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Chlorinated dibenzo-*p*-dioxins, dibenzofurans, and biphenyl profiles of workers with trichlorophenol and pentachlorophenol exposures

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ABSTRACT

We examined the serum lipid adjusted levels of 2,3,7,8-substituted chlorinated dioxins and furans, and four coplanar PCBs for 98 workers. We found workers who worked only in the trichlorophenol units had mean lipid adjusted 2,3,7,8-TCDD levels of 36.8 ppt significantly higher ($p < 0.05$) than 6.0 ppt in the reference group. Workers who worked only in the pentachlorophenol units had mean lipid adjusted levels for 123478-HxCDD of 14.8 ppt, 123678-HxCDD of 156.4 ppt,123789-HxCDD of 23.7 ppt, 1234678-HpCDD of 234.6 ppt, and OCDD of 2,778.2 ppt significantly higher ($p < 0.05$) than the reference group levels for the same congeners of 7.5, 71.8, 8.0, 67.5, and 483.2 ppt, respectively. While we did find 12378-PeCDD levels higher than the reference group in trichlorophenol and pentachlorophenol workers, the differences are small, and could be attributed to normal variation. All furan levels among the trichlorophenol or pentachlorophenol only workers were not significantly different than the reference group. Workers with both trichlorophenol and pentachlorophenol exposures had mean dioxin levels consistent with complex chlorophenol exposures. Tradesmen who worked throughout the plant had congener profiles consistent with both trichlorophenol and pentachlorophenol exposures. PCB 169, 23478-PeCDF, 123478-HxCDF, and 123678-HxCDF levels were also significantly greater ($p < 0.05$) in these tradesmen than in the reference group. We found distinct patterns of dioxin congeners many years after exposure among workers with different chlorophenol exposures. We were effectively able to distinguish past trichlorophenol exposures from pentachlorophenol exposures based on differing serum dioxin profiles among workers.

1. Introduction

Polychlorodibenzo-*p*-dioxins and polychlorodibenzofurans may be formed as unintended by-products in the production of 2,4,5-trichlorophenol (TCP) and pentachlorophenol (PCP). Studies of persons with significant TCP exposures find 2,3,7,8 tetrachlorodibenzo-*p*-dioxin (2378-TCDD) levels above background with some of these studies also reporting elevated 12378-PeCDD levels (Nygren et al., 1988; Beck et al., 1989; Papke et al., 1992; Piacitelli et al., 1992; Smith et al., 1992; Ott et al., 1993; Littorin et al., 1994; Flesch-Janys et al., 1996; Heederik et al., 1998; Ryan and Schecter, 2000). Persons exposed to PCP often have 123478-HxCDD, 123678-HxCDD, 123789-HxCDD, 1234678-HpCDD, and OCDD levels above background. Some studies also report higher 12378-PeCDD, 123478-HxCDF, and 1234678-HpCDF levels (Ryan et al., 1987; Papke et al., 1992; Littorin et al., 1994; Schecter et al., 1994; Flesch-Janys et al., 1996; Schecter et al., 1996; Coenraads et al., 1999).

We examined serum dioxin, furan, and PCB levels among former workers in production of TCP and PCP, and compared these levels with workers at the same plant without potential for workplace exposures. These chlorophenol workers have been studied previously in several epidemiology studies (Townsend et al., 1982; Bond et al., 1983; Bond et al., 1989; Bodner et al., 2003). The current study is unusual because workers may have been exposed to either or both TCP and PCP. Thus this study provides a rare opportunity to compare 2,3,7,8-substituted chlorinated dioxins and furans profiles among two types of chlorophenol workers. We will determine if the dioxin and furan profiles for our workers differ from previous studies of TCP and PCP workers, and how distinct the dioxin "fingerprints" are for these chlorophenols many years after workplace exposures have ceased.

