SYDNEY HARBOUR FISHERMAN AND FAMILIES: ELEVATED LEVELS OF DIOXINS RESULTING FROM CONSUMPTION OF TCDD-CONTAMINATED FISH

Symons R[1], Paepke O[2], Lohmann N[2], Harley J[3] and Callan A[4]

[1]National Measurement Institute, PO Box 385, Pymble NSW 2073, Australia
[2]eurofins | ERGO, Geierstrasse 1, 22305 Hamburg, Germany
[3]Australian Broadcasting Corporation, 700 Harris Street, Ultimo NSW 2007, Australia
[4]Seven Network (Operations) Limited, 52 Martin Place, Sydney NSW 2000, Australia

Introduction

In 2001, Australian Government established the National Dioxins Program that involved a range of studies measuring emissions from sources such as bushfires, as well as dioxin levels in the environment, food, agricultural commodities and its population. One study concentrating on the aquatic environment detected dioxin-like chemicals in all Australian aquatic sediments analysed, with middle-bound concentrations ranging from 0.002 to 520 pg WHO-TEQ g^{-1} dry matter (dm). Highest concentrations were found in a sediment sampled from the Parramatta River estuary (100 and 520 pg WHO-TEQ g^{-1} dm) and the western section of Port Jackson (78 and 130 pg WHO-TEQ g^{-1} dm). [1] In close proximity to where these sediments had been collected were a number of industries located along the Rhodes peninsula bordering Homebush bay which manufactured a range of chemicals from 1928 to 1986 including xanthates, aniline, nitrobenzene, phenol, chlorophenol, chlorobenzene, 2,4,5-T and 2,4-D herbicides, chlorine, DDT, bisphenol-A and phenol-formaldehyde. Industrial practices during this time lead to contamination of the sediments of Homebush Bay with a number of these chemicals with subsequent studies have found levels of dioxins ranging from 31.5 to 4,352.5 pg WHO-TEQ g^{-1} dm with a mean of 711.5 pg WHO-TEQ g^{-1} dm. [2] Remediation of the soil from the manufacturing sites together with some of the most contaminated sediment started in early 2006. A baseline study of the levels of dioxins (PCDDs/PCDFs) and dioxin-like polychlorinated biphenyls (DL-PCBs) in prawns and bream from areas both upstream and downstream of the remediation site was undertaken in order to assess the efficacy of the remediation works. Levels determined were assessed by an Expert Panel convened by the New South Wales Food Authority and they recommended that "seafood caught in Sydney Harbour/Parramatta River posed a possible public health risk and should not be consumed on a regular long term basis until further data demonstrates the safety of the product." [3] Furthermore, on 2 December 2005 the NSW Minister for Primary Industries initiated a ban on the taking of all prawns in Port Jackson and its tributaries and on 24 January 2006 initiated a ban on commercial fishing in Sydney Harbour.
Fisherman and their families that had consumed fish caught within these areas for a considerable time were contacted by investigative teams from two media organisations with regards to their willingness to provide blood samples for analysis of dioxins. This paper discusses the results of the investigation of blood serum levels of PCDDs/PCDFs and DL-PCBs and compares them with levels found in the general Australian population.

Materials and Methods

Samples and Sampling

The sampling was organized in cooperation with local health centres. Sampling was done in March and April 2006. Participants A and B belong to two different families. Samples were sent in frozen state by an international courier service to ERGO in Hamburg/Germany where they were stored below -18°C until the beginning of the analyses. Some background information for the individuals who donated the six blood samples are given below.

