

PCDD/PCDF LEVELS IN HUMAN BLOOD AND BREAST MILK IN THE REGION OF OPORTO, PORTUGAL

José Manuel Calheiros¹, Miguel Coutinho², Carlos Borrego², Rui Santos³ and Olaf Papke⁴

¹Institute of Biomedical Sciences Abel Salazar, University of Porto, Portugal

²IDAD, Institute of Environment and Development, University of Aveiro, Portugal

³Centro de Saúde de Castelo da Maia, Portugal

⁴ERGO Forschungsgesellschaft, Hamburg, Germany

Introduction

In the municipal solid waste (MSW) management plan adopted for Oporto, in Portugal, it was built a MSW incinerator with the capacity of 400 000 ton.a⁻¹ commonly referred as LIPOR II. This waste treatment facility is under operation since January 2000, being located in the boarder between the municipalities of Maia and Matosinhos. An External Monitoring Plan (EMP) for the LIPOR II was designed with the objective of assessing the potential impact over the environment of the construction and operation of this facility¹.

One of the main concerns of the EMP is to fulfil the lack of information about the atmospheric levels of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD and PCDF). The EMP covers a large set of environmental matrices namely, air, soils and river sediments, as well as biological matrices, such as vegetables, chicken eggs and cow milk produced locally. PCDD and PCDF levels in these matrices have been presented elsewhere^{2,3}. The ultimate objective of the EMP is to verify the potential contamination of human beings living in the surroundings of the MSW incinerator. As a result of this concern, mother milk and human blood samples have been collected during 2001. Taking into account that the incinerator was in operation for only 12 months for a life span of 20 – 70 years for the donors, the levels reported in this paper could be considered as background levels.

Results and Discussion

Sampling and analytical procedure

The sampling was organized in cooperation with local health centres. For obtaining blood samples a protocol with an explanation with the broader objectives of the EMP was proposed to healthy people visiting the health centres-. Milk samples were obtained during the regular visits that mothers do to local health centres during the first 4 months of the newborn baby.

Samples were sent in frozen state by a courier service to ERGO where they were stored at -18°C until the beginning of the analyses. Before the extraction ¹³C-UL-labeled internal standards were added to the sample. After the spiking, the samples were extracted with pentane/diethyl ether after the addition of potassium oxalate and ethanol. The cleanup was done on multicolumn systems involving carbon-on-glassfibre or carbon-on-celite. The measurement was performed by means of high resolution gas chromatography and high resolution mass spectrometry (HRGC/HRMS) with VG-AutoSpec Finnigan MAT 95 XL using DB-5 capillary columns. For each substance 2 isotope masses were measured. The quantification was carried out with the use of internal and external standards (isotope dilution method). The 17 2,3,7,8 chlorine substituted congeners were reported.

HUMAN EXPOSURE I

Human blood

During the first semester of 2001 blood from 46 donors was sampled in the municipalities of Maia and Matosinhos. Data obtained are compiled in Table 1 that includes the congener pattern of individual donors with minimum and maximum WHO-TEQ level. Donor's age ranged between 21 and 70 years, with an average of 43. 70 % of the donors were women but average age was similar for male and female sub-samples. PCDD and PCDF levels expressed as WHO-TEQ ranged between 10.4 to 54.8 pg/g lipid based, with an average of 21.7 ± 8.2 pg/g. 4 of the congeners were responsible for *circa* 80 % of these values.

Table 1. PCDD and PCDF levels in human blood in Maia and Matosinhos, Portugal.

