

SERUM DIOXINS, FURANS, AND PCB LEVELS AMONG NEW ZEALAND TRICHLOROPHENOL WORKERS

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Introduction

The Dow AgroSciences site in New Plymouth, New Zealand manufactured 2,4,5-trichlorophenoxy acetic acid (2,4,5-T) from 1962 to 1988 and 2,4,5-trichlorophenol (TCP) from 1969 to 1987. 2,3,7,8 tetrachlorodibenzo-p-dioxin (TCDD) is the major dioxin contaminant in these products.¹ Studies of serum dioxins among workers in TCP or 2,4,5-T production routinely report TCDD levels above background many years after exposures have ended.²⁻⁶

We examined serum dioxin, furan, and PCB levels among current and former workers who had potential contact with TCP or 2,4,5-T, and compared their levels with workers at the same site without potential for such workplace exposures. The current study provides an opportunity to determine if TCP and 2,4,5-T workers have elevated body levels of dioxins particularly TCDD and examine the range of current body levels among these workers. We also determine if TCDD is the only elevated dioxin congener among workers with TCP and 2,4,5-T exposure. These serum results will provide exposure estimates for health studies.

Materials and Methods

We collected all blood at a single clinic in September of 2005, July through August of 2006, and May of 2007. Approximately 80 milliliters of blood was collected in vacutainer tubes without anticoagulant or serum separator. Whole blood was allowed to clot for at least 20 minutes then centrifuged for 15 minutes at 2,500 rpm. All serum was transferred to rinsed glass vials with Teflon seals and stored at -20°C until laboratory analysis.

Serum samples were analyzed byASUREQuality Laboratory, Wellington, New Zealand. The analytical procedure measured levels of the seven 2378-substituted dioxins (2378-TCDD, 12378-P₅CDD, 123478-H₆CDD, 123678-H₆CDD, 123789-H₆CDD, 1234678-H₇CDD, OCDD), the ten 2378-substituted furans (2378-TCDF, 12378-P₅CDF, 23478-P₅CDF, 123478-H₆CDF, 123678-H₆CDF, 234678-H₆CDF, 123789-H₆CDF, 1234678-H₇CDF, 1234789-H₇CDF, OCDF), and 4 PCBs (PCB-77, -81, -126, and -169).

The laboratory used high resolution gas chromatography/mass spectrometry to determine the levels for 2378-substituted dioxins and furans following the procedures described in EPA Method 8290⁷ and Method 1668 for PCB measurement. When levels were below the limit of detection (LOD), we assumed the serum value equaled the LOD divided by the square root of two.⁸ All results were lipid adjusted. The lipid determination followed the procedure used by the Centers for Disease Control and Prevention.⁹ We calculated the total toxic equivalency (TEQ) using the 2006 TEQ factors.¹⁰

There were jobs in several departments with potential exposure to TCDD. We classified jobs in the same department with the same exposure potential into similar exposure grouping. This was done by reviewing past potential exposures with several long-term employees, examining past biomonitoring results for trichlorophenol, and considering past engineering and process changes.

Results and Discussion

Workers may have held several jobs at the site including both exposed and unexposed jobs. Of the 1,599 workers at the site, we estimated from the above procedures that 1,134 workers would have potential exposure to TCDD based on one or more of their job in their work histories and/or were involved in the 1986 accidental release as detailed in Table 1. We were able to sample 241 of these workers or 21% (241/1,134) of the total. The average level of serum TCDD among workers with one or more potentially exposed job was 9.9 ppt lipid adjusted and these workers spent an average of 32.5 months in a job with potential exposure. There were 465 workers who were never exposed to TCDD based on their work

histories and 105 of these workers (23%, or 105/465) participated in the serum study. The average serum dioxin TCDD level was 4.9 ppt and these workers spent an average of 53.9 months in these jobs.

Table 1. Mean Lipid Adjusted 2,3,7,8 TCDD levels by Department and Exposure Level.

