ACCUMULATION AND PARTITION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS (PCDD/F) IN DIFFERENT TISSUES OF FISH AND THEIR TOP-PREDATORS IN A HEAVILY POLLUTED LAKE AREA

K.-W. Schramm[1], W.Z. Wu[2], Y. Xu[2], B. Henkelmann[1], A. Kettrup[1]

[1]GSF-National Research Centre of Environment and Health, Institute of Ecological Chemistry, Ingolstädter Landstr.1, D-85764 Neuherberg, Germany
[2]State Key Laboratory of Freshwater Ecology and Biotechnology, Institute of Hydrobiology, Chinese Academy of Sciences, Wuhan, 430072, P.R. China

Introduction

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) are ubiquitous pollutants in all environmental media. A lot of studies are still continuing to determine the effects of PCDD/F on human health affected by the transfer from water to fish and other aquatic and terrestial top-predators like birds and mammals via the foodweb. The lack of standardization for sampling and reporting makes results difficult to compare, and only a few theoretically derived relationships have been developed and confirmed between e.g. the concentration in the whole fish and its tissues and organs [1] from field monitoring. Such relationships would enable some normalization of results on different weight basis. An important point is that PCDD/F concentrations in fish, whole or as fillets, are of limited use on their own unless the lipid content of the fish is also known since lipid contents of different fish species vary. Those species with a higher lipid content are expected to have a higher PCDD/F concentration per wet weight. These environmental interrelationships could be nicely studied and confirmed in a highly gradually and stratified polluted lake area in Wuhan, PR China.

Materials, Methods, History, and Location

Fish were taken of five ponds of Ya-Er Lake during July 1996 to September 1997. Before 1962, the Ya-Er Lake was an oligotrophic lake. During 1962-1978, the lake was seriously polluted by the waste effluent from a large chemical plant. In 1979, a series of five ponds were built for the waste effluent treatment by self-oxidative purification. The water depth of the lake is 2-3m and the pH of the water is 7.5-7.9 [2].

After homogenization, the samples were freeze-dried and grounded. The PCDD/F analysis has been performed using the isotope dilution technique. About 20g dried sample was weighted and spiked with $^{13}C_{12}$ labeled 2,3,7,8-substituted PCDD/F internal standards. Extraction was carried out by Soxhlet using 180ml toluene for 24 hours. Details including the validation and quality assurance of the method is described elsewhere [2]. Quantification and detection were performed on a high-resolution gas chromatography (60m Rtx 2330 polar capillary column, Restek) coupled with mass spectrometry (Finnigan MAT95s, R=10000) in EI mode by tracing the M^+, $(M+2)^+$, or the most intensive ions of the isotope cluster.

Results and Discussion

In general, lipid-rich tissues preferentially accumulate PCDD/F because of their strongly hydrophobic properties. As most organic contaminants, PCDD/F accumulate in certain tissues with the highest proportions found in the liver of vertebrates. Thus, it is expected that liver accumulates high levels of PCDD/F and exhibit high TEQ values because liver is the tissue that usually is very rich in lipids.

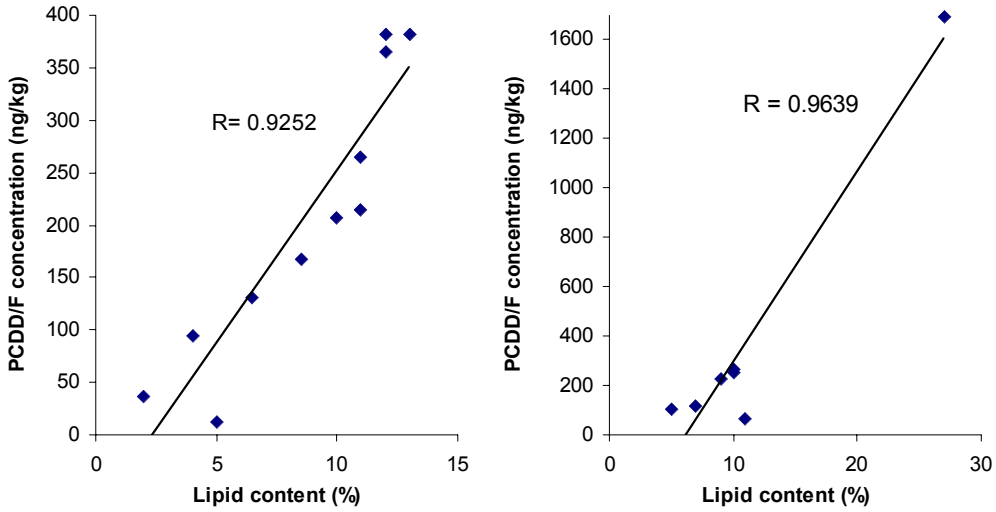

Figure 1: PCDD/F concentrations versus percent lipid content in the different tissues in fish-eating bird (right) and fish (left). All correlations are significant at the 95% level

