TRENDS IN DIOXIN AND PCB CONCENTRATIONS IN MEAT SAMPLES FROM SEVERAL DECADES OF THE 20TH CENTURY

Dwain L. Winters[a], Susan Anderson[b], Matthew Lorber[c], Joseph Ferrario[d], Christian Byrne[d]

[a]Office of Prevention, Pesticides, and Toxic Substances, US EPA, 401 M St., SW, Washington, DC 20460; [b] Versar, Inc., 6850 Versar Center, Springfield, VA, 22151; [c]National Center for Environmental Assessment (8623D), US EPA, 401 M St., SW, Washington, DC 20460; Environmental Chemistry Lab, US EPA, John C. Stennis Space Center, MS 39529

INTRODUCTION

Data from several studies suggest that concentrations of dioxins rose in the environment from the 1930s to about the 1960s/70s and have been declining over the last decade or two. The most direct evidence of this trend is lake core sediments, with some other evidence from older vegetation, soil, and sludge samples[1,2,3,4,5]. It has been generally assumed, but not empirically demonstrated, that dioxin levels in the human diet follow the same general pattern. Pinsky and Lorber[6] investigated this possibility using body burden data for 2,3,7,8-TCDD from the 1970s, 80s, and 90s, combined with simple first-order, single-compartment pharmacokinetic modeling. Using a Bayesian statistical approach, they back-calculated doses of 2,3,7,8-TCDD through the 20th century. Their best-fit 2,3,7,8-TCDD temporal dose regime showed low doses at the beginning of the century, rising to a peak in the late 1960s and early 1970s, and then dropping to current doses. Their predicted peak dose of 2,3,7,8-TCDD was up to an order of magnitude higher than current doses.

The study of this paper takes this general investigation one step further. Exposures to dioxin occur primarily through food consumption, and in particular, through animal fat consumption. If exposure was higher in earlier decades of the 20th century, it should be reflected in higher animal fat concentrations of these compounds. Fourteen preserved meat samples from various decades of the 20th century were obtained and analyzed for the 17 2,3,7,8- substituted dioxin and furan congeners, as well as for 7 dioxin-like coplanar PCBs. This paper examines trends from the analysis of these 14 samples.

DESCRIPTION OF SAMPLES

Sample collection was conducted through inquiries to a broad range of government and historical institutions that might have preserved food products. Samples from the second half of the century were most readily available, while the accumulation of product samples from the early part of the century relied on incidental discoveries. A total of 14 samples, spanning 80 years, were found for this effort. The food types examined included three poultry, one dairy, five pork, three beef, one mixture of beef and ground wheat, and one mixture of beef and pork.

Samples were provided by the U.S. military, a U.S. government research facility, a museum, the U.S. space program, and a private individual.

The earliest sample was a 1908 "Emergency Ration," which was the first official U.S. Army food ration. The ration consisted of a mixture of beef and cooked ground wheat, a dried chocolate powder component, and salt and pepper for seasoning. This ration, provided by the U.S. Army Quartermaster Museum, is one of the earliest examples of canning as a technique for food preservation. The 1945 beef and pork loaf was packaged in a can as a pre-cooked ready-to-eat "K Ration." The 1957 dried cream sample was contained in the "Accessory Pack" of a "C Ration." These ration samples were also provided by the U.S. Army.

Two 1968 pork samples, provided by the Smithsonian Institution, consisted of a commercially prepared can of deviled ham and a maritime survival pouch containing a pre-cooked, ready-to-eat bacon bar. These food samples were from supply packs taken on the expedition of the S.S. Manhattan, an icebreaking research vessel that attempted to cross the Northwest Passage to find a course for the transport of oil from Alaska to the East Coast of the United States.

The National Aeronautics and Space Administration (NASA) Johnson Space Center supplied two 1971 beef slices and bacon wafer samples. These products were pre-cooked and dried; sealed in cans; and used in the space program. Two 1977 chicken samples were provided by the United States Department of Agriculture (USDA) Russell Research Laboratory. These samples were from a research study examining the quality and nutritional performance of chicken (both cooked and uncooked) packaged in retort pouches. A private individual supplied the 1979 "C-Ration" containing pork slices with juice from her personal storage.

