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MONSANTO RESEARCH CORPORATION *Inter-Office Correspondence*

From LOCATION: F. D. Hileman, Analytical Technology, Dayton cc:

DATE: 24 February 1981

SUBJECT: Chlorinated Dibenzofurans in PCBs

REFERENCE:

MAR 2 1981 John Craddock

TO : Clayton Callis
St. Louis - 83CA

Enclosed you will find a copy of the analyses carried out by our laboratory on several samples each labeled "Bulk Aroclor" and two transformer oil samples. This work was done using packed column GC/MS and therefore no isomer specificity on the tetrachlorodibenzofurans (TCDBF) is given. We have recently repeated the analysis on "bulk #4" using capillary column techniques and found that less than 50 ppb of the original 116 ppb resulted from the 2,3,7,8-TCDBF with the remainder present in other TCDBF isomers. This number for 2,3,7,8-TCDBF could go lower as we get better isomer specificity.

I have also included a copy of a pertinent section from the rough draft of the Government Interagency Criteria Document on Dibenzofurans. Hopefully this will serve to bring you up to date on furan problems in PCBs. If I can be of any further help, let me know.

854-406

Fred D. Hileman

FDH/cvd
Enc.

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Dayton Lab Analyses

TABLE 1. ANALYSES FOR TCDBF IN [redacted] PCB SAMPLES

Sample	Ng TCDBF gm
#80-00175 Transformer 637	102
#80-00175 Transformer 637 (replicate)	94
#80-00176 Bulk #3	13
#80-00177 Bulk #4	116
#80-00179 Bulk #7	30
Solvent Blank	N.D.

The only identification on these samples were the terms "Bulk Aroclor"

Lower Detection Limit = 10 Ng/g

Sample	Ng TCDBF/gm Found	Ng TCDBF/gm Added	Recovery
#80-00176 Bulk #3 Low Spike	56.2	40	106%
#80-00177 Bulk #3 High Spike	180	200	83%

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synthesis of CDBFs from chlorobenzenes is also discussed in Section 4.4.1.2.2.

The average concentration of the 2,3,7,8-tetra-CDD in technical 2,4,5-T used in Agent Orange manufacture ranged from 1 to 32 ppm (Young, et al. 1978). Levels in Agent Purple (n-butyl 2,4-D: n-butyl 2,4,5-T: iso-butyl 2,4,5-T:: 5:3:2) formulated in the mid-1950s appear to be even higher than those in Agent Orange. Levels of 2,3,7,8-tetra-CDD in the technical 2,4,5-T used for its formulation have been estimated to be as high as 90 ppm (Young, et al. 1978). Other herbicides containing 2,4,5-T used in Vietnam, namely, Agent Pink (n-butyl 2,4,5-T/isobutyl 2,4,5-T:: 3:2), Agent Green (n-butyl ester of 2,4,5-T), Dinoxol (1:1 butoxyethanol esters of 2,4,5,-T and 2,4-D) and Trinoxol (40 percent butoxyethanol ester of 2,4,5-T), have never been intensively studied for their CDD or CDBF contents.

4.4.2.4 CDBFs in Hexachlorophene

The bactericide, hexachlorophene, is prepared commercially from 2,4,5-trichlorophenol (Nilsson, et al. 1978) However, it is purified during this process and levels of 2,3,7,8-tetra-CDD are less than 30 ug/kg. Nevertheless, hexachlorophene can contain 100 ppm of the 1,2,4,6,8,9-hexachloroxanthene (Gothe and Wachmeister, 1972). The CDBFs identified included hepta- and octa-CDBFs the latter being present in concentations ranging from 0.35 to 58.3 ppm (Villanueva, et al. 1974).