Table 1 Information on study participants

Code	Age	Fish consumption, caught in Sydney harbour, during fishing season
A #1	74	Seafood (prawns, bream, whiting, squid, crabs, octopus, flathead), 3 to 4 times a week
A #2	6	Seafood (prawns, calamari, octopus, crabs), 3 times a week
A #3	40	Seafood (prawns, crabs, calamari, octopus, whiting, bream), 3 times a week
A #4	45	Seafood (prawns, crabs, calamari, whiting), 3 times a week
B #1	77	Seafood (fish, prawns, crabs and calamari)
B #2	45	Seafood (fish, prawns, crabs and calamari)

Analysis

Before the extraction 13C-UL-labeled internal standards for all 17 PCDDs/Fs and 12 PCBs were added to the sample. After spiking, the samples were extracted with appropriate solvents using a solid/liquid extraction for blood. The cleanup was done on multicolumn systems involving carbon-on-glass fibre. The measurement was performed by means of high resolution gas chromatography and high resolution mass spectrometry (HRGC/HRMS) with VG-AutoSpec operating on a resolution of approximately 10,000 using DB-5 capillary column. For each substance two isotope masses were measured. The quantification was carried out with the use of internal and external standards (isotope dilution method). Methods applied are described in detail elsewhere. [4,5]

The analytical methods used at the ERGO laboratory are validated and successfully applied by participation at international quality control studies. [6,7] All calculations presented in this study are based on the most recent revised version of WHO-TEF values used. [8]

Results and Discussion

The results for the determination of dioxins and dioxin-like PCBs of the fisherman and their families are provided in Table 2. When comparing the results for the six individuals with actual human background for Australia [9], it is striking that all samples show elevated levels for 2,3,7,8-TCDD. This elevation for TCDD can be seen from Figures 1 to 3 as well.

Table 2: PCDDs/PCDFs and Dioxin-like PCBs in Human Blood of Sydney Harbor Fish Consuming Individuals, Values in pg/g, lipid based

Person No.	A #1	A #2	A #3	A #4	B #1	B #2
Age	**74**	**6**	**40**	**45**	**77**	**45**
2.3.7.8-Tetra-CDD	45	8,8	25	6,2	232	26
1.2.3.7.8-Penta-CDD	9,9	2,4	3,9	2,1	26	5,2
1.2.3.4.7.8-Hexa-CDD	5,1	n.d.(2)	1,7	1,9	8,7	n.d.(2)
1.2.3.6.7.8-Hexa-CDD	36	8,9	16	13	80	18
1.2.3.7.8.9-Hexa-CDD	5,7	2,4	2,4	1,8	11	3,1
1.2.3.4.6.7.8-Hepta-CDD	45	11	12	12	56	7,5
OCDD	332	152	121	173	270	119
2.3.7.8-Tetra-CDF	n.d.(1)	n.d.(1)	n.d.(1)	n.d.(1)	3,2	n.d.(1)
1.2.3.7.8-Penta-CDF	n.d.(1)	n.d.(1)	n.d.(1)	n.d.(1)	2,2	n.d.(1)
2.3.4.7.8-Penta-CDF	12	2,2	5,0	1,9	24	5,9
1.2.3.4.7.8-Hexa-CDF	5,0	1,8	2,9	1,4	9,9	2,3
1.2.3.6.7.8-Hexa-CDF	2,4	1,9	1,7	1,3	13	1,7
1.2.3.7.8.9-Hexa-CDF	n.d.(1)	n.d.(2)	n.d.(1)	n.d.(1)	n.d.(2)	n.d.(2)
2.3.4.6.7.8-Hexa-CDF	n.d.(1)	n.d.(2)	n.d.(1)	n.d.(1)	1,9	n.d.(1)
1.2.3.4.6.7.8-Hepta-CDF	3,9	9,9	4,5	2,2	4,0	2,6
1.2.3.4.7.8.9-Hepta-CDF	n.d.(1)	n.d.(2)	n.d.(1)	n.d.(1)	n.d.(2)	n.d.(3)
OCDF	n.d.(3)	n.d.(3)	n.d.(2)	n.d.(2)	n.d.(5)	n.d.(10)
3,3',4,4'-TetraCB (No #77)	n.d.(21)	n.d.(22)	n.d.(18)	n.d.(17)	n.d.(49)	n.d.(35)
3,4,4',5-TetraCB (No #81)	n.d.(4)	n.d.(2)	n.d.(2)	n.d.(1)	6,8	n.d.(1)
3,3',4,4',5-PentaCB (No #126)	130	n.d.(10)	19	7,1	263	25
3,3',4,4',5,5'-HexaCB (No #169)	57	8,0	27	9,9	99	20
2,3,3',4,4'-PentaCB (No #105)	11654	791	2421	1116	27554	3046
2,3,4,4',5-PentaCB (No #114)	3695	189	544	227	5949	892
2,3',4,4',5-PentaCB (No #118)	79782	4791	16146	6035	174150	20235
2',3,4,4',5-PentaCB (No #123)	1509	73	317	145	1914	215
2,3,3',4,4',5-HexaCB (No #156)	35551	1365	7478	1698	58324	7413
2,3,3',4,4',5'-HexaCB (No #157)	8329	354	1848	355	15743	1896
2,3',4,4',5,5'-HexaCB (No #167)	13125	500	2244	607	24399	2953
2,3,3',4,4',5,5'-HeptaCB (No #189)	2246	99	797	171	4209	535
TEQ (WHO) based on PCDDs/Fs	67	14	34	11	284	36
TEQ (WHO) based on PCBs	47	1,6	9,1	2,7	88	10
TEQ (WHO)	**113**	**16**	**43**	**14**	**372**	**47**