2. Methods

We reported the design and the determinants of the dioxin levels for these workers and the impact of age and body fat on dioxin levels previously (Collins et al., 2006, 2007). In the present study,

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we now examine the dioxin and furan profiles by occupational exposure source. Briefly, a sample of men living within 50 miles of the Dow Chemical plant in Midland, Michigan who worked at the plant during chlorophenol production was included in the study. These workers had potential exposure to the chlorinated dioxins from production of TCP and PCP. Production occurred from 1937 to 1980 for PCP and 1942–1979 for TCP. We determined duration of time spent in either or both the TCP or PCP units based on detailed job histories available on all workers (Ott et al., 1987). Workers were then classified into one of 4 exposed groups: chlorophenol workers with only PCP exposure (26 workers), chlorophenol workers with only TCP exposures (12 workers) chlorophenol workers with both TCP and PCP exposures (14 workers), and tradesmen who had plant-wide exposures (10 workers). Tradesmen included workers with the job classifications of boilermaker, electrician, janitor, machinist, maintenance, millwright, painter, or pipe-fitter that had plant-wide responsibilities. We also collected blood from 36 workers employed in non-chlorophenol departments who had no documented workplace dioxin exposure to serve as referents for the exposed workers. We subsequently refer to these groups as PCP-only, TCP only, PCP and TCP, tradesmen, and the referents.

We collected serum at a company medical facility in September and October of 2004. Participants were instructed to eat a low fat meal on the day of the blood draw. Weight and height were measured to provide an estimate of body mass index (weight in kilograms divided by weight squared), and date of birth was taken from the work record. Approximately 80 mm of blood was collected in vacutainer tubes without anticoagulant or serum separator. Whole blood was allowed to clot for at least 20 min and then centrifuged for 15 min at 2500 rpm. The serum was transferred to rinsed glass vials with Teflon seals and stored at −20 °C until laboratory analysis.

We shipped the serum samples to Alta Analytical Laboratory, El Dorado Hills CA, USA. The analytical procedure determined the levels for 2,3,7,8-substituted dioxins (2378-TCDD, 12378-PeCDD, 123478-HxCDD, 123678-HxCDD,123789-HxCDD, 1234678-HpCDD, OCDD), furans (2378-TCDF, 12378-PeCDF, 23478- PeCDF, 123478-HxCDF, 123678-HxCDF, 234678-HxCDF, 123789-HxCDF, 1234678-HpCDF, 1234789-HxCDF, OCDF), and 4 coplanar PCBs (PCB77, PCB81, PCB126, and PCB169). The laboratory used high-resolution gas chromatography/mass spectrometry to measure the levels for 2,3,7,8-substituted dioxins and furans following the procedures described in EPA Method 8290 (Tondeur and Beckert, 1994) and Method 1668 for PCB measurement. The lipid determination followed the procedure used by the centers for disease control (Phillips et al., 1989). When results were below the limit of detection (LOD), we used the LOD divided by the square root of 2 to infer average levels of dioxins, furans and PCBs (Hornung and Reed, 1990). All results were lipid adjusted.

We calculated mean serum dioxin, furan and PCB levels and the 25% and 75% quartiles for each group of workers mentioned above. We also estimated the percentage of the dioxin, furan and PCB levels of the total toxic equivalency (TEQ) of the WHO established in 2005 (van den Berg et al., 2006). Each group of exposed workers was compared to the unexposed workers for both the mean levels and percentages of TEQ using a Student's *t*-test. We calculated correlations among the dioxins, furans and PCBs for all workers, exposed and unexposed. We compared profiles of selected dioxin and furan congeners among the PCP-only and TCP-only workers

Table 1
Lipid adjusted (pg/g lipid) serum 2,3,7,8 substituted dioxin and furan levels for each congener by exposure group