[redacted]

The abundance and distribution of PCBs in the environment have been the subjects of many papers since their discovery in

Swedish wildlife in 1966 almost four decades after their first commerical production (Jensen, 1966). In the late 1960s, a significant difference in toxicity to chick embryos was discovered among three supposedly identical PCB formulations originating from three different countries (Vos and Koeman, 1970). Large amounts of polar contaminants were detected in a German PCB (Clophen A-60) and a French PCB (Phenoclor DP-6) but not in an American PCB (Aroclor 1260). Two of the contaminants in the German PCB were identified by GC/MS as a tetra- and a penta-CDBF (Vos, et al. 1970); these compounds accounted for the observed toxicity of the whole PCB formulation. CDBFs were found also in American PCBs but not as much as in the European formulations (Bowes, et al. 1973). Kanechlors from Japan were also found to contain CDBFs (Bowes, et al. 1975; Roach and Pomerantz, 1974). The average CDBF content in Aroclors 1248, 1254, and 1260 from the United States was then put at between 1 to 2 ppm. Less than ppt levels were detected in Aroclor 1016 (Bowes, et al. 1975). The 2,3,7,8- tetra- and 2,3,4,7,8-penta-isomers were found to be present in Aroclors 1248 and 1254, and in Kanechlors 200 and 500 (Bowes, et al. 1975); Clophen A-60 contained approximately 8 ppm CDBFs, and Phenoclor DP-6 contained around 14 ppm. The PCBs with the highest CDBF contents were toxic to chick embryos.

In 1968, some 1,200 Japanese people consumed a rice oil ("Yusho") contaminated with 800-1000 ppm of a Japanese PCB formulation, Kanechlor 400, leaked from a heat exchanger (Nagayama, et al. 1975). Several months before this incident, half a million chicks were killed by a crude bran oil from the

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Table 4.15. Chlorodibenzofuran Content in Some Polychlorinated Biphenyls and in Yusho Oil.

Substrate	CDBF Content (ppm) Tri	Tetra	Penta	Hexa	Total	Reference
Yusho oil	0.15	1.4	2.5	1.6	5.7	Buser, et al. 1978c
Yusho oil	?	?	?	?	5.0	Nagayama, et al. 1976
Used Japanese PCB (Mitsubishi-Monsanto T-1248)	4.2	4.5	5.5	1.4	16	Buser, et al 1978c
Yusho oil	0.02	0.52	1.3	0.81	2.7	Morita, et al. 1977
2 Kanechlor 300	-	6.7	1.6	-	8.3	Morita, et al. 1977
Kanechlor 300	-	-	1.3	-	1.3	Nagayama, et al. 1976
3 Kanechlor 400	0.3	12.2	10.3	0.9	24	Morita, et al. 1977
Kanechlor 400	?	?	?	-	18	Nagayama, et al. 1976
Kanechlor 400	?	1	?	?	?	Roach and Pomerantz, 1974
2 Kanechlor 500	0.2	1.7	1.1	3.1	6.1	Morita, et al, 1977
Kanechlor 500	-	-	?	?	3.3	Nagayama, et al. 1976
2 Kanechlor 600	-	0.2	0.5	0.4	1.1	Morita, et al. 1977
Kanechlor 600	-	?	?	?	4.0	Nagayama, et al. 1976
Phenoclor DP 4	-	1.7	1.6	0.5	3.8	Morita, et al. 1977

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Table 4.15. Chlorodibenzofuran Content in Some Polychlorinated Biphenyls and in Yusho Oil. (continued)

Substrate	CDBF Content (ppm) Tri	Tetra	Penta	Hexa	Total	Reference
Phenoclor DP 5	-	4.6	2.7	2.6	9.9	Morita, et al. 1977
Phenoclor DP 6	0.2	2.1	2.6	5.6	11	Morita, et al. 1977
Phenoclor DP-6	-	0.7	10.0	2.9	13.6	Bowes, et al. 1975
Aroclor T-64	-	4.8	9.4	2.0	16	Morita, et al. 1977
Aroclor T-241	-	2.4	2.7	0.8	5.9	Morita, et al. 1977
Aroclor T-1254 (1969)	-	0.1	0.2	1.4	1.7	Bowes, et al. 1975
Aroclor T-1254 (1970)	-	0.2	0.4	0.9	1.5	Bowes, et al 1975
Aroclor T-1254	-	0.1	3.6	1.9	5.6	Morita, et al. 1977
Aroclor T-1200 (1969)	-	0.1	0.4	0.5	1.0	Bowes, et al. 1975
Aroclor T-1260 (lot AK 3)	-	0.2	0.3	0.3	0.8	Bowes, et al. 1975
Aroclor T-1260	-	0.8	0.9	0.5	2.2	Morita, et al. 1977