Sample structure	M	F	range	Average	Standard deviation	Minimum donor	Maximum donor
Age			21-70	42.7	12.0	34	45
Sex	14	32					
Congener	Positive results	Not detected					
2,3,7,8 TD	29	1	nd-9.2	2.73	1.31	1.4	9.2
1,2,3,7,8 PD	30	0	4.1-18.1	8.16	2.89	4.2	18.1
1,2,3,4,7,8 HxD	29	1	nd-15.8	5.61	2.47	3.4	15.8
1,2,3,6,7,8 HxD	30	0	10.9-73.1	30.88	13.92	14.8	73.1
1,2,3,7,8,9 HxD	30	0	2.7-13.9	6.25	2.24	3.5	13.9
1,2,3,4,6,7,8 HpD	30	0	15.9-216.2	87.45	47.3	70.8	197.8
OD	30	0	192.2-1352.1	611.24	288.48	240.6	1352.1
2,3,7,8 TF	2	28	nd-3.7	0.17	0.62	nd	nd
1,2,3,7,8 PF	6	24	nd-3.0	0.32	0.64	nd	1.2
2,3,4,7,8 PF	30	0	2.1-23.7	8.46	4.00	2.4	23.7
1,2,3,4,7,8 HxF	30	0	2.3-15.7	6.14	2.65	3.3	15.7
1,2,3,6,7,8 HxF	30	0	2.4-13.8	5.38	2.35	2.8	13.8
1,2,3,7,8,9 HxF	0	30	nd	nd	-	nd	nd
2,3,4,6,7,8 HxF	16	14	nd-4.4	1.26	1.40	nd	nd
1,2,3,4,6,7,8 HpF	30	0	3.9-24.6	9.05	4.86	7.6	22.6
1,2,3,4,7,8,9 HpF	0	30	nd	nd	-	nd	nd
OF	2	28	nd-18.5	0.69	3.29	nd	nd
Total D			245.0-1680.0	752.3	344.4	338.7	1680.0
Total F			14.5-77.0	31.5	12.9	16.1	77.1
D/F ratio			10.1-50.8	23.9	8.9	21.0	21.8
Total D+F			265.9-1757.0	783.8	353.8	354.8	1757.1
WHO-TEQ			10.4-54.8	21.7	8.2	10.4	54.8
I-TEQ			8.5-47.0	18.2	7.0	8.5	47.0

Average results obtained through this work are comparable with data published for Germany⁴. Papke and other authors identified a clear temporal reduction of PCDD/F levels in human blood in Germany, from levels above 40 pg/g I-TEQ in 1988 to levels between 14 to 16 pg/g I-TEQ in 1998-99. Within

this trend, levels reported for the region of Oporto are closer to the levels reported for Germany in 1994 and considerably lower than the levels reported for the USA during the 1990's⁵.

Breast milk

In August 2001, breast milk samples from 19 mothers were collected. Results obtained in this campaign are reported in Table 2. Mother's age ranged between 19 and 45 years with an average of 28. WHO-TEQ levels ranged between 5.5 and 46.0 pg/g lipid based with an average of 12.4 ± 9.6 pg/g. As it was previously referred the sum of TD, 1,2,3,7,8-PD, 1,2,3,6,7,8, HxD and 2,3,4,7,8 PF is responsible for approximately 80% of the total TEQ level.

Table 2. PCDD and PCDF levels in breast milk in Maia and Matosinhos, Portugal.

	range	Average	Standard deviation	Minimum donor	Maximum donor		
Age of mother (yr)	19-45	27.6	5.5	23	23		
Age of baby (days)	5-120	32.1	31.3	12	90		
Congener	Positive results detected	Not detected					
2,3,7,8 TD	19	0	0.6-2.7	1.2	0.48	0.6	2.7
1,2,3,7,8 PD	19	0	1.9-13.9	4.1	2.88	1.9	13.9
1,2,3,4,7,8 HxD	19	0	1.0-14.7	3.3	3.33	1.2	14.7
1,2,3,6,7,8 HxD	19	0	7.1-136.6	26.5	35.11	9.2	136.6
1,2,3,7,8,9 HxD	19	0	1.3-20.7	3.6	4.35	1.7	20.7
1,2,3,4,6,7,8 HpD	19	0	5.2-469.2	64.5	102.17	14.8	469.2
OD	19	0	33.0-1246.7	251.1	304.14	95.2	1246.7
2,3,7,8 TF	17	2	nd-2.1	0.5	0.46	Nd	0.2
1,2,3,7,8 PF	19	0	0.1-0.7	0.3	0.16	0.2	0.3
2,3,4,7,8 PF	19	0	2.5-6.3	4.4	1.32	2.5	5.9
1,2,3,4,7,8 HxF	19	0	1.7-21.4	4.0	4.27	1.8	21.4
1,2,3,6,7,8 HxF	19	0	1.3-14.5	2.9	2.87	1.3	14.5
1,2,3,7,8,9 HxF	0	19	nd	nd	nd	Nd	nd
2,3,4,6,7,8 HxF	17	2	nd-4.6	1.2	0.99	Nd	4.6
1,2,3,4,6,7,8 HpF	19	0	1.1-35.7	4.9	7.35	2.7	35.7
1,2,3,4,7,8,9 HpF	17	2	nd-4.5	0.6	0.95	Nd	4.5
OF	12	7	nd-5.4	1.3	1.46	nd	5.4
Total D			55.8-1904.5	354.4	439.4	124.6	1904.5
Total F			8.5-92.5	20.0	17.8	8.5	92.5
D/F ratio			6-54.3	15.7	10.5	14.7	20.6
Total D+F			65.1-1997.0	374.3	455.4	133.1	1997.0
WHO-TEQ			5.5-46.0	12.4	9.6	5.5	46.0
I-TEQ			4.6-40.2	10.6	8.4	4.6	40.2

