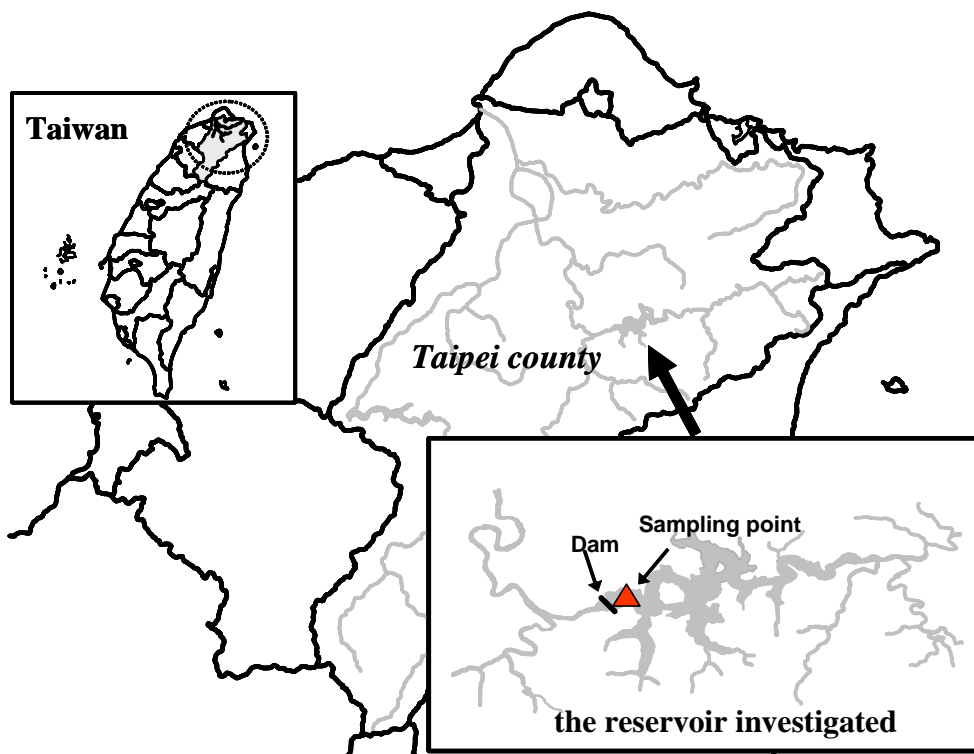


Figure 1 Sampling point and location of the reservoir investigated.

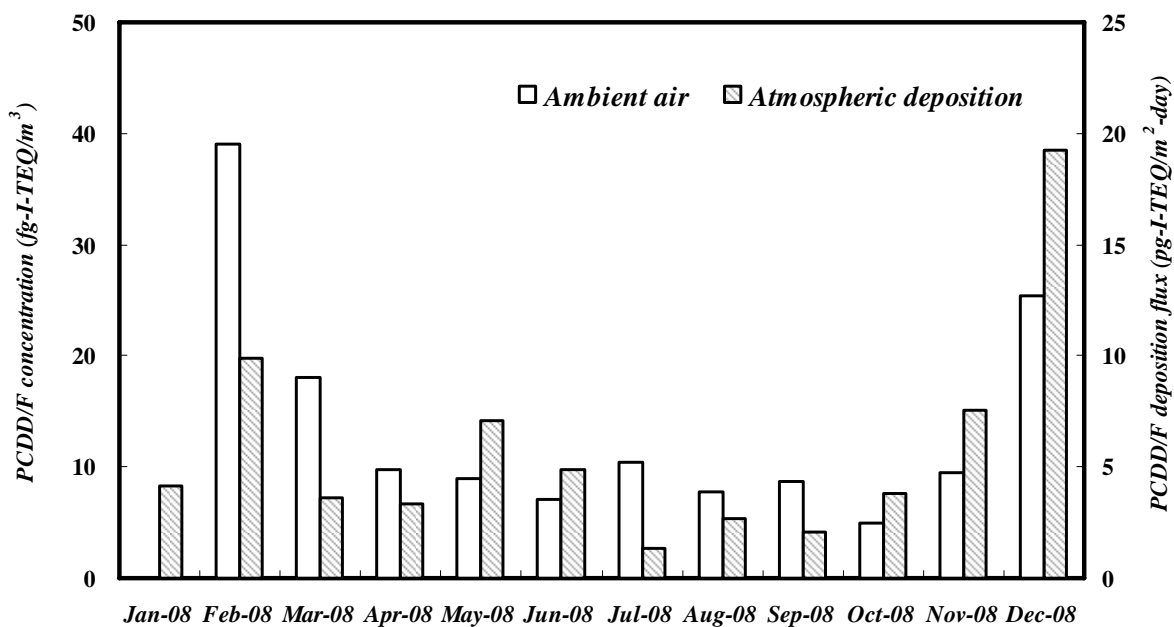


Figure 2 Atmospheric PCDD/F concentration and deposition flux measured in the vicinity area of the reservoir investigated.

