POLYCHLORINATED DIBENZO-*P*-DIOXIN/FURAN AND DIOXIN-LIKE PCB CONCENTRATIONS IN SEDIMENTS AND MUSSEL TISSUES FROM KENTUCKY LAKE, USA

Bommanna G. Loganathan[1], Kurunthachalam Senthilkumar[2], Naomasa Iseki[2] and Shigeki Masunaga[2]

[1]Department of Chemistry and Center for Reservoir Research, Murray State University, 456 Blackburn Science Building, Murray, KY 42071-3346, USA. [2]Graduate School of Environment and Information Sciences, Yokohama National University, 79-7 Tokiwadai, Hodogaya-ku, Yokohama 240-8501 Japan

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs) and dioxin-like PCB congeners are among the most toxic chemicals in a variety of animals species including humans[1,2]. PCDDs, PCDFs are found as byproducts in the production of PCBs, polychlorinated naphthalenes and chlorinated phenols. These pollutants are widely dispersed in the environment[2,3] and the residues of these chemicals have been reported in air, water, soil, sediment, aquatic and terrestrial organisms including humans[4-7]. Due to persistent and bioaccumulative properties of these compounds, animals which belongs in higher trophic level receives the largest amount of these contaminants and are implicated in a variety of health effects including, body weight loss, thymic atrophy, dermal disorder, hepatic damage, terratogenicity, reproductive toxicity and immunotoxicity in some animals[8-10]. The westernmost Kentucky, USA is endowed with the highest densities of major rivers and reservoirs in the world, variety of industries and state-of-the-art agricultural operations. However, little is known on the levels of highly toxic dioxins, furans and dioxin-like polychlorinated biphenyls in sediments and biota of this watershed. The objective of the study was to determine the concentrations of 2,3,7,8-chlorine substituted PCDDs, PCDFs and non- and mono-*ortho*-chlorine substituted PCBs in surface sediment and mussels tissues collected from selected locations of Kentucky Lake and Kentucky Dam Tailwater.

Materials and Methods

Sampling locations and Samples

Kentucky lake is one the major man-made lakes in the U.S. Figure 1 shows the map of westernmost Kentucky, the Kentucky lake watershed and the sediment and mussel sampling locations. Ledbetter embayment of Kentucky Lake is considered relatively unpolluted, whereas Kentucky Dam Tailwater receives industrial wastewater from several industries (chemical, metallurgical etc.,) located in the Calvert City Industrial Complex. Selected locations in the Kentucky Lake including Ledbetter embayment and Kentucky Dam Tailwater were sampled for sediments and freshwater mussels during 1999 and 2000. Surface sediments (0-5 cm) samples were collected using PONAR grab sampler. Freshwater mussel samples were collected by SCUBA diving. The mussels were identified, measured for length, height and width, wet weight and age were determined. Mussel species collected and analyzed included, mapleleaf (*Quadrula*

quadrula), threeridge (*Amblema plicata*), ebonyshell (*Fusconaia ebena*) and washborard (*Megalonaias nervosa*).

Chemical Analysis

Sediment and mussel samples were freeze-dried and Soxhlet extracted using methylene chloride for 16h. Details of the analytical procedures were described elsewhere[11]. Identification and quantitation of 2,3,7,8-substituted congeners of PCDDs/DFs and dioxin-like PCBs were performed using a Hewlett Packard 6890 Series High Resolution Gas Chromatography interfaced with a Micromass Autospec - Ultima High Resolution Mass Spectrometer.

