LESSONS LEARNED ON PERFORMING MORE THAN 15,000 DIOXIN ANALYSES

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Introduction

A demand for dioxin analyses in 1984 in Hamburg lead to the development of the ERGO department "Ultra Trace Analysis". Due to high 2,3,7,8-TCDD concentration found in oil effluents from a dumpsite in Hamburg and due to the lack of analytical possibilities of responsible authorities in Hamburg, we developed methods to move into the dioxin field . ERGO started with only one customer from Hamburg - the Environmental Agency - and less than 100 dioxin analyses in the first year. Meanwhile we have analysed more than 5 000 human samples and more than 10 000 non human samples like environmental, ambient air, stack gas, food and feeding stuff samples for PCDDs/PCDFs.

In the following, some results of our analytical work is presented and compared with data published by different groups. In this paper priority will be given to the field of human exposure.

Human exposure

The most important route for human exposure to dioxins is food consumption, contributing > 95 % of total exposure, with products of animal origin making the greatest contribution of this exposure. This kind of uptake of dioxins by the human body results in the background.

In the early years of dioxin analysis in human tissues, adipose tissue was used almost exclusively for exposure estimation. Due to of the low lipid content of blood it was not possible to analyze blood with only background contamination. Improvements in sensitivity of analytical equipment opened the path to analyse human blood. Patterson et al. /1/ demonstrated the good correlation of 2,3,7,8-TCDD between serum and adipose tissue. This result was found by analyzing serum and adipose samples from 50 individuals. For other PCDD/F congeners Schecter at al. /2/ showed good correlation between the concentration in whole blood and adipose tissue originating from the same persons.

Beck et al. /3/ and Fürst et al. /4/ reported the first background data for adipose tissue and for human milk respectively for Germany. The first data for human blood where reported in 1989 by our group /5/. In table 1 PCDD/F background contamination of human blood from Germany, is summarised.

Table 1: Time trend of PCDD/F background contamination in human blood, Germany

Year of collect-ion	n	I-TEQ, mean values in pg/g lipid based	Reference	Year of collect-ion	n	I-TEQ, mean values in pg/g lipid based	Reference
1988	10	45,8	Päpke et al. 5	1993	70	21,7	Päpke et al. 10
1989-90	102	40,8	Päpke et al. 6	1994	134	19,1	Päpke et al. 11
1991	56	44,4	Kieselrotst. 7	1996	180	16,5	Päpke et al. 12
1991+	94*	42,7	Schrey et al. 8	1998	55	14,7	Päpke et al. 13
1992	44	26,0	Päpke et al. 9	1999	43	15,3	Päpke et al. 13

* includes 56 persons from Kieselrot study

A time trend for PCDD/Fs in humans was first observed in German mothers milk by Fürst at al. /14/ in 1992. This time trend is shown for blood in table 1 as well. Between the end of the 1980s and 1999 the decline of PCDD/Fs was shown to be more than 70 %. These results indicate that efforts to reduce emissions in the industry have notable effects. For example, the dominating number of stack gas measurements performed for Waste Incinerators were found by us in the early 1980s in the range of low ng/m^3, in some cases much higher. The introduction of an emission limit value at 0,1 ng/m^3 for Waste Incinerators lead to much lower emission rates. Meanwhile all incinerators fulfil these emission requirements in Germany. A number of measurements documented that values of 0,01 or even 0,001 ng/m^3 are possible.

Looking at background data for PCDD/Fs and the dioxin-like (coplanar) PCBs from other countries – presented in table 2 - it is quite surprising that a wide range of exposure can be observed for the population of different countries. In countries of low industrialisation like Albania and Pakistan - at the end of the table - quite low PCDD/F and PCB levels are observed. The populations of highly industrialised countries show higher concentrations. The highest values in this "ranking list" are found for Inuit from North Quebec and from Greenland. As can be seen here, for Greenland Inuit dioxin levels are 10 to 20 times higher compared to levels of the population of industrialised countries. The reason for this surprisingly high exposure has to be expected in the specific consumption habits.

