2,3,7,8 Chlorine Substituted Dioxin and Dibenzofuran Congeners in 2,4-D, 2,4,5-T and Pentachlorophenol

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Abstract
The herbicide 2,4-D is generally believed not to contain toxic (2,3,7,8 chlorine substituted) dioxins or dibenzofurans. The herbicide 2,4,5-T has generally been considered to be contaminated with 2,3,7,8-tetrachlorodibenzo-p-dioxin only. Pentachlorophenol is characteristically contaminated with higher chlorinated polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Because of the improved analytic techniques now available, we analyzed specimens of these compounds recently obtained from the United States, Israel (of European manufacture), Palestinian areas (Gaza and the West Bank) and Russia. Unexpectedly, we found low levels of some toxic PCDDs/PCDFs in the 2,4-D samples and higher levels of many PCDDs/PCDFs in the 2,4,5-T as well. Pentachlorophenol from the United States contained many higher chlorinated PCDD/PCDF congeners, as expected.

Introduction

2,4-dichlorophenoxyacetic acid (2,4-D) is a commonly used phenoxy herbicide in the United States and elsewhere. 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) is no longer used in the United States, with a few exceptions such as railroads and power lines. Agent Orange, a herbicide used during the Vietnam War which was a 1:1 mixture of 2,4-D and 2,4,5-T, has been thought to have been contaminated only with 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). Pentachlorophenol (PCP) has been used chiefly in fungicides, disinfectants, and wood preservatives. There have been few recent congener-specific PCDD/PCDF analyses of these compounds.

Methods

Two brands of 2,4-D were purchased in Gaza City, Gaza and one in Bethlehem, West Bank. These three samples of 2,4-D purchased in Palestine were manufactured in Western Europe and packaged in Israel. One sample of 2,4-D was purchased from Sigma Chemical Co. in the United States, but was a product of England. Another sample of 2,4-D was purchased in Lake Charles, Louisiana and packaged by American Brand Chemical Co. of Bonham, Texas. Several other brands were purchased in Binghamton, NY. The final sample of 2,4-D was manufactured at the Chimprom factory in Ufa, Russia[1]. The sample of 2,4,5-T, which was purchased from Sigma Chemical Co., was labeled "Bell Fibre Products Co., Columbus, Georgia." The PCP was recently found stored in a barn in Vermont. Analytic methods used by ERGO Forschungsgesellschaft, mbH laboratory were previously described and will not be repeated here[1,2].

Results

Table 1 summarizes the PCDD and PCDF congener analyses and dioxin toxic equivalents (TEQs) for selected 2,4-D samples. As expected, 2,3,7,8-TCDD was not detectable in any of the samples, but some other toxic congeners were found at low levels. The TEQs were calculated two ways for each of the samples; once giving a value of zero where congeners were not detected (ND = 0), and alternatively using ½ the detection limit as the value for congeners not detected (ND = ½). For the United States samples, the total PCDD/PCDFs TEQ when ND = ½ is between 2 and 3 times greater than the total TEQ when ND = 0. Table 2 presents the PCDD and PCDF congeners and TEQs for two analyses of the 2,4,5-T sample and for the PCP analysis. Surprisingly, 14 of 17 toxic dioxin and dibenzofuran congeners were detected in the 2,4,5-T sample purchased from Sigma Chemical Co. (USA).

Discussion and Conclusions

The finding of low levels of certain toxic PCDD/PCDF congeners in 2,4-D was unexpected. The findings of higher chlorinated dioxins in PCP was as expected. The finding of many PCDD and PCDF congeners in the 2,4,5-T sample was a surprise. Only 2,3,7,8-TCDD has been thought to be a dioxin contaminant of 2,4,5-T. To date, in Vietnamese, Vietnam veterans, and others exposed to 2,4,5-T in Agent Orange, only elevations of 2,3,7,8-TCDD in blood, adipose tissue, or milk has been reported[3,4,5,6]. We have no ready explanation for the unexpected finding of numerous PCDD/PCDF congeners in the 2,4,5-T sample. Analysis of other 2,4,5-T samples with the improved analytic methodology currently available seems indicated.

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TABLE 1. DIOXIN AND DIBENZOFURAN CONGENERS AND TOXIC EQUIVALENTS IN 2,4-D SAMPLES FROM PALESTINE, ISRAEL, UNITED STATES AND RUSSIA (ng/g, ppb)