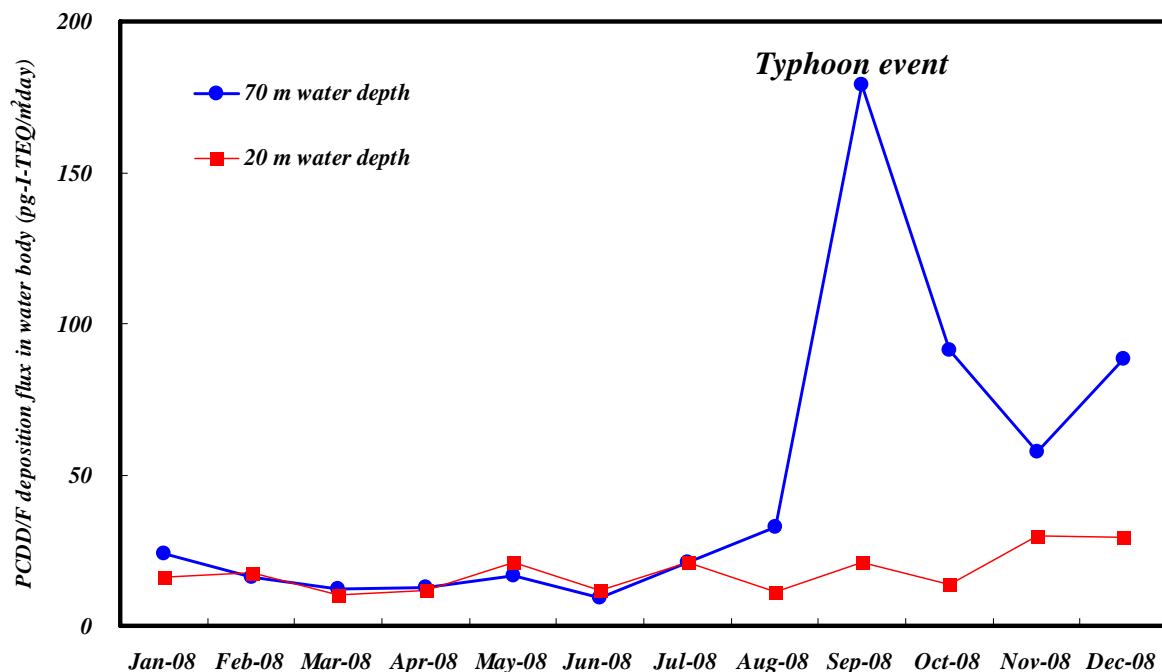


Figure 3 PCDD/F deposition flux in water body at the down stream of the reservoir investigated.

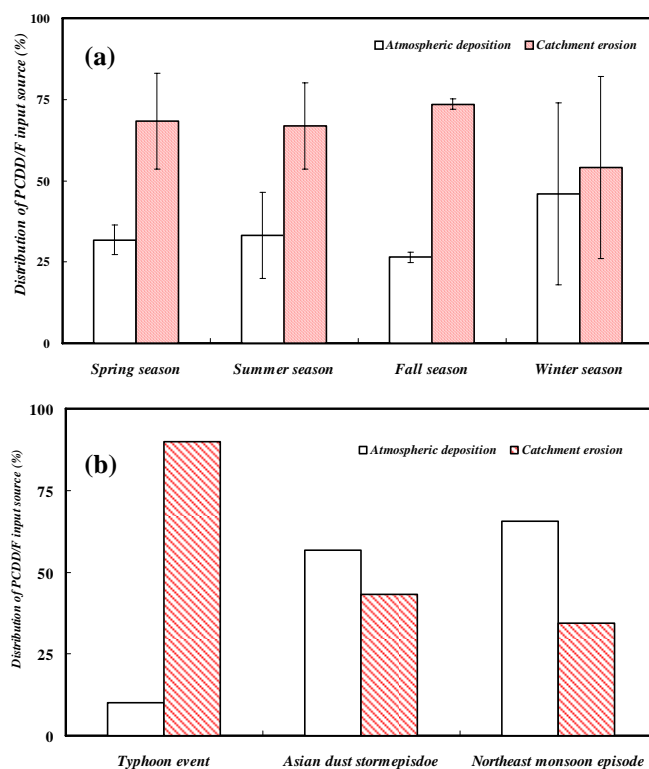


Figure 4 Contribution of PCDD/F input sources of the reservoir investigated during (a) normal periods and (b) specific events.