Due to a great number of occupational exposure situations in the chlorine industry a demand for dioxins analyses of human tissue - especially blood - has to be met by qualified laboratories worldwide. A further need for analyses concurred in connection with certain incidents or in connection of consequences on involved humans of these incidents. Important incidents of questions happened at Monsanto (1949), BASF (1953), Bayer (1954), Dow Chemical (1964), Rhone Poulenc (1994) and the Chemiewerke Linz (1997).

The most important incident resulting trough the explosion of a reactor vessel at the Icmesa plant in Seveso, Italy, happened in 1976. An amount of 0,5 –1 kg of 2,3,7,8-TCDD was distributed in the vicinity of Seveso. Some thousand residents have been treated by this incident, of whom about 200 have been diagnosed as having chloracne. Beside the enormous consequences resulting after the accident of Seveso the knowledge on consequences of dioxins on humans increased considerably.

When analyzing blood samples from 3 groups of different exposure with no, moderate and severe chloracne, Mocarelli et al. /15/ found in the group with severe chloracne the highest value ever found for 2,3,7,8-TCDD in human blood till 1998: 56 000 pg/g lipid.

In early 1998, two blood samples originating from 2 females with diagnosed chloracne were analysed in our laboratory. The values found were unexpected high at 26 000 and 144 000 pg 2,3,7,8-TCDD/g lipid /16,17/. The source of TCDD and the route of exposure have not yet been identified. After having knowledge of these incident certain measures followed with respect to therapy for the patients. We learned that in early stage of elimination the half live for TCDD was - instead of about 7 years as expected - observed at less than one year for both patents. Further information gained are the possibility of increase of fecal excretion of TCDD by application of Olestra (a non absorbable dietary fat substitut), the percutanous desorption/18/, the good correlation for TCDD between different tissues at high levels and others. We will try to continue our work under the aspect to provide best support for the patients within our possibilities.

Analyses to avoid human exposure

Due to two contamination incidents, thousands of dioxin analyses have been performed in many laboratories world wide during the last tree years. Both incidents are to be seen in connection with contaminated feeding material from Brazil and from Belgium respectively.

The Brazilian incident had its origin in contaminated Citrus Pulp Pellets (CPP) used in feeding material for cattle management. The contamination was discovered by Malisch et al. /19/ when they found in cows milk unexpected high dioxin levels. As a result of the findings of high dioxin concentrations in cattle feed, the European Union closed temporarily the market for Brazilian CPP.

Table 2: **Recent Background Contamination for PCDD/Fs (D/F) and coplaner PCBs of Humans Worldwide, Values in pg/g, lipid based**