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Table 4.15. Chlorodibenzofuran Content in Some Polychlorinated Biphenyls and in Yusho Oil. (continued)

Substrate	CDBF Content (ppm) Tri	Tetra	Penta	Hexa	Total	Reference
Clophen A-30	1.6	2.3	1.0	-	4.9	Morita, et al. 1977
Clophen A-40	1.5	5.4	6.9	-	14	Morita, et al. 1977
Clophen A-50	0.7	8.3	4.1	1.8	15	Morita, et al. 1977
Clophen A-60	-	1.4	5.0	2.2	8.4	Bowes, et al. 1975

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same origin as Yusho oil but the warning went unheeded (Kohanawa, et al. 1969). The composition of Kanechlor 400 resembled that of Aroclor 1248. Six of the GC peaks assigned to CDBFs made up 2 ppm of the PCB. However, reports of the total CDBF content varied greatly from investigator to investigator. For example, Roach and Pomerantz (1974) detected 1 ppm, Nagayama, et al. (1975) 18 ppm, and Kashimoto (Kuratsune, et al. 1976) reported 33 ppm. These values were obtained on conventional packed GC columns and so are expected to be maximal figures. Later work confirmed a level of 2 to 5 ppm (Nagayama, et al. 1977; Rappe, et al. 1977), with the major CDBFs being the toxic 2,3,7,8-tetra- (0.45 ppm) and the 2,3,4,7,8-penta- (approximately 0.2 ppm) isomers. It was calculated that the contaminating Kanechlor 400 PCB contained a CDBF level 250 times greater than the value found for an unused Kanechlor 400 formulation (Nagayama, et al. 1975). However, a fourfold increase of CDBFs (15 to 20 ppm) occurred when a PCB was used for two years in a heat exchanger in a situation similar to the suspected source of Yusho contamination (Morita, et al. 1977). More than 40 isomers were found of which the 2,3,7,8-tetra- was the most abundant (1.25 ppm). The chromatographic profile of the CDBF fraction was very similar to that of Yusho oil (Buser, et al. 1978c; Rappe, et al. 1977). A summary of the levels of CDBFs in various PCB formulations and in Yusho oil is given in Table 4.15.

Table 4.16 gives the suspected maximum levels of the toxic 2,3,7,8-tetra- and 2,3,4,7,8-penta-CDBFs in these formulations (Morita, et al. 1977). The levels of the 2,3,7,8-derivatives were identified via retention time of the pure standard, and were

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subsequently confirmed by GC/mass fragmentography by Buser, et al. 1978c. If the same order of elution is followed on the GC columns utilized by these workers, probably peaks 6 to 10 and 13 to 19 of Buser, et al. (1978c) correspond to peaks 2 and 3 respectively of Morita, et al. (1977). Similarly, peaks 23 to 33, 37 to 40, 44 to 47, 51 to 52, 53 to 56, 58 to 66, 68 to 70, 71 to 73, 77 to 78, and 85 denoted by Buser, et al. (1978c), correspond to peaks 3,5,6,9,10,11,12,14,16, and 17 of Morita, et al. (1977). The 2,3,7,8-tetrachloro derivative, therefore constitute more than 90 percent of peak 6 of Morita, et al. (1977), accounting for the near equivalence of the levels of the 2,3,7,8-tetra- derivative found in Yusho oil by both sets of workers. However, the actual level of the 2,3,4,7,8-penta-CDBF is probably about 70 percent of the levels quoted in Table 4.13, since peak 68 of Buser, et al. (1978c) is 70 percent of the combined height of peaks 68, 69, and 70. The figures quoted in Table 4.16 are therefore unlikely to have an error greater than 30 percent provided that the elution profiles on the two GC columns are comparable. Thus, these two toxic isomers may have made up between 5 and 34 percent of the total CDBFs in the PCBs. The low values for the Aroclors T-1242 and T-1260 are to be noted. The low toxicity and low toxic CDBF levels of Aroclor 1260 thus correlate (Vos and Koeman, 1970).