Figure 1: Comparison of PCDD/PCDF Pattern, Family A

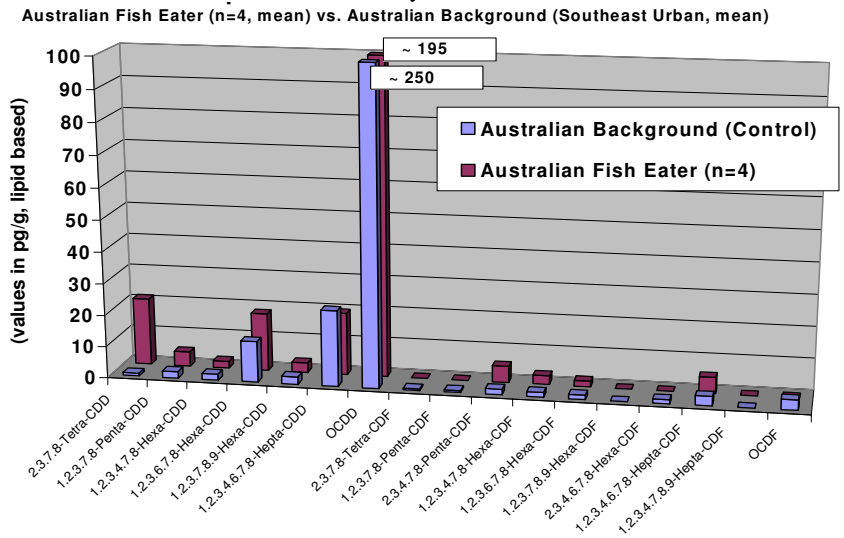


Figure 2: Comparison of PCDD/PCDF Pattern, Family B

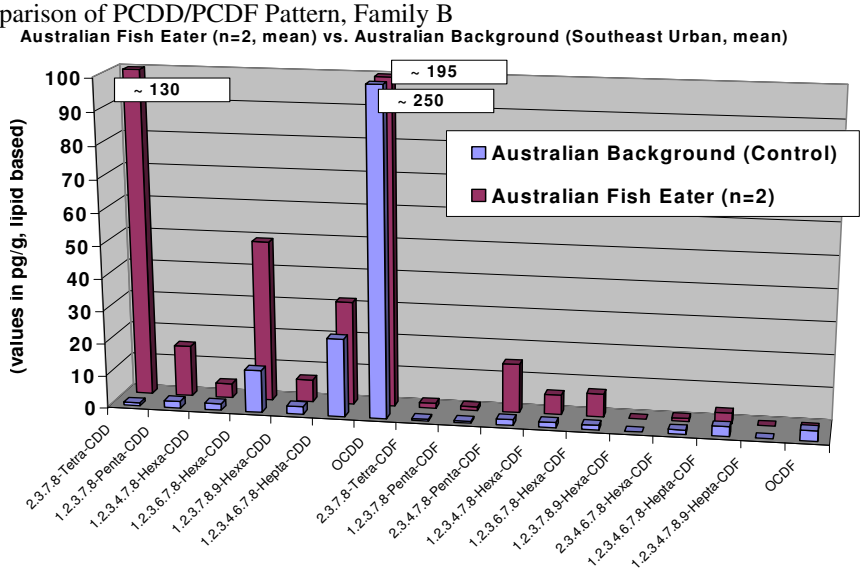
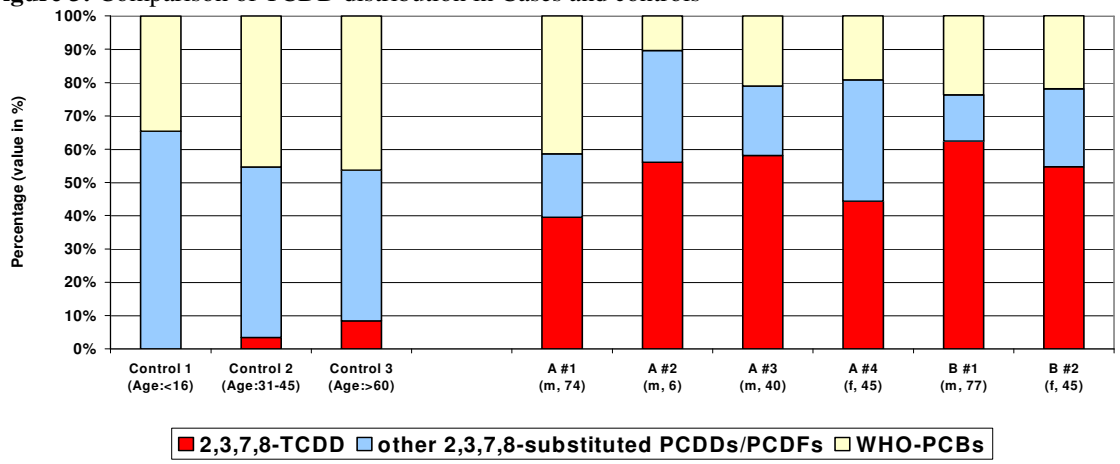


Figure 3: Comparison of TCDD distribution in Cases and controls



In Table 3 we compare the results of other studies where the consumption of fish and/or seafood was observed to be highly relevant for elevated levels in humans.

Table 3: Other studies considering distinct fish consumption (summary of main findings of studies in blood carried out under special consideration of distinct fish consumption)

Observed area	2,3,7,8-Tetra-CDD (in pg/g)		TEQ based on PCDDs/PCDFs (in pg/g)		TEQ based on PCDDs/PCDFs and PCBs (in pg/g)		Literature
	Control	Fish eater	Control	Fish eater	Control	Fish eater	
Sweden	2	8	18*	26 – 64*	n.a.	n.a.	[10]
	n.a.	n.a.	37 – 54*	42 – 154*	n.a.	n.a.	[11]
Finland	2 - 7	3 - 110	10 – 70*²	34 – 500*²	n.a.	51 – 900*²	[12]
Norway	n.a.	n.a.	21*³	61 – 110*³	n.a.	n.a.	[13]
Vietnam	1 - 2	3 - 415	n.a.	n.a.	n.a.	n.a.	[14]

n.a. = not available * I-TEQ *² WHO-TEQ *³ Nordic-TEQ

Acknowledgment
We would like to thank the families of Sydney Harbour fisherman for providing the blood samples.