Table 1: The ratios of TEQ and PCDD/F, PCDD/F and lipid content, PCDD and PCDF in the different tissues of fish and bird

Fish				Bird			
	$\frac{TEQ}{PCDD/F}$	$\frac{PCDD/F}{Lipid}$	$\frac{PCDD}{PCDF}$		$\frac{TEQ}{PCDD/F}$	$\frac{PCDD/F}{Lipid}$	$\frac{PCDD}{PCDF}$
egg	0.03	29.35	1.26	brain	0.07	5.98	1.21
gill	0.01	19.69	6.01	heart	0.23	24.78	0.56
glue	0.06	20.24	0.92	liver	0.33	62.73	0.10
heart	0.01	19.52	0.57	muscle	0.27	20.35	0.36
kidney	0.02	24.11	2.15	stomach	0.25	16.20	0.29
liver	0.02	30.45	4.48	egg_1	0.43	25.17	0.08
muscle	0.07	18.35	1.04	egg_2	0.43	26.26	0.08
brain	0.03	2.49	1.02				
skin	0.07	23.50	0.81				
intestine	0.05	31.87	0.71				
spleen	0.02	20.71	3.38				

Figure 1 plot the PCDD/F concentrations versus lipid content, showing significant correlations among the different tissues. This makes the relative accumulation potential in fish and bird tissues predictable. At a given concentration in water and a tissue lipid content, the equilibrium tissue concentration for PCDD/F may be predicted mainly by the octanol-partition-value of the compound.
Accumulation in animals can be highly variable, even in apparently similar individuals and same tissues of a species from the same site.
Tissues have different capacities for bioaccumulation and biotransformation and we also find variable proportions of TEQ throughout the body. The effect of different lipid properties is obvious in the case of brain tissue, which is more rich in phospholipids. In fish the ratios of TEQ and PCDD/F concentration in various tissues range from 0.01 to 0.07. Interestingly, in bird, the ratios range from 0.07 to 0.43 (Table 1). This species difference in tissue distribution may be explained by the top-predator function of the bird. The bird seems to eliminate substantial amounts of PCDD/F via the eggs. Its tissues contain significantly more toxic congeners than fish which can be explained by the impact and its enhanced metabolic capacity. PCDD are enriched in the brain, whereas in case of fish PCDD are enriched in gill, liver and spleen. Although the liver based PCDD/F are enhanced in fish liver, the bird liver accumulated much more PCDD/F. Further data about the extend of pollution of sediment, soil, vegetables, pigs, breast milk, and human hair as well as the relationships among these webnodes will be highlighted.

Conclusion
The bioaccumulative and metabolic capacity in several tissues is different. Therefore, the bioaccumulation patterns of PCDD/F in fish and bird are also different. Biotransformation is one of the most important processes in higher organisms and the evaluation of metabolic capacity and disposition of PCDD/F must be included in any study of PCDD/F bioaccumulation in predators to accurately assess fate and impact of PCDD/F to those foodweb nodes. A lipid based presentation of the data allow to predict (a) the partition between different tissues especially in fish (b) obtain the succesful confirmation of this approach from the ecosystem for PCDD/F and probably persistent organic toxins (PBT) where PCDD/F belong to.

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References
[1] Schramm K-W, Marth P, Wolf A, Hahn K, Oxynos K, Schmitzer J, Kettrup A.; *UWSF* **1999** (in press)
[2] Schramm K-W, Henkelmann B, Kettrup A, Xu, Y, Wu W (Report), Sources, Fate, Bioaccumulation and Sinks of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in the People's Republic of China. Especially Ya-Er Lake Aerea, near Wuhan, GSF- Forschungszentrum, **1999**, ISSN 0721-1694