Congeners	Mean lipid adjusted serum concentration (25% and 75% quartiles)				
	Pentachlorophenol only workers	Trichlorophenol only workers	Pentachlorophenol and trichlorophenol workers	Tradesmen	Reference group (no known workplace exposure)
2378-TCDD	7.8 (3.2–8.7)	36.8[a] (7.6–42.6)	13.3 (4.2–14.5)	20.7 (10.1–24.1)	6.0 (2.4–7.8)
12378-PeCDD	18.0 (10.3–23.5)	18.4 (8.8–24.8)	23.7[a] (10.5–30.7)	31.7[a](18.4–39.3)	10.9 (6.3–14.2)
123478-HxCDD	14.8 (8.1–14.6)	9.4 (5.6–10.5)	20.9[a] (6.7–31.6)	21.5[a] (8.6–34.2)	7.5 (4.8–10.3)
123678-HxCDD	156.4 (80.9–173.0)	100.0 (56.6–129.5)	234.0[a] (75.8–362.2)	150.4 (77.0–211.0)	71.8 (46.0–94.0)
123789-HxCDD	23.7[a] (8.3–28.2)	9.6 (4.7–11.1)	23.0[a] (8.7–37.9)	21.0 (6.3–33.7)	8.0 (5.2–11.0)
1234678-HpCDD	234.6[a] (55.2–347.0)	61.9 (36.5–85.2)	280.7[a] (78.4–317.0)	264.4 (46.2–299.0)	67.5 (47.0–85.4)
OCDD	2778.2 (793.0–3120.0)	605.1 (248.5–819.5)	4928.3[a] (642.0–4630.0)	2502.6 (683.0–2650.0)	483.2 (255.0–608.5)
2378-TCDF	0.5 (0.2–0.7)	0.3 (0.2–0.3)	0.5 (0.3–0.5)	0.6 (0.2–0.9)	0.6 (0.3–0.6)
12378-PeCDF	0.5 (0.3–0.7)	0.4 (0.3–0.4)	0.6 (0.3–0.7)	0.7 (0.2–1.0)	0.6 (0.3–0.6)
23478-PeCDF	9.9 (6.3–13.5)	9.7 (7.3–12.2)	10.9 (8.4–12.6)	15.2[a] (10.9–19.9)	9.2 (6.1–11.4)
123478-HxCDF	10.2 (6.7–13.2)	7.2 (4.5–8.7)	11.3 (7.1–15.2)	13.7[a] (6.6–18.9)	7.7 (5.3–10.0)
123678-HxCDF	9.2 (6.2–11.4)	6.9 (4.3–8.0)	10.0 (7.0–11.0)	12.0[a] (7.0–15.6)	7.3 (5.0–9.3)
234678-HxCDF	2.1 (1.2–2.3)	1.1 (0.0–1.8)	2.9[a] (1.7–4.7)	1.9 (0.5–2.9)	1.6 (0.7–2.4)
123789-HxCDF	0.4 (0.3–0.6)	0.5 (0.2–0.5)	0.4 (0.3–0.5)	0.6 (0.4–0.7)	0.4 (0.4–0.4)
1234678-HpCDF	15.9 (10.8–17.2)	16.6 (8.4–12.6)	19.3 (10.4–25.0)	14.5 (10.8–17.8)	11.3 (7.8–13.7)
1234789-HpCDF	0.5 (0.3–0.5)	0.5 (0.4–0.6)	0.5 (0.3–0.7)	0.6 (0.4–0.9)	0.5 (0.3–0.6)
OCDF	1.9 (1.1–1.8)	1.5 (1.1–1.9)	1.7 (1.3–2.1)	2.1 (1.4–2.5)	4.5 (1.2–2.1)
PCB77	3.5 (2.9–3.9)	3.8 (3.1–4.2)	4.2 (2.6–5.9)	4.2 (2.6–5.6)	4.5 (2.6–4.9)
PCB81	2.0 (0.8–2.3)	1.7 (1.0–2.6)	1.7 (1.1–1.6)	2.3 (1.0–2.9)	1.8 (0.8–2.2)
PCB126	34.4 (15.6–37.0)	20.9 (12.3–28.0)	36.4 (23.3–48.1)	49.8 (14.8–88.4)	28.0 (13.6–33.9)
PCB169	33.7 (19.2–40.7)	49.5 (29.9–68.8)	44.0 (26.0–55.3)	64.8[a] (51.4–75.4)	40.7 (25.6–43.75)
Number	26	12	14	10	36
Mean age	56.6	72.3	62.7	71.0	64.0
Mean body mass index	33.0	27.3	31.2	32.2	28.8
Mean months employed at site	266.3	391.0	375.8	412.44	303.6
Mean months employed in chlorophenol units	29.4	55.6	46.4	0.0[b]	0.0
Range of last year exposed to chlorophenols	1944–1980	1954–1979	1961–1980	Unknown	NA

NA = not applicable.
[a] Significance <0.05 based on a Student's *t*-test.
[b] While tradesmen were not formally assigned to chlorophenol units, they had plant-wide responsibilities which may have taken them into chlorophenol units.