References

1. Müller J, Muller R, Goudkamp K, Shaw M, Mortimer M, Haynes D, Paxman C, Hyne R, McTaggart A, Burniston D, Symons R, Moore M. *Dioxins in Aquatic Environments in Australia*, National Dioxins Program Technical Report No. 6, Australian Government Department of the Environment and Heritage, Canberra, Australia, 2004. (http://www.deh.gov.au/industry/chemicals/dioxins/report-6/pubs/report6a.pdf)
2. Birch GF, Harrington C, Symons RK, Hunt JW.: The source and distribution of polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofurans in sediments Port Jackson, Australia. *Marine Pollution Bulletin* 2006, submitted.
3. NSW Food Authority. *Dioxins in Seafood in Port Jackson and its Tributaries* Report of the Expert Panel 24 February 2006 (http://www.foodauthority.nsw.gov.au/pdf/Report_of_the_Expert_Panel_on_Dioxins_in_Seafood.pdf)
4. Päpke O, Ball M, Lis ZA, Scheunert K.: PCDD/PCDF in Whole Blood Samples of Unexposed Persons. *Chemosphere* 1989;19:941.
5. Smith LM, Stalling DL, Johnson JL.: Determination of Part-per-trillion Levels of Polychlorinated Dibenzofurans and Dioxins in Environmental Samples. *Anal. Chem.* 1984;56:1830.
6. WHO Regional Office for Europe. *Consultation on the third round of interlaboratory quality control studies on levels of PCBs, PCDDs and PCDFs in human milk, blood, cows milk and fish.* EUR/ICP EHAZ 94 05 / B03(1), Denmark 1995.
7. *International Comparison on Dioxins in Food 2000, 2001, 2003, 2004, 2005* Final Reports 2000 to 2005, Folkehelsa, National Institute of Public Health, Norway.
8. Van den Berg M, Birnbaum L, Bosveld BTC, Brunström B, Cook P, Feeley M, Giesy J, Hanberg A, Hasegawa R, Kennedy SW, Kubiak T, Larsen JC, van Leeuwen FXR, Liem AKD, Nolt C, Peterson RE, Poellinger L, Safe S, Schrenk D, Tillitt D, Tysklind M, Younes M, Wærn F, Zacharewski R: Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. *Environm. Health Persp*. 1998;106:775.
9. Harden F, Müller J, Toms L, Gaus C, Moore M, Päpke O, Ryan J, Hobson P, Symons R, Horsley K, Sim M, Van den Berg M, Fürst P. *Dioxins in the Australian Population: Levels in Blood* National Dioxins Program Technical Report No. 9, Australian Government Department of the Environment and Heritage, Canberra, Australia May 2004.
10. Svensson BG, Nilsson A, Hansson M, Rappe C, Akesson B, Skerfving S.: Exposure to dioxins and dibenzofurans through the consumption of fish. *N. Engl. J. Med.* 1991;324:8.
11. Svensson BG, Nilsson A, Jonsson E, Schutz A, Akesson B, Hagmar L.: Fish consumption and exposure to persistent organochlorine compounds, mercury, selenium and methylamines among Swedish fishermen. *Scand. J. Work Environ. Health* 1995;21:96.
12. Kiviranta H, Vartiainen T, Tuomisto J.: Polychlorinated Dibenzo-p-dioxins, Dibenzofurans, and Biphenyls in Fishermen in Finland. *Environ. Health Persp.* 2002;110:355.
13. Johansen HR, Alexander J, Rossland OJ, Planting S, Løvik M, Gaarder PI, Gdynia W, Bjerve KS, Becher G.: PCDD, PCDF and PCB in human blood in relation to consumption of crabs from contaminated fjord area in Norway. *Environ. Health Persp.* 1996;104:756.
14. Schecter A, Dai LC, Päpke O, Prange J, Constable JD, Matsuda M, Thao VD, Piskac AL.: Recent Dioxin Contamination From Agent Orange in Residents of a Southern Vietnam City. *JOEM* 2001;43:435.