Four samples were obtained from the early 1980's. One, from 1980, was a canned military "C Rations" containing precooked beef steak with gravy from the Quartermaster Museum. A 1982 pre-cooked heat processed and thermostabilized ham slice packaged in a retort pouch was prepared for the space program. Finally, the Quartermaster Museum supplied two "Meals-Ready-to-Eat"; one with beef slices in barbecue sauce, and one with diced turkey with gravy, from 1983. These samples were packaged in foil pouches, pre-cooked, and freeze-dehydrated.

RESULTS

All samples were analyzed using a procedure that extracted the entire lipid content from each of the samples and then subjected the lipid to acid/base, alumina and carbon clean-up preparation prior to analysis by high resolution gas chromatography, high resolution mass spectrometry. Further details on the analytical methods and a listing of the analytical results for the 17 2,3,7,8–substituted dioxin and furan congeners, and 7 coplanar PCBs, can be found in a companion paper also presented at this conference.[7]

The data were evaluated by comparing the concentration in historic samples to current dioxin concentrations derived from the national food surveys for beef[8,9], pork[10], poultry[11], and milk[12] conducted by EPA. All the surveys were conducted after 1993, and their principal objective was to determine the national average concentration of the dioxin-like compounds in the lipids of these animal fat products. The lipid-adjusted concentrations were converted to the 2,3,7,8-TCDD TEQ using the International-Toxic Equivalence Factor (I-TEFs) scheme[13] for PCDD/Fs and the WHO recommendations for coplanar PCBs[14]. National mean TEQ concentrations from these surveys are shown in Table 1.

Table 2 shows the PCDD/F and PCB TEQ concentrations of the 14 samples. It also shows TEQ concentrations normalized and expressed as a percent of current concentrations for the most similar food type. For example, the 1908 beef ration percentage of 38% means that the 0.34 pg TEQ/g lipid PCDD/F (calculated at ND = ½ LOD) is 38% of the current beef concentration of 0.89 pg TEQ/g lipid (calculated at ND = ½ LOD), which is from the recent national EPA beef survey[8].

The 14 samples analyzed represent a very limited data base and should not be assumed to necessarily be representative of these food types or for their respective time period. It is, however, noteworthy that all 10 samples from 1957 to 1982 were higher in PCDD/F TEQ than the current mean concentrations (at ND = ½ LOD) and that 12 of the 13 samples taken from 1945 through 1983 were higher for PCB TEQ. If the samples are indicative of past concentrations of dioxin-like compounds, normalized TEQ suggests PCDD/F 2-3 times higher during the period of peak environmental loading while PCB TEQ may have been over 10 times current concentrations. EPA plans to continue analyzing historic meat and dairy products as additional samples become available.

REFERENCES

(1) Kjeller, L; Rappe, C. *Environ. Sci. Technol.* **1995**, 29, 346-365.

(2) Kjeller, L; Jones, K; Johnston, A; Rappe, C. *Environ. Sci. Technol.* **1991**, 25, 1619-1627.

(3) Alcock, R.E.; Jones, K.C. *Environ. Sci. Technol.* **1996**, 30, 3133-3143.

(4) Cleverly, D.; Monetti, M; Phillips, L; Cramer, P.; Heit, M.; McCarthy, S.; O'Rourke, K; Stanley, J; Winters, D. *Organohalogen Compounds* **1996**, 28, 77-82.

(5) Beurskens, J; Mol, G; Barreveld, H.L.; Van Munster, B; Winkels, H. *Environ. Tox. and Chem.* **1990**, 12, 1549-1566.

(6) Pinsky, P.F.; Lorber, M.N.; *J. Exp. Anal. and Environ. Epid.* **1998**, 8, 187-206.

(7) Ferrario, J.F; Byrne, C.; Dupuy, A.; Winters, D.L.; Lorber, M.; Anderson, S. Analytical method and results from the analyses of USEPA historical food samples for dibenzo-p-dioxins/-furans/coplanar PCBs. **1998.** This conference.

(8) Winters, D.; Cleverly, D.; Meier, K.; Dupuy, A.; Byrne, C.; Deyrup, C.; Ellis, R.; Ferrario, J.; Harless, R.; Leese, W.; Lorber, M.; McDaniel, D.; Schaum, J.; Walcott, J. *Chemosphere*, **1996**, 32(3), 469-478.