Congener	Acbar Super Gaza City, Gaza	Amco Super Gaza City, Gaza	Bethlehem, West Bank	Sigma Co. United States	"American Brand" United States	Chimprom factory Ufa, Russia
DIOXINS						
2,3,7,8-TCDD	- (0.1)	- (0.1)	- (0.1)	- (0.002)	- (0.002)	- (0.02)
1,2,3,7,8-PeCDD	+	- (0.1)	+	- (0.002)	- (0.002)	+
1,2,3,4,7,8-HxCDD	- (0.1)	- (0.1)	- (0.1)	- (0.002)	- (0.002)	+
1,2,3,6,7,8-HxCDD	- (0.1)	+	+	- (0.002)	- (0.002)	+
1,2,3,7,8,9-HxCDD	- (0.1)	- (0.1)	+	- (0.002)	- (0.002)	- (0.02)
1,2,3,4,6,7,8-HpCDD	+	+	+	+	+	+
1,2,3,4,6,7,8,9-OCDD	+	+	+	+	+	+
DIBENZOFURANS						
2,3,7,8-TCDF	+	- (0.1)	- (0.1)	+	+	- (0.1)
1,2,3,7,8-PeCDF/ 1,2,3,4,8-PeCDF	- (0.1)	+	+	- (0.002)	- (0.002)	+
2,3,4,7,8-PeCDF	- (0.1)	- (0.1)	+	- (0.002)	- (0.002)	+
1,2,3,4,7,8-HxCDF/1,2,3,4,7,9-HxCDF	- (0.1)	+	+	+	+	+
1,2,3,6,7,8-HxCDF	- (0.1)	- (0.1)	+	- (0.002)	- (0.002)	+
1,2,3,7,8,9-HxCDF	- (0.1)	- (0.1)	- (0.1)	- (0.002)	- (0.002)	- (0.02)
2,3,4,6,7,8-HxCDF	- (0.1)	- (0.1)	+	- (0.002)	- (0.002)	+
1,2,3,4,6,7,8-HpCDF	+	+	+	+	+	+
1,2,3,4,7,8,9-HpCDF	- (0.1)	- (0.1)	- (0.1)	+	+	+
1,2,3,4,6,7,8,9-OCDF	+	+	+	+	+	+
Total PCDDs TEQ, ND=0	**0.051**	**0.035**	**0.703**	**0.00017**	**0.00006**	**0.0252**
Total PCDFs TEQ, ND=0	**0.031**	**0.032**	**0.146**	**0.00118**	**0.00185**	**0.1086**
Total PCDD/Fs TEQ, ND=0	**0.082**	**0.066**	**0.850**	**0.00134**	**0.00191**	**0.1338**
Total PCDDs TEQ, ND=1/2	**0.116**	**0.120**	**0.758**	**0.00197**	**0.00186**	**0.0362**
Total PCDFs TEQ, ND=1/2	**0.079**	**0.077**	**0.157**	**0.00203**	**0.00270**	**0.1146**
Total PCDD/Fs TEQ, ND=1/2	**0.195**	**0.197**	**0.915**	**0.00399**	**0.00456**	**0.1508**

"+" = detected. "-" = not detected;detection limit follows in ( ).
"ND=0" = calculation done by giving no value to congeners not detected.
"ND=1/2" = calculation done by giving 1/2 the detection limit to congeners not detected.

TABLE 2. DIOXIN AND DIBENZOFURAN CONGENERS AND TOXIC EQUIVALENTS FROM UNITED STATES SAMPLES OF 2,4,5-T AND PENTACHLOROPHENOL (PCP) (ng/g, ppb)

Congener	TEF	2,4,5-T Sigma Chem. Co.* Analysis 1	2,4,5-T Sigma Chem. Co.* Analysis 2	PCP Vermont
DIOXINS				
2,3,7,8-TCDD	1	+	+	- (10)
1,2,3,7,8-PeCDD	0.5	+	+	- (10)
1,2,3,4,7,8-HxCDD	0.1	+	+	- (10)
1,2,3,6,7,8-HxCDD	0.1	+	+	+
1,2,3,7,8,9-HxCDD	0.1	+	+	+
1,2,3,4,6,7,8-HpCDD	0.01	+	+	+
1,2,3,4,6,7,8,9-OCDD	0.001	+	+	+
DIBENZOFURANS				
2,3,7,8-TCDF	0.1	+	+	- (10)
1,2,3,7,8-PeCDF/ 1,2,3,4,8-PeCDF	0.05	+	+	- (10)
2,3,4,7,8-PeCDF	0.5	+	+	- (10)
1,2,3,4,7,8-HxCDF/1,2,3,4,7,9-HxCD	0.1	+	+	+
1,2,3,6,7,8-HxCDF	0.1	+	+	- (20)
1,2,3,7,8,9-HxCDF	0.1	- (0.012)	n.a.	- (20)
2,3,4,6,7,8-HxCDF	0.1	+	n.a.	- (20)
1,2,3,4,6,7,8-HpCDF	0.01	+	+	+
1,2,3,4,7,8,9-HpCDF	0.01	+	n.a.	+
1,2,3,4,6,7,8,9-OCDF	0.001	+	+	+
Total PCDDs TEQ, ND=0		**2.5185**	**2.6477**	**749.21**
Total PCDFs TEQ, ND=0		**0.3582**	**0.4941**	**61.34**
Total PCDD/Fs TEQ, ND=0		**2.8767**	**3.1418**	**810.55**
Total PCDDs TEQ, ND=1/2		**2.5188**	**2.6477**	**757.21**
Total PCDFs TEQ, ND=1/2		**0.3592**	**0.4941**	**67.59**
Total PCDD/Fs TEQ, ND=1/2		**2.878**	**3.1418**	**824.8**

"+"= detected. "-" = not detected;detection limit follows in ( ). n.a. = not analysed.
"ND=0" = calculation done by giving no value to congeners not detected.
"ND=1/2" = calculation done by giving 1/2 the detection limit to congeners not detected.
*Purchased from Sigma Chemical Co., product number T-5785, Lot 16H3625