Department	Estimated Exposure Level	Serum TCDD level
<i>Continuous Exposure</i>		
Trichlorophenol	Low	23.4
	High	21.9
Phenoxy	Low	12.4
	Medium	13.9
	High	17.9
Formulations	Very low	8.6
	Low	5.9
Herbicides	Low	6.6
Pilot Plant	High	7.5
<i>Intermittent Exposure</i>		
Construction & Maintenance (includes Despatch, Field Service Unit, Maintenance, and some jobs in Triazines)	Very Infrequent	8.4
	Infrequent	13.1
	Monthly	13.9
Mechanics and Transport (Includes Distribution, Drum Processing, Materials Flow & Raw Materials)	Very Infrequent	6.6
	Infrequent	19.1
	Monthly	22.1
Phenoxy Laboratory	Daily	3.6
TCDD Laboratory	Daily	5.9
Other Laboratories, R&D	Very Infrequent	3.7
	Infrequent	3.5
	Monthly	3.9
Professional Personnel (includes Engineering and Manufacturing)	Very Infrequent	15.8
	Infrequent	6.2
	Monthly	10.0
	Daily	17.5
<i>Accident</i>		
1986 Accident	NA	37.9
<i>Unexposed Workers</i>		
Never Exposed Workers	NA	4.9

NA-Not applicable

Workers involved in the 1986 accidental release had the highest current serum dioxin levels averaging 37.9 ppt. Among workers with routine continuous exposures, workers in the TCP department had levels of 21.9 or 23.4 ppt depending on job type. Workers with jobs in formulations, herbicides, and the pilot plant had the lowest current levels, ranging from 5.9 to 8.6 ppt, and workers with jobs in the phenoxy plant had current levels between these groups ranging from 12.4 to 17.9 ppt. Workers with jobs with intermittent exposure potential to TCDD including construction and maintenance, mechanics and transports, and the professional personnel had current levels generally consistent with many of the continuous exposure jobs. However, the laboratory workers generally had the lowest current dioxin levels with the possible exception of the TCDD laboratory workers who had a mean TCDD exposure of 5.9 ppt.

Table 2 presents dioxin, furan, PCB levels, and the TEQs for unexposed and exposed workers. The levels of TCDD are significantly higher among the ever exposed workers (mean = 9.9 ppt) compared to the never exposed workers (mean = 4.9 ppt). There are no significant differences between the two groups on the remaining dioxins, the furans or PCBs. However, the TEQ of 24.1 ppt for exposed workers is significantly higher than 19.2 ppt for unexposed workers. We also compared the remaining dioxin, furans, and PCBs

with the New Zealand national population sample.¹¹ The serum levels for both exposed and unexposed workers on these other congeners are similar to the New Zealand population.

Table 2. Comparison of lipid-adjusted (pg/g lipid) serum 2,3,7,8-substituted dioxins and furans, and PCB levels for each congener and the toxic equivalency (TEQ) for workplace never exposed and ever exposed workers.

