NEW FINDINGS OF DIOXINS, DIBENZOFURANS, PCBS, DDT/DDE, HCB, AND HCH IN FOOD FROM A VIETNAM TCDD CONTAMINATED AREA AND ACOMPARISON AREA

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Introduction

Joint Vietnamese-American research on TCDD and other dioxins began in 1970 measuring human tissue and food levels and continues to the present time ¹⁻⁷. Initial findings in the 1970s found extremely high 2,3,7,8-TCDD in human milk, up to 1,850 ppt lipid, and over 800 ppt in fish on a whole weight, not lipid, basis¹⁻². This research was resumed in 1982 and over 3,200 persons were studied for dioxin, dibenzofuran and PCB levels³⁻⁵ There were almost uniformly low dioxin levels in the north of Vietnam where Agent Orange defoliant, contaminated with TCDD, was not sprayed during the Vietnam war. Large amounts, however, were sprayed over 10 to 20 % of the south of Vietnam from 1962-1971. We found areas with higher and lower levels of TCDD from Agent Orange, and higher chlorinated dioxins from different sources. One area was found with very elevated TCDD levels in blood, with a high of over 400 parts per trillion (ppt) and 95 % of those sampled had elevated blood TCDD⁶. We also found over 1 million ppt TCDD in the highest soil sample, and elevated TCDD in the sediment in a stream. This city was Bien Hoa, 35 km north of Ho Chi Minh City, with a population of 390,000⁶⁻⁷. We did not previously obtain food from this area. We report here dioxin levels in recently collected food from this area and others, as well as levels of other orghanochlorine chemicals.

Methods and Materials

Food was collected in Vietnam by one of us (HTQ) in dioxin contaminated lake and from markets around Bien Hoa City. Specimens were frozen after the collection and shipped to Germany on dry ice. Analytical methods were described elsewhere and are referenced here⁸. The usual cleanup and separation for dioxins and the other chemicals was performed. High resolution gas chromatography high resolution mass spectroscopy was employed. The amount of lipid was determined gravimetrically. Additional samples were collected in Ho Chi Minh City and Hanoi, where we expect intermediate or high, and low dioxin levels, respectively.

Results and Discussion

Results are shown in Tables 1 and 2 for dioxins, dibenzofurans, PCBs, HCH, hexachlorobenzene, DDT, DDD, and DDE. Elevated 2,3,7,8-TCDD can be noted in four out of seven food samples in Table 1. Fish 1 and the toad sample had TCDD levels of 65 and 56 ppt, respectively. Both free-range duck samples were very elevated, 276 and 331 ppt wet weight. All samples came from the contaminated Bien Hung Lake area or a nearby market.

Table 1. Dioxin, dibenzofuran, PCBs, and other organochlorines in food samples from Bien Hoa

 City, Vietnam (pg/g or ppt wet weight).