The present dietary intake of PCB from fish is about 175 ug/day (Cordle, et al. 1978). If the amount of 2,3,7,8-tetra-CDBF is the same as in a used Kanechlor-400 formulation (similar to Aroclor 1248) i.e., 1.25 ppm, the amount of this isomer stored assuming no excretion would be approximately 0.2 ng/day.

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Table 4.16. Suspected Maximum Levels of Toxic CDBFs in Various PCBs and in Yusho Oil (calculated from Morita, et al. 1977)

Formulation	CDBF Levels (ppm) 2,3,7,8-a	2,3,4,7,8-b	Total	Percentages of total CDBFs for these two derivatives
Yusho oil	0.28	0.42	2.68	26
Phenoclor				
DP-4	0.7	0.4	3.8	29
DP-5	2.2	0.8	9.9	30
DP-6	0.9	0.6	10.5	14
Kanechlor				
KC-300	2.2	0.6	8.3	34
KC-400	1.6	0.9	23.8	11
KC-500	0.7	0.7	6.1	23
KC-600	0.1	0.1	1.1	18
Aroclor				
T-64	2.4	2.3	16.2	29
T-241	1.1	0.4	5.9	25
T-1242	0.2	0.1	4.5	7
T-1248	0.2	0.8	2.8	36
T-1248*	.1	1.4	12.4	20
T-1254	-	1.6	5.6	29
T-1260	-	0.1	2.2	5
Clophen				
A-30	1.0	0.1	4.9	22
A-40	2.1	0.7	13.8	20
A-50	3.6	0.6	14.9	28

- below detection limit; *Used PCB;
[a]=based on GC retentin time, but subsequently confirmed by Buser, et al. 1978.
[b]assumed the order of elution obtained by Buser, et al. 1978, is followed by the GC column utilized.

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Miyata, et al. (1979) recently showed that Yusho oil and Kanechlor-400 also contained polychloroquaterphenyls (600 to 3,000 ppm) and polychloroquaterphenyl ethers. The roles of these other compounds in the observed toxicology have not as yet been elucidated.

Workplace air levels of Aroclor 1242 can range as high as 2.22 mg/m^3 (Ouw, 1974). If it is present as fume, it would contain approximately 3 ng/m^3 of the 2,3,7,8-CDBF, if one makes the same assumptions as used to estimate the levels of this isomer in fish The levels of PCBs reported for various environmental compartments are as follows: ambient air ($\sim$100 ng/m^3), surface waters (10 to 50 ng/liter), foundry effluent (12 to 335 ppb), paper mill effluents (0.01 to 25 ppb), snow (0.17 to 0.24 ppb), waste water ($\sim$ 520 ng/liter) and sewage sludge (16 mg/kg). The last source appears to be the most important source of CDBFs since sewage sludge is often incinerated (see Section 4.4.2.7.). PCB residues in human adipose tissues in the U.S. are low: below detection limit (34.2 percent), <1 ppm (33.3 percent), 1 to 2 ppm (27.3 percent), and exceeding 5.2 ppm (5.2 percent) (Yobs, 1972). Human milk can contain up to 100 ppb of PCBs (Savage, et al. 1973).

4.4.2.6 Brominated DBFs in PBBs

The PBBs gained their greatest notoriety as a result of a severe contamination of cattle in Michigan in October, 1973 (Cordle, et al. 1978). The contaminant, Firemaster BP-6, contained 2 percent tetrabromobiphenyls, 10.6 percent pentabromobiphenyls, 62.8 percent hexabromobiphenyls, 13.8 percent

heptabromobiphenyls and 11.4 percent other bromobiphenyls. It was manufactured by the Michigan Chemical Corporation. As a result of mismanagement, Firemaster BP-6 was added to cattle feed instead of magnesium oxide. The levels of contamination were: lot 405, 2.4 ppm; lot 410, 1790 ppm; and lot 407, 4300 ppm. Milk from affected herds contained from 2.8 to 271 ppm on a fat basis. Contaminated butter (1 to 2 ppm), cheese (1.3 to 15 ppm) and canned milk (1.2 to 1.6 ppm) were later seized and destroyed.