(9) Winters, D.; Cleverly, D.; Lorber, M.; Meier, K.; Dupuy, A.; Byrne, C.; Deyrup, C.; Ellis, R.; Ferrario, J.; Leese, W.; Schaum, J.; Walcott, J. *Organohalogen Compounds*, **1996**, 27, 386-390.

(10) Lorber, M.; Saunders, P.; Ferrario, J.; Leese, W.; Winters, D.; Cleverly, D.; Schaum, J.; Deyrup, C.; Ellis, R.; Walcott, J.; Dupuy, A; Byrne, C.; McDaniel, D. *Organohalogen Compounds*, **1997**, 32, 238-244.

(11) Ferrario, J.; Byrne, C.; Lorber, M.; Saunders, P.;Leese, W.; Dupuy, A.; Winters, D.; Cleverly, D.; Schaum, J; Pinsky, P.; Deyrup, C.; Ellis, R.; Walcott, J. *Organohalogen Compounds*, **1997**, 32, 245-251.

(12) Lorber, M.N., Winters, D.W.; Griggs, J.; Cook, R.; Baker, S.; Ferrario, J.; Byrne, C.; Dupuy, A.; Schaum, J. A national survey of dioxin-like compounds in the United States milk supply. **1998**. This conference.

(13) US EPA. Interim procedures for estimating risks associated with exposures to mixtures of chlorinated dibenzo--p-dioxins and -dibenzofurans (CDDS and CDFs) and the 1989

Update. Risk Assessment Forum, Washington, DC; EPA/625/3-89/016. **1989**.
(14) Ahlborg, U.G.; Becking, G.C.; Birnbaum, L.S.; Brouwer, A.; Derks, H.J.G.M; Feeley, M.; Golor, G.; Hanberg, A; Larsen, L.C.; Liem, A.K.D.; Safe, S.H.; Schlatter, C.; Waern, F.; Younes, M.;Yrjanheikki, E. *Chemosphere* **1994**, 28, 1049-1067.

Table 1. United States mean PCDD/F and PCB TEQ concentrations in beef, pork, poultry, and milk (results assume ND = ½ LOD; results calculated at ND = 0 shown in parenthesis).

Description	Beef[8,9]	Pork[10]	Poultry[11]	Milk[12]
PCDD/F, pg TEQ/g lipid	0.89 (0.35)	1.30 (0.46)	0.64 (0.41)	0.84 (0.84)
PCB, pg TEQ/g lipid	0.46 (0.46)	0.06 (0.06)	0.28 (0.28)	0.43 (0.43)

Table 2. PCDD/F and PCB TEQ concentrations and percent differences from current levels (results assume ND = ½ LOD; results calculated at ND = 0 shown in parenthesis).

Description	PCDD/F TEQ, pg/g lipid	PCB TEQ, pg/g lipid	Percent difference from current PCDD/F levels	Percent difference from current PCB levels
1908 beef ration	0.34 (0.15)	0.07 (0.07)	38 (42)	15 (15)
1945 beef and pork	0.98 (0.75)	0.36 (0.36)	89 (197)	140 (146)
1957 dried cream	2.05 (0.81)	3.56 (3.54)	244 (96)	827 (824)
1968 bacon bar	3.01 (2.94)	1.05 (1.05)	231 (638)	1747 (2620)
1968 deviled ham	3.73 (3.71)	0.61 (0.61)	287 (805)	1019 (1529)
1971 beef	1.36 (0.02)	2.48 (1.98)	153 (7)	540 (540)
1971 bacon wafer	1.75 (1.62)	1.98 (1.98)	135 (352)	3301 (4952)
1977 raw chicken	1.29 (1.18)	2.72 (2.72)	202 (287)	970 (970)
1977 cooked chicken	1.33 (1.20)	2.83 (2.83)	209 (292)	1009 (1009)
1979 pork slices	1.46 (1.20)	0.04 (0.04)	112 (262)	72 (105)
1980 beef steak	0.94 (0.73)	0.93 (0.93)	106 (207)	203 (203)
1982 ham slice	1.36 (1.04)	0.07 (0.07)	105 (227)	119 (178)
1983 beef in bbq	0.50 (0.03)	0.79 (0.79)	56 (8)	171 (171)
1983 turkey with gravy	0.55 (0.23)	0.32 (0.31)	85 (57)	113 (113)