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	Fish 1	Fish 2	Fish 3	Fish 4	Duck 1	Duck 2	Toad
Fat content %:	0.43	1.1	41	4.0	52	64	0.68
2.3.7.8-TCDD	65	0.13	0.22	0.062	276	331	56
1.2.3.7.8-PnCDD	0.80	0.011	0.24	0.028	6.4	7.4	9.3
1.2.3.4.7.8-HxCDD	0.098	n.d.(0.01)	0.10	0.021	1.0	1.1	9.4
1.2.3.6.7.8-HxCDD	0.27	n.d.(0.008)	0.28	0.044	1.9	2.2	39
1.2.3.7.8.9-HxCDD	0.079	n.d.(0.007)	0.11	0.016	0.43	0.48	1.6
1.2.3.4.6.7.8-HpCDD	0.59	n.d.(0.03)	0.37	0.079	2.7	3.0	19
OCDD	0.96	n.d.(0.2)	0.47	n.d.(0.2)	3.7	4.1	13
2.3.7.8-TCDF	0.60	0.044	1.2	0.47	17	21	0.083
1.2.3.7.8-PnCDF	0.057	n.d.(0.004)	0.35	0.095	0.48	0.56	0.17
2.3.4.7.8-PnCDF	0.093	0.0077	0.24	0.053	0.90	1.1	5.2
1.2.3.4.7.8-HxCDF	0.072	n.d.(0.005)	0.17	0.029	1.2	1.5	8.8
1.2.3.6.7.8-HxCDF	0.022	n.d.(0.004)	0.092	0.0090	0.49	0.47	2.1
1.2.3.7.8.9-HxCDF	n.d.(0.01)	n.d.(0.008)	n.d.(0.02)			0.056	0.11
2.3.4.6.7.8-HxCDF	0.014	n.d.(0.007)	0.036	n.d.(0.01)		0.16	0.91
1.2.3.4.6.7.8-HpCDF	0.016	0.017	n.d.(0.04)	n.d.(0.02)	0.53	0.43	0.62
1.2.3.4.7.8.9-HpCDF	n.d.(0.01)	n.d.(0.001)	n.d.(0.03)	n.d.(0.01)	0.21	0.25	0.089
OCDF	n.d.(0.04)	0.098	n.d.(0.06)	n.d.(0.02)	0.23	0.19	0.27
PCB 81	0.16	0.078	0.71	0.13	2.0	2.3	3.0
PCB 77	2.7	2.0	12	n.d.(1)	53	58	2.1
PCB 126	2.7	0.25	3.7	0.32	9.5	11	51
PCB 169	0.25	n.d.(0.05)	1.3	0.079	1.6	1.8	6.6
PCB 105	143	14	116	28	397	490	310
PCB 114	7.6	n.d.(0.5)	n.d.(8)	2.1	n.d.(17)	n.d.(12)	33
PCB 118	261	28	306	91	912	967	4023
PCB 156	54	3.7	36	7.6	156	161	1005
PCB 157	14	n.d.(0.8)	n.d.(15)	n.d.(1)	57	22	295
PCB 167	20	1.9	22	4.1	70	47	617
PCB 189	4.5	n.d.(1)	n.d.(18)	n.d.(2)	n.d.(21)	n.d.(17)	146
TEQ PCDD/PCDF	66	0.16	0.81	0.18	285	341	74
TEQ non-ortho PCB	0.28	0.026	0.38	0.033	0.97	1.1	5.2
TEQ mono-ortho	0.079	0.0068	0.074	0.017	0.25	0.25	1.1
SUM TEQ	66	0.19	1.3	0.23	286	343	80
α-НСН	2.3	11	78	6.0	8.7	28	2.4
β-НСН	3.0	4.7	114	9.7	351	418	87
γ-НСН	3.3	5.6	46	0.76	25	64	5.3
Hexachlorbenzene	563	n.d.(32)	231	n.d.(4)	1145	1391	129
pp'-DDD	358	338	2596	403	4322	5605	969
op'-DDT	1.9	9.8	233	69	42	48	36
pp'-DDT	179	118	2368	709	23468	26823	6115
pp'-DDE	4989	305	8141	613	55342	68099	8003
n d = non-detected limit of	datastian in t	a hraaltata					

n.d. - non-detected, limit of detection in the brackets.

Table 2. Dioxin, dibenzofuran, PCBs, and other organochlorines in food samples from Bien Hoa City, Vietnam (pg/g or ppt wet weight).