Bromo DBFs were found in pyrolyzed PBBs by O'Keefe (1978)(see Section 4.4.2.7). Bromo DBFs were not found in one study on unheated Firemaster FF-1 (Hass, et al. 1978). Since this latter group did not give recoveries by their technique with authentic known bromodibenzofuran standards, their results must be regarded as tentative. The bromodibenzofurans are less polar than the chlorodibenzofurans, so that use of the same column-chromatographic techniques as used for CDBFs may be inappropriate. Hass et al. 1978 concluded that the amount of BDBFs must be less than 0.5 ppm, and that penta- and hexabromonaphthalenes were present to the extent of 150 and 70 ppm, respectively. A metabolite of Firemaster BP-6 in dogs, 6-hydroxy-2,2',4,4', 5,5'-hexabromobiphenyl, decomposed at 230 to 260°C on an OV-101 column in a gas chromatograph to form two pentabromodibenzofurans (Gardner, et al. 1979). Thus, BDBFs can be formed from pyrolysis on GC columns as well as being originally present in PBB formulations. Such artifacts need to be investigated before BDBF contamination of PBB formulations is considered confirmed.

4.4.2.7 Halodibenzofurans formed by Incineration and Heating

The formation of CDBFs and BDBFs by air incineration is the most likely source in the environment. The formation of parts-per-hundred amounts of CDBFs during pyrolysis of specific PCBs in quartz ampoules between 500 and 700°C was described in Section 4.4.1.2.2 and summarized in Table 4.8 (Buser, et al. 1978a b, c: Buser and Rappe, 1979). Their production in parts per million quantities from specific chlorobenzenes (Buser, 1979) under similar pyrolytic conditions has also been discussed (Section 4.4.1.2.2; Table 4.9). The levels of CDBFs in PCBs increase with the length of time in service at high temperatures as heat exchange media (Morita, et al. 1977; Buser, et al. 1978c), as originally suggested by Kuratsune, et al. (1976). The isomeric composition of the CDBF fraction was very similar to that of the CDBF fraction from Yusho oil (Buser, et al. 1978c). Aroclor 1254 on pyrolysis also contained the major toxic CDBFs but the relative amounts of the products differed somewhat from those obtained from the Mitsubishi-Monsanto T 1248 (Buser, et al. 1978b). The major CDBFs identified in the used Mitsubishi-Monsanto T 1248 were the 2,3,7,8-tetra- (1.25 ppm), the 2,3,4,7,8-penta-CDBF (the pyrolysis product of 2,4,5,2',4',5'-hexachlorobiphenyl), 1,2,3,7,8-penta-, 2,3,4,6,8-penta-, 1,2,3,4,8-penta-, 1,3,4,7,8-penta- (also from pyrolyis of 2,4,5,2'4'5'-hexachlorobiphenyl and the 2,3,4,6,7,8-hexa-isomers. Whereas the used Mitsubishi-Monsanto T-1248) was exposed for years to elevated temperatures in the liquid phase, the laboratory pyrolyses of Aroclor 1254 and 1260 were performed in the gas phase for a few seconds up to a maximum temperature of 700°C (Buser, et al. 1978b). With Aroclor 1254