Congener	Mean Concentrations (5%, 50%, 95% quantile)	
	Never Exposed Workers	Ever Exposed Workers
2378-TCDD	4.9 (1.1, 3.2, 13.0)	9.9 (1.0, 3.8, 45.1)*
12378-P ₃ CDD	4.7 (1.9, 4.3, 8.7)	5.3 (1.8, 4.2, 11.2)
123478-H ₆ CDD	2.4 (0.9, 2.2, 5.1)	2.7 (0.9, 2.1, 4.9)
123678-H ₆ CDD	14.3 (5.6, 13.4, 26.7)	15.0 (5.9, 13.2, 32.6)
123789-H ₆ CDD	3.3 (1.5, 2.8, 6.3)	3.4 (1.2, 2.7, 7.8)
1234678-H ₇ CDD	25.7 (6.2, 23.0, 65.2)	24.9 (6.8, 19.5, 57.4)
OCDD	241.2 (90.4, 213.0, 565.0)	231.5 (69.9, 183.0, 557.0)
2378-TCDF	0.9 (0.4, 0.8, 1.4)	0.9 (0.4, 0.7, 1.8)
12378-P ₃ CDF	0.6 (0.2, 0.5, 1.0)	0.6 (0.2, 0.5, 1.2)
23478-P ₃ CDF	4.7 (2.2, 4.1, 9.9)	4.4 (2.0, 4.1, 8.1)
123478-H ₆ CDF	2.1 (1.0, 1.8, 4.0)	2.1 (0.9, 1.8, 4.2)
123678-H ₆ CDF	2.4 (1.1, 2.0, 5.3)	2.5 (1.0, 2.1, 5.3)
234678-H ₆ CDF	1.1 (0.3, 0.9, 2.2)	1.1 (0.3, 0.9, 2.2)
123789-H ₆ CDF	1.0 (0.2, 0.6, 2.6)	1.0 (0.2, 0.7, 2.5)
1234678-H ₇ CDF	4.8 (1.4, 3.0, 17.3)	7.7 (1.4, 3.4, 30.5)
1234789-H ₇ CDF	1.5 (0.3, 1.0, 4.5)	1.5 (0.3, 0.9, 4.2)
OCDF	2.8 (0.6, 1.8, 8.6)	2.5 (0.6, 1.7, 7.0)
PCB77	32.2 (8.2, 21.8, 72.3)	34.0 (8.8, 22.9, 83.0)
PCB81	13.1 (4.1, 10.6, 29.7)	13.4 (4.3, 10.5, 27.0)
PCB126	37.5 (12.0, 24.6, 74.1)	30.0 (11.5, 25.3, 70.5)
PCB169	33.8 (14.1, 29.1, 69.0)	31.4 (14.0, 28.5, 60.1)
TEQ	19.2 (8.5, 15.4, 39.7)	24.1 (7.5, 16.6, 76.1)*
Total Workers	105	241

* P-value <0.05 comparing ever exposed to never exposed using t-test.

The serum study we completed at the New Plymouth site is one of the larger studies with 239 exposed workers. This is the first study to our knowledge to assess exposure to workplace dioxins through serum evaluations among workers by sampling all workers at the site regardless of exposure potential. Most previous serum studies have limited serum evaluations to workers holding jobs with clear potential for exposure. We found that many jobs with potential exposure exhibited dioxin levels above background levels. Further, workers in departments which had high dioxins levels in previous serum dioxin studies also had high levels in our study. For instance, workers in the TCP department had some of the highest serum levels. This is consistent with other studies where TCP was made.³ We also found that workers who worked throughout the site in jobs such as maintenance often had TCDD levels above background. This has also been seen in other studies indicating that intermittent exposures may also contribute to body dioxin levels.^{3,6} We also found that some workers who had no history of potential workplace dioxin exposures according to work records had dioxin levels above background. In most cases, these high levels could be associated with workplace dioxin exposure that was either not recorded on the work history or resulted from dioxin exposures in other jobs before or after work at the site. However, in most other cases the work records accurately reflect potential exposure. While a direct comparison of our serum TCDD levels with the New Zealand national sample is not possible, we found that most unexposed workers had TCDD levels consistent with New Zealand background levels.

The exposed workers at the New Plymouth site appear to have low current serum dioxin levels compared to virtually every other study of highly exposed workers. While it is difficult to compare these studies since

the time between last exposure and the blood draw varies, the TCDD serum levels at this site are at the low end of the range of these studies.

This study finds a distinct dioxin “fingerprint” from TCP exposure in the TCP department, in the departments where TCP was used to make the product 2,4,5-T, and in the packaging of 2,4,5-T. TCDD was the only dioxin, furan, or PCB that was elevated among exposed workers. Other than high levels of TCDD, we found no evidence of elevated dioxins, furans or PCBs in the serum of TCP or 2,4,5-T workers compared to never exposed workers or the New Zealand population. Even though exposure occurred many years ago, we were able to effectively distinguish exposed jobs and department from unexposed jobs based on TCDD levels. There appears to be little or no exposure to TCDD among workers at the New Plymouth site who did not have direct exposure to TCP or 2,4,5-T.

The TCDD levels in this study will be useful to better determine who was exposed and how high past exposures were for epidemiology studies. This study confirms that many of the workers with exposures to TCP and 2,4,5-T had TCDD levels above background many years after workplace exposures had ended and provides justification for studying these exposed workers for the potential health effects from industrial dioxin exposures.

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