	Pork 1	Pork 2	Beef 1	Beef 2	Chicken 1	Chicken 2	Chicken 3
Fat content %:	52	64	3.3	12	65	29	37
2.3.7.8-TCDD	0.86	0.025	0.082	0.082	15	0.031	0.034
1.2.3.7.8-PnCDD	n.d.(0.02)	0.049	0.0060	0.039	8.5	0.088	0.055
1.2.3.4.7.8-HxCDD	n.d.(0.02)	0.14	0.0029	0.013	8.2	0.14	0.056
1.2.3.6.7.8-HxCDD	n.d.(0.01)	0.19	0.0067	0.058	38	0.35	0.19
1.2.3.7.8.9-HxCDD	n.d.(0.01)	0.027	0.0037	0.021	4.7	0.12	0.038
1.2.3.4.6.7.8-HpCDD	0.068	0.78	0.023	0.093	63	0.56	1.1
OCDD	0.39	1.1	0.10	0.55	122	0.38	2.6
2.3.7.8-TCDF	0.078	n.d.(0.05)	0.012	0.016	4.7	0.21	0.084
1.2.3.7.8-PnCDF	n.d.(0.01)	n.d.(0.02)	0.0035	0.0072	4.6	0.32	0.045
2.3.4.7.8-PnCDF	0.018	0.11	0.0062	0.034	4.4	0.16	0.039
1.2.3.4.7.8-HxCDF	0.018	1.8	0.0051	0.020	5.7	1.9	0.069
1.2.3.6.7.8-HxCDF	n.d.(0.01)	0.60	0.0026	0.012	2.5	0.98	0.038
1.2.3.7.8.9-HxCDF	n.d.(0.02)	n.d.(0.03)	n.d.(0.001)	n.d.(0.005)	0.32	0.12	n.d.(0.02)
2.3.4.6.7.8-HxCDF	n.d.(0.02)	0.068	n.d.(0.004)	n.d.(0.006)		0.18	n.d.(0.05)
1.2.3.4.6.7.8-HpCDF	n.d.(0.04)	2.5	0.012	0.033	3.5	1.5	0.13
1.2.3.4.7.8.9-HpCDF	n.d.(0.02)	1.1	n.d.(0.001)	n.d.(0.007)	0.34	0.99	n.d.(0.02)
OCDF	n.d.(0.06)	0.93	0.0099	0.039	1.5	1.00	0.11
PCB 81	n.d.(0.1)	n.d.(0.2)	n.d.(0.02)	n.d.(0.06)	19	n.d.(0.4)	n.d.(0.3)
PCB 77	n.d.(5)	n.d.(5)	n.d.(0.6)	n.d.(1)	145	n.d.(10)	n.d.(9)
PCB 126	n.d.(0.9)	n.d.(0.9)	n.d.(0.10)	0.40	108	n.d.(2)	n.d.(1)
PCB 169	0.15	0.34	0.027	0.15	8.2	n.d.(0.2)	n.d.(0.2)
PCB 105	100	92	n.d.(6)	n.d.(13)	7189	n.d.(50)	n.d.(75)
PCB 114	n.d.(13)	n.d.(11)	n.d.(1.0)	n.d.(2)	318	n.d.(4)	n.d.(9)
PCB 118	369	176	17	n.d.(38)	14182	n.d.(154)	n.d.(192)
PCB 156	113	n.d.(5)	2.3	n.d.(1)	2461	9.9	10
PCB 157	24	n.d.(18)	n.d.(0.9)	n.d.(3)	603	n.d.(5)	n.d.(7)
PCB 167	51	26	n.d.(0.3)	n.d.(0.8)	1076	n.d.(5)	9.4
PCB 189	30	n.d.(18)	n.d.(1)	n.d.(6)	176	n.d.(10)	n.d.(11)
TEQ PCDD/PCDF	0.91	0.46	0.095	0.16	33	0.64	0.18
TEQ non-ortho PCB		0.096	0.010	0.042	11	0.16	0.13
TEQ mono-ortho	0.13	0.046	0.0045	0.0088	3.9	0.031	0.041
SUM TEQ	1.1	0.60	0.11	0.21	48	0.83	0.35
α-НСН	29	32	38	20	48	129	91
β-НСН	78	98	69	14	846	202	139
ү-НСН	39	40	20	20	25	215	115
Hexachlorbenzene		n.d.(1001)		n.d.(165)	n.d.(687)		n.d.(1537)
pp'-DDD	384	507	163	105	6513	103	1112
op'-DDT	67	97	4.4	20	629	13	536
pp'-DDT	762	1717	46	71	44722	336	4203
pp'-DDE	867	1261	575	643	149409	565	1303

n.d. - non-detected, limit of detection in the brackets.