(tri- to hepta-PCBs), mostly mono- to penta-CDBFs were formed at a level of approximately two percent. With Aroclor 1260 (penta- to octa-PCBs), mostly tri- to hepta-CDBFs were produced at a similar level. The toxic 2,3,7,8-tetra isomer was the most abundant tetra-CDBF, most likely derived from 2,4,5,2',4',5'-hexachlorobiphenyl, or from 2,4,5,3',4'-pentachlorobiphenyl. The toxic 1,2,3,7,8- and 2,3,4,7,8-penta derivatives were major constituents of the penta-CDBFs. The former probably is produced from pyrolysis of 2,3,4,2',4',5'-hexachlorobiphenyl, and the latter from 2,4,5,2',4',5'-hexachlorobiphenyl or 2,3,4,5,2'4'5'-heptachlorobiphenyl or 2,3,4,5,2',4',5'-heptachlorobiphenyl. Aroclor 1254 also contained significant amounts of 1,3,4,7,9-penta-CDBF, although this identification was tentative. In the same study, it was suggested that the presence of CDBFs in the fly ash of municipal incinerators could be explained by the pyrolysis of PCBs. Flyash samples from an industrial heating facility at Aarau and a municipal incinerator in Zurich, both in Switzerland, were analyzed. Both CDDs and CDBFs were found in both locations, the levels being 0.3 and 0.1 ppm for the Aarau and Zurich samples respectively, and were one-third to one-half the total CDDs present. The levels of PCBs were the same as for CDBFs. Polychlorinated naphthalenes were also present in smaller quantities. The CDBF isomer profile from flyash was very similar to that from pyrolysed commercial PCBs, suggestive of a common source. Eighteen tri-, 21 tetra- (mainly the 2,3,7,8-), 17 penta- (including the toxic 1,2,3,7,8- and 2,3,4,6,8-), 7 hexa- and 4 hepta- (1,2,3,4,6,7,8- most abundant) CDBFs were detected. Flyash

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samples contained large amounts of 2,3,4,6,8- and 1,2,3,4,8-penta- and other penta-isomers relative to pyrolysed Aroclor. These data support the levels of CDBFs detected in municipal incinerator flyash and flue gases by Olie, et al. (1977) and Buser and Bosshardt (1978). Olie, et al. (1977) also detected large amounts of chlorobenzenes and chlorophenols in the flyash of municipal incinerators in the Netherlands, but did not provide any quantitative data. The Dow Chemical Company in 1978 and Bumb, et al. 1980 suggested that CDDs were ubiquitous products of the combustion of all chlorinated material, including that found in municipal incinerators. Flyash from two Japanese, one Dutch and two Canadian municipal incinerators were analysed for many compounds (Eiceman, et al. 1979). Dibenzofuran itself was found only in a Canadian sample which also contained tetra-, penta-, hexa-, and hepta-CDBFs (Table 4.17). The numbers quoted in Table 4.17 are relative only and do not give information on absolute concentrations. The remarkable feature is that, in general, CDBFs predominate over CDDs for the four- and five-chlorine containing isomers for one Canadian and the two Japanese samples but CDDs predominate for six- to eight-chlorine containing isomers. This is very similar to the results obtained for levels of CDDs and CDBFs in chlorophenols (see Table 4.13). PCBs were also found in the Ontario 2 and The Netherlands sample. The latter was donated by Dr. Hutzinger and may have been the sample investigated by Olie, et al. (1977). Combustion in the municipal incinerators sampled occurred in the temperature range 750° to 900°C. Higher temperatures may solve the CDBF residue problem as indicated by a

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Table 4.17. Comparison of Mass Spectral Abundances of Corresponding CDBFs and CDDs in Fly Ashes (Eiceman, et al. 1979)

Sample		Mass Spectral Abundances									
		Tetra		Penta		Hexa		Hepta		Octa	
		CDBF	CDD	CDBF	CDD	CDBF	CDD	CDBF	CDD	CDBF	CDD
Ontario, Canada	(1)	3272	1396	5697	2177	1415	4385	967	1524	-	-
	(2)	-	-	-	-	-	-	-	-	-	-
Japan	(1)	789	1038	3691	-	1069	1856	2389	2603	1120	4126
	(2)	-	5561	3827	-	-	6378	2555	4391	2341	4126
Netherlands		-	-	-	-	-	-	-	1808	-	8178