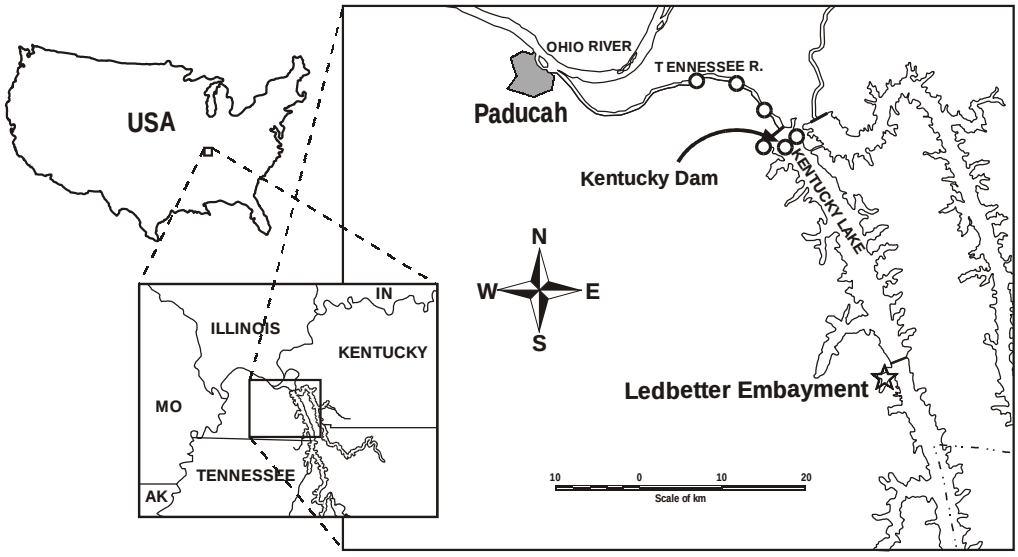

Figure 1. Map showing sediment and mussel sampling locations in the Ledbetter embayment (★) and the Kentucky Dam Tailwater (o).

Results and Discussion

Sediment and mussel tissues were analyzed for non-*ortho* and mono-*ortho*-chlorine substituted PCBs, polychlorinated dibenzo-*p*-dioxins and furans (PCDDs/DFs) and the mean concentrations of the analytes are presented in Tables 1. Average total dioxin-like PCBs in sediment from Ledbetter embayment were 120 pg g^{-1} dry wt. Mussel tissues from the same general location recorded 35, 000 pg g^{-1} fat wt. Elevated concentrations of the dioxin-like PCBs were found in sediments (570 pg g^{-1} dry wt.) and mussel tissues (390,000 ng g^{-1} dry wt.) collected from Kentucky Dam Tailwater indicating relatively higher exposure to these compounds in this region. Among 2,3,7,8- substituted PCDD and PCDF concentrations in sediments and mussel tissues from Ledbetter embayment and Kentucky Dam Tailwater, OCDD/DF were most prominent detects in all of the samples analyzed (Table 1).

Table 1. Mean concentrations of dioxin-like PCBs, polychlorinated dibenzo-*p*-dioxins (PCDDs) dibenzofurans (PCDFs) and TEQs in sediment (pg g^{-1} dry wt) and mussel tissues (pg g^{-1} fat wt) from Ledbetter embayment of Kentucky Lake and Kentucky Dam Tailwater, USA.

Compound	**Sediment**		**Mussel Tissue**	
	Ledbetter Embayment(n=5)	KY Dam Tailwater(n=5)	Ledbetter Embayment(n=5)	KY Dam Tailwater(n=5)
Non-*ortho* PCBs				
81	0.04	15	9.2	9.4
77	5.1	56	1300	1200
126	0.6	41	3100	110
169	0.1	5.3	22	12
Mono-*ortho* PCBs				
105	26	81	7900	8200
114	3.2	8.3	170	370
118	75	270	19000	24000
123	3.6	16	<0.1	<0.1
156	6.1	44	1400	2600
157	2.0	11	520	610
167	2.4	17	1200	1500
189	0.5	3.0	67	560
TEQ (Mean)	0.1	0.3	19	0.7
PCDDs				
2,3,7,8-D	0.04	0.1	11	4.5
1,2,3,7,8-D	0.1	0.2	73	8.9
1,2,3,4,7,8-D	0.3	0.5	98	6.2
1,2,3,6,7,8-D	0.6	0.1	88	13
1,2,3,7,8,9-D	0.1	0.2	11	1.6
1,2,3,4,6,7,8-D	24	490	310	140
OCDD	830	1500	5400	2800
TEQ (Mean)	0.6	0.6	110	17
PCDFs				
2,3,7,8-F	0.2	0.6	66	88
1,2,3,7,8-F	0.1	0.9	470	25
2,3,4,7,8-F	0.1	0.3	83	13
1,2,3,4,7,8-F	0.3	3.8	63	27
1,2,3,6,7,8-F	0.2	1.2	57	15
2,3,4,6,7,8-F	0.1	0.3	93	11
1,2,3,7,8,9-F	0.03	0.2	64	4.4
1,2,3,4,6,7,8-F	2.1	22	68	48
1,2,3,4,7,7,8,9-F	0.1	2.8	71	29
OCDF	3.2	170	140	320
TEQ (Mean)	0.2	0.4	62	14
Total TEQ	**0.9**	**1.3**	**190**	**32**