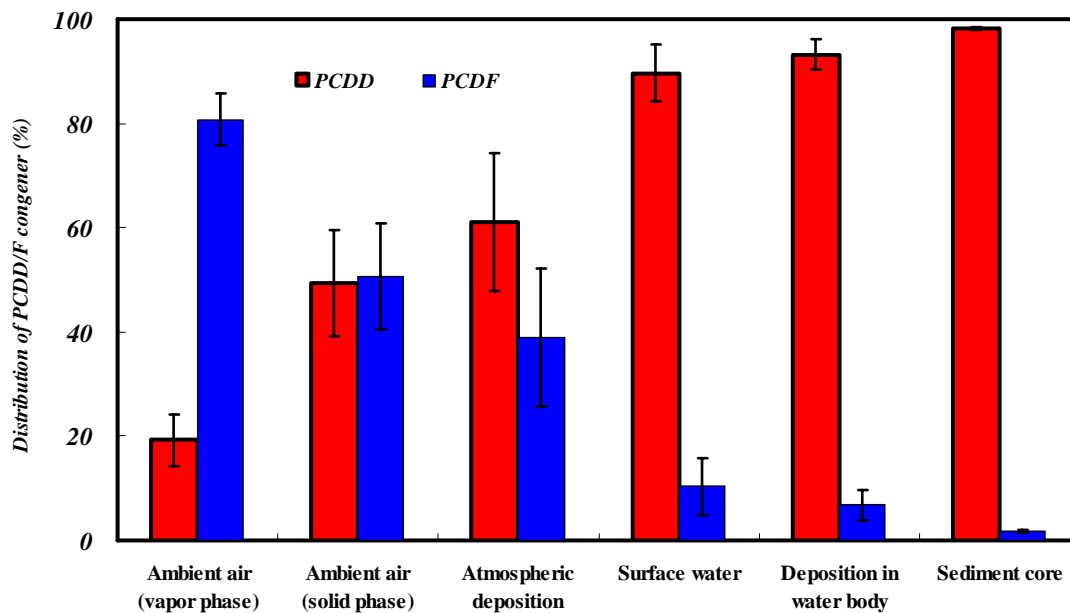


Figure 5 Distribution of PCDD/F homologue in different environmental matrix.

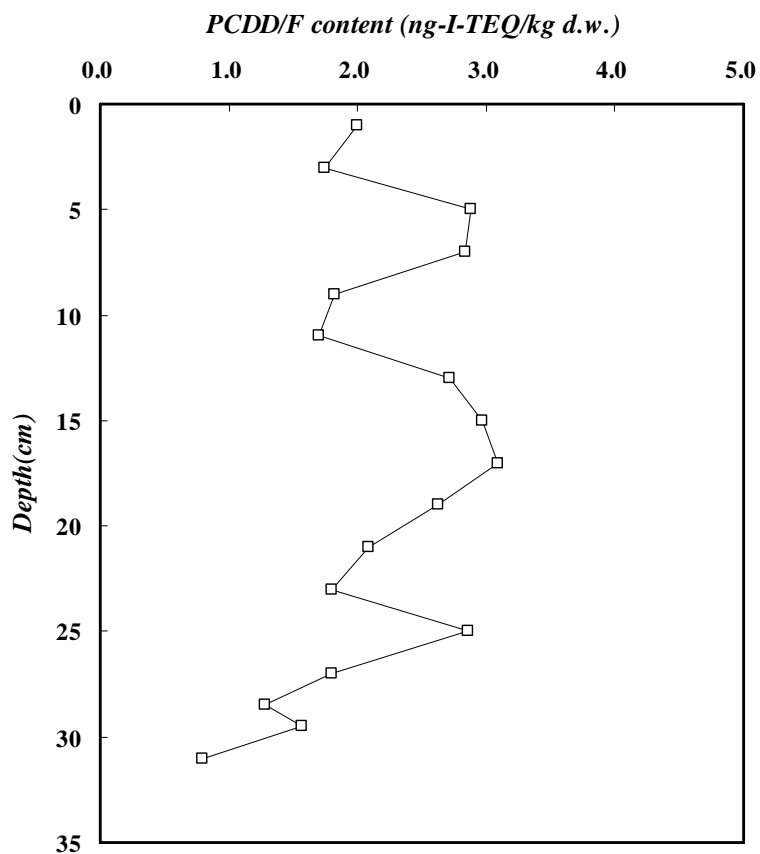


Figure 6 PCDD/F content in sediment core at different depth in the reservoir investigated.