Table 2 presents results for pork, beef, and chicken samples. Elevated TCDD level of 15 ppt wet weight was found in Chicken 1 sample but other chicken samples, and pork and beef samples show no elevation in TCDD levels. Fish 3, Chicken 3, beef 1, and pork 1 were purchased at Bien Hoa City market. Mono-ortho PCBs 105 and 118 in particular, but also 156 and 167, were elevated in all samples with elevated TCDD but also, to a lesser degree, in some food samples with no elevation of TCDD (fish 3-4, pork 1-2). As expected, levels of DDT and its metabolites were elevated in all samples.

At least some of the sources of extremely elevated blood TCDD in residents of Bien Hoa have been identified. Food of animal origin, including fish, ducks, chickens, and toad or frog probably constitutes the major source of elevated TCDD in the residents of Bien Hoa City. It is remarkable that between 30 and 40 years after spraying ended, humans and their food are still contaminated with this persistent dioxin. Avoiding eating contaminated food seems the best method of keeping body burden of TCDD low in these contaminated areas. The elevated PCBs, of unknown origin, can also be avoided by diet restrictions. Further study of food and human organochlorine contamination including dioxins and PCBs in Vietnam seems indicated. The source of the PCBs found here is not known to us. DDT usage was for mosquito control, to prevent malaria and other mosquito borne diseases.

Acknowledgements

We wish to thank the funding agencies, the CS Fund, the Kundstadter Family Foundation, the Samuel Rubin Foundation, and the Zumwalt Foundation.

References:

- 1. Baughman, R.W., and Messelson, M. (1973) An analytic method for detecting TCDD (dioxin) levels of TCDD in samples from Vietnam. Environ. Health Perspect. 9:27-35.
- 2. Baughman, R.W. (1974) Tetrachlorodibenzo-p-dioxins in the environment: high-resolution mass spectrometry at the picogram level. Dissertation. Boston: Harvard University.
- 3. Schecter, A.J., Ryan, J.J. and Constable, J.D. (1986) Chlorinated dibenzo-p-dioxin and dibenzofuran levels in human adipose tissue and milk samples from the North and South of Vietnam. Chemosphere 15(9-12): 1613-1620.
- 4. Schecter, A.J., Ryan, J.J. and Constable, J.D. (1987) Polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran levels in human breast milk from Vietnam compared with cow's milk and human breast milk from the North American continent. Chemosphere 16(8-9): 2003-2016.
- Schecter, A.J., Dai, L.C., Thuy, L.T.B., Quynh, H.T., Minh, D.Q., Cau, H.D., Phiet, P.H., Phuong, N.T., Constable, J.D., Baughman, R., Päpke, O., Ryan, J.J., Fürst, P., and Raisanen, S. (1995) Agent Orange and the Vietnamese: the persistence of elevated dioxin levels in human tissues. Am. J. Public Health 85:516-522.
- Schecter, A., Dai, L.C., Päpke, O., Prange, J., Constable, J.D., Matsuda, M., Thao, V.D., and Piskac, A.L. (2001) Recent dioxin contamination from Agent Orange in residents of a southern Vietnam city. J. Occup. Environ. Med. 43:435-443.
- Schecter, A., Pavuk, M., Constable, J.D., Dai, L.C., and Päpke, O. (2002) A follow-up: high level of dioxin contamination in Vietnamese from Agent Orange, three decades after the end of spraying. Letter. J. Occup. Environ. Med. 44:218-220.
- Ball, M., Päpke, O., Lis, Z. A., and Scheunert, K. (1989) PCDD and PCDF in mice from various environments. Chemosphere 18:759–765.