Country	Area	Matrix	Sampling-year	n	Pool/ Single	Age	TEQ			Author	Ref
							DF	Coplanar PCBs	DF / co-planar PCBs		
Greenland		A		30	s		332	290	622	Ryan et al, 1996	20
Canada	Nunavik	B	1992	499	p(20)		39.6	26.3	65.9	Ayotte P. et al, 1997	21
Japan	Fukuoka	A		36	s	56	31.1	27.3	58.4	Hirakawa et al, 1994	22
Japan	Fukuoka	B	1996	4	p	40-46	29	11	40	Matsueda et al, 1996	23
USA		B	1995/96	44	p		27	2	29	Schecter A. et al, 1996	24
Russia	Irkutsk	A	1997	5	s	35-72	26	22	48	Mamontova et al, 1998	25
Belgium		M	1993	34	p(8/20/6)		24.8	3.2	28	Liem D. et al, 1996	26
Netherlands		M	1993	103	s		23.5	8.8	32.3	Liem D. et al, 1995	26
Spain		M	1993	29	p(19/10)		22.5	5.3	27.8	Liem D. et al, 1996	26
Sveden		B		5	s	63	21	13	34	Rappe C. et al, 1994	27
Slovak Rep.		B	1993	30	s	21-52	20			Kocan A. et al, 1996	28
Finland	Urban	M	1992/94	14	s		19.9			Kiviranta H. et al, 1998	29
Russia	Irkutsk	A	1997	5	s	28-69	19.2	22.9	42.1	Mamontova et al, 1998	25
USA	Ohio	B		16	s	<20-+60	19.1			Tepper A. et al, 1997	30
Korea	Western	A	1994/95	32	s	53	18			Kang Y-S et al, 1997	31
Estonia		M	1991	6	p		17.5			Mussalo R. et al, 1995	32
Palestine		B	1996	20	p		16.9			Schecter A. et al, 1997	33
Finland		M	1993	34	p(10/24)		16.8	1.5	18.3	Liem D. et al, 1996	26
Denmark		M	1993/94	10	s		16.7	6.2	22.9	Hilbert G. et al, 1996	34
Germany		M	1993	10	s		16.6	9	25.6	Liem D. et al, 1996	26
United Kingd.		M	1993	43	p(20/23)		16.6	2.6	19.2	Liem D. et al, 1996	26
Russia	Kola	M	1993	30	s	24	15.5			Polder A. et al, 1996	35
Czech Rep.		M	1993	22	p(11/11)		15.3	3.3	18.6	Liem D. et al, 1996	26
Germany		B	1999	43	s	44	15.3			Päpke O. et al, 1999	13
Denmark		M	1993	48	s		15.2	2.3	17.5	Liem D. et al, 1996	26
Lithuania		M	1993	36	p(12/12/12)		14.8	12.4	27.2	Liem D. et al, 1996	26
Canada		M	1993	100	s		14.6	3.8	18.4	Liem D. et al, 1996	26
Canada	S-Quebec	B	1992	15	p(3)	30	14.6	5.2	19.8	Ayotte P. et al, 1997	21
Slovak		M	1993	20	p(10/10)		13.9	5	18.9	Liem D. et al, 1996	26
Finland	Rural	M	1992/94	28	s		13.6			Kiviranta H. et al, 1998	29
New Zealand		B		10	s	30-39	13.1			Hannah D. et al, 1994	36
Israel		B	1996	100	p		13.1			Schecter A. et al, 1997	33
Ukraine		M	1993	10	p(5/5)		12.2	7.6	19.8	Liem D. et al, 1996	26
Korea		B	1996	16	s		12	1.9	13.9	Kang D. et al, 1997	37
Croatia		M	1993	23	p(10/13)		11	4.5	15.5	Liem D. et al, 1996	26
Austria		M	1993	34	p(13/21)		10.8	8.9	19.7	Liem D. et al, 1996	26
Norway		M	1993	30	p(10/10/10)		10.6	10.1	20.7	Liem D. et al, 1996	26
Palestine Gaza		B	1996	39	p		8.4			Schecter A. et al, 1997	33
Hungary		M	1993	30	p(20/10)		8.2	0.9	9.1	Liem D. et al, 1996	26
Spain	Madrid	B	1993	11	s	19-55	7	22.7	29.7	Jiménez et al, 1996	38
Albania		M	1993	20	p(10/10)		4.3	1.2	5.5	Liem D. et al, 1996	26
Pakistan		M	1993	14	s		3.9	1.9	5.8	Liem D. et al, 1996	26

A = adipose
B = blood
p = pool
M = milk
n = number of samples
s = single analysis

Additionally, the EU established a limiting value for CPP at 500 pg/kg. The contamination of the CPP resulted for the Brazilian citrus industry in high economic losses.

The second event - the Belgian feed poisoning - was a problem at a much higher extent. In early 1999 highly contaminated Belgian feeding stuff was distributed to farms - mainly in Belgium - and mainly fed to chicken. On a certain extent, it was fed to other animals as well. First dioxin analyses of chicken meat and eggs resulted at high values of 600 to 900 pg I-TEQ/g lipid. In a few months we had to analyze more than thousand food and feeding stuff samples. Surprisingly only less than 10 samples out of thousand were found to be elevated when compared to given preliminary action values for dioxins in food.

After the Belgian incident and the resulting remarkable losses for the Belgian economy it is our impression that higher input is given to archive food and feed free of contamination.

Looking at the results of the incidents described above it has to be learned that a higher level of attention is essential to archive a further decline of human background contamination.

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