Altogether, PCDD homologues were abundant contaminants in all analyzed samples indicating multiple local sources in Kentucky Dam and its surrounding areas. Greater concentrations of OCDD and OCDF suggested the usage of pentachlorophenol herbicide (PCP) in the agriculture probably the reason.

In general, TEQs (calculated using WHO-TEFs proposed in 1998 [for sediment-mammal TEFs and for mussel-fish TEFs]) indicated that sediments from KY Dam Tailwater (1.3 pg g^{-1} dry wt) and mussel tissues (190 pg g^{-1} fat wt) from Ledbetter embayment of KY Lake higher toxic potential than sediment from Ledbetter embayment and mussel tissues from KY Dam Tailwater respectively (Table 1). On the whole, PCDD homologues greatly contributed to the toxicity in all the sample followed by PCDFs, non-*ortho* PCBs and mono-*ortho* PCBs. In particular, 2378-TCDD, 12378-PnCDD, 2378-TCDF, 12378-PnCDF and 23478-PnCDF comprised greater composition in toxic equivalencies. Elevated concentrations of PCDD/DFs in mussel tissues indicate bioaccumulation of these compounds (Table 1). Very little is known on the concentrations of dioxins and dioxin-like compounds in Kentucky Lake watershed. Further studies with greater number of samples from this watershed is needed to elucidate distribution, source, bioaccumulation and toxic effects.

Acknowledgements
NSF-CRUI, Murray State University, Murray, KY, USA and Japan Society for the Promotion of Science (JSPS Fellowship to KS, Yokohama, National University, Japan) supported this research. The authors are thankful to Mr. Kosta Seaford for his help in the sample analysis and Mr. Carl Woods (MSU Science Resource Center) for his help in preparation of this manuscript.

References

1. Loganathan, B.G., Kannan, K., Watanabe, I., Kawano, M., Irvine, K., Kumar, S. and Sikka, H.C. (1995) Environ Sci Technol. 29, 1832-1838.
2. Schecter, A. (1998) Environ Health Perspect 106, 737-742
3. Haug, L.S., Nicolayasen, T. and Lindström, G. (2000) Organohalogen Compounds 47, 353-356.
4. Safe, S.H. (1995) *Pharmacol Ther.* ***67,*** 247-281.
5. Smith, L.M., Stalling, D.L. and Johnson, J.L. (1984) Anal Chem 56, 1830-1842.
6. Rappe, C. and Kjeller, L.O. (1987) Chemosphere 16, 1775-1780
7. Patterson, D.G., Todd, G.D., Turner, W.E., Maggio, V., Alexander, L.R. and Needham, L.L. (1994) Environ Health Perspect 102,(Suppl. 1), 195-204.
8. Kennedy, S.W., Lorenzen, A. and Norstrom, R.J. (1996) Environ Sci Technol. 30, 706-715.
9. Safe, S. (1994) Crit Rev Toxicol 24, 87.
10. Grasman, K.A., Fox, G.A., Scanlon, P.F. and Ludwig, P.F. (1996) Environ Health Perspect 104 (Suppl 4), 829-842.
11. Senthil Kumar, K.; Kannan, K.; Paramasivan, O.N.; Shanmugasundaram, V.P.; Nakanishi, J.; Masunaga S. (2001) Environ Sci Technol, (in press).