PCDD/F levels determined under the framework of this project are lower than levels reported for Germany and the USA by Schecter and Papke⁵. These authors present an average level of 16 to 23 pg/g

HUMAN EXPOSURE I

I-TEQ in sampling campaigns performed between 1988 and 1994. Data compiled in Table 2 shows a strong consistency with data published for an extensive sampling work performed in Japan in 415 mothers⁶. This later work reports an average level of 12.3 ± 4.6 pg/g WHO-TEQ, with 72% of the samples in the range 5.0-14.9 pg/g and a maximum of 32.0 pg/g. Special care should be drawn to the sample that reported the maximum level of 46.0 pg/g WHO-TEQ on the Oporto region. Analysis of the congener pattern of this sample reveals an unusually high contribution of the hexa- and hepta-chlorinated dioxins and a relatively low presence of 2,3,4,7,8 PF, creating a high dioxin/furan ratio.

Conclusions

This paper presents the levels of PCDD and PCDF found in human blood and breast milk of residents of Maia and Matosinhos, in the region of Oporto, in Portugal. Data will be used as baseline levels for the assessment of the potential impact of the operation of a MSW incinerator.

PCDD/PCDF levels measured in the atmosphere of the region of Oporto were relatively high with an average value above 200 fg/m³ I-TEQ revealing the presence of important pollutant sources. In spite of this fact, no evidence of a measurable influence on the concentrations of these organic compounds on human blood and breast milk has been found. Similar conclusions have been found by other authors⁷.

Acknowledgements

The authors want to express their gratitude to all participants and local general practitioners, as well as to "LIPOR - Sistema Intermunicipal de Tratamento de Lixos da Região do Porto" for the promotion and support of the External Monitoring Program.

References

1. Coutinho, M., Conceição, M., Borrego, C. and Nunes, M., *Atmospheric impact assessment and monitoring of dioxin emissions of municipal solid waste incinerators in Portugal*, Chemosphere, Vol. 37, 2119-2126, 1998.
2. Coutinho, M., Bóia, C., Borrego, C., Mata, P., Costa, J., Rodrigues, R., Gomes, P. and Neves, M., *Environmental Baseline Levels of Dioxins and Furans in the region of Oporto*, Organohalogen Compounds, Vol. 43, 131-136, 1999.
3. Coutinho M., Ferreira J., Gomes P. and Borrego C.; *Atmospheric levels of PCDD/PCDF during the test phase of a municipal solid waste incinerator, in Portugal*, Organohalogen Compounds, 46, 447-450, 2000.
4. Papke O., Herrmann Th. and Schilling B.; *PCDD/Fs in humans, follow up of background data for Germany, 1998/9*, Organohalogen Compounds, 44, 221-224, 1999.
5. Schecter A. and Papke O.; *Dioxin levels in milk and blood from Germany and the USA. Are dioxin blood levels decreasing in both countries?*, Organohalogen Compounds, 48, 68-71, 2000.
6. Nakamura Y., Matsuura N., Kondo N. And Tada Y.; *Polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, and coplanar polychlorinated biphenyls in breast milk in Japan*, Organohalogen Compounds, 48, 1-4, 2000.
7. Dolgner R., Ranft U., Abel J. and Vogel C.; *A comparison of polychlorinated dibenzodioxins and dibenzofurans concentration patterns in outdoor air and human blood*, Organohalogen Compounds, 30, 76-79, 1996.