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study of the PCB, CDBF, and CDD content of the residual ash of a cement kiln. Residual PCB of approximately 10 mg/kg was detected for a chamber pyrolysis time of five seconds at 700 to 1000°C (Ahling and Lindskog, 1978) but this was drastically lowered at 1400 to 1450°C (Ahling, 1979). No PCBs were found in the flue gases, and no CDDs or CDBFs were found in the kiln residues, although peaks corresponding to the expected retention time for octachlorodibenzofuran did appear. No PCBs were detected in one study of the municipal sewage sludge ashes from the incinerators of ten American cities but CDDs and CDBFs were not sought (Furr, et al. 1979). The polybrominated biphenyl, Firemaster FF-1, when pyrolysed for 20 minutes at 380 to 400°C in open glass tubes, produced 40 ppm tetra- and 4 ppm penta-BDBFs based on PBB content. Only trace amounts (around 1 ppm) were found if the pyrolysis was done in a nitrogen atmosphere (O'Keefe, 1978). It was postulated that since 2,4,5,2',4',5'-hexabromobiphenyl was the major hexabromobiphenyl present, then nearly all of the tetrabromo-isomer was the 2,3,7,8-isomer. The larger yield is expected from the weaker ring carbon-bromine bond relative to that of carbon-chlorine.

Chlorodiphenylethers are also common contaminants of PCBs. It was found that any degradation of the 2,4,2',4'-, 2,3,4'5'-, 2,4,6,4'-, 2,4,5,4'-tetrachlorodiphenyl ethers at 380°, 770° and 980°C had to be less than one percent (Norstrom, et al. 1977).

Lindahl, et al. (1980) observed yields of 0.7 to 4.5 percent between 500° and 600°C for various chlorodiphenylethers.

Chlorophenolates burned for fifteen minutes on birch leaves or wood wool, or heated at 280°C for thirty minutes, evolved CDD's but not many CDBFs (Rappe and Marklund, 1978). Originally, both

types of formulations studied (Servarex Teknisk and Kymmene KY-5, both containing 5 percent 2,4,6-tri-, 50 percent 2,3,4,6-tetra-, and 10 percent penta-chlorophenols as the sodium salts) contained 10 ppm each of tetra-, penta-, and octa-CDBFs and 70 ppm each of the hexa- and hepta-CDBFs, with 40-50 isomers present (see Section 4.6.2.2; Table 4.12). The burnt samples produced only ten isomers and levels were lower than the original levels (Table 4.18). Nevertheless, the major tetra-CDBF (unknown) increased 100-fold during burning (from 0.04 to 5 ppm) and two others were not in the original formulation. The 2,3,7,8-isomer was a very minor component, e.g., in the starting material, 0.1 percent of the total CDBFs. When the pure phenols were micropyrolyzed, no CDBFs could be detected. Thus, the newly formed CDBFs had to arise from impurities in the technical products, e.g., PCBs, but not chlorodiphenylethers (Norstrom, et al. 1977).

The production of CDDs and CDBFs from the 2-butoxyethyl ester of 2,4,5-T was studied by pyrolyzing the ester for 0.6 to 1 second when the ester (1 kg) was mixed with leaves or sawmill wood chips (Ahling, et al. 1977). The CDBF levels usually exceeded CDD levels (Table 4.18) but not between 100 and 625°C, even though CDBFs were more concentrated in the original formulation (which also contained 47 mg/g 2,4,5-T, 230 ug/g of 2,4,5-trichlorophenol, 12 ug/g pentachlorophenol in addition to the CDBFs and CDDs cited in Table 4.19). It was thought that the chlorophenols could not be the source of the CDDs or CDBFs but that a complex mechanism was involved.

It might be noted here that stack emissions and flyash from a

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Table 4.18. Levels of Trapped CDBFs and CDDs on Charcoal from Burning Chlorophenolate-Impregnated Leaves and Wood Wool (Rappe and Marklund, 1978)

Commercial Chlorophenol	Substrate	CDBF and CDD collected in ug/g chlorophenate									
		Tetra		Penta		Hexa		Hepta		Octa	
		CDBF	CDD	CDBF	CDD	CDBF	CDD	CDBF	CDD	CDBF	CDD
2,3,4,6-Tetra- (Servarex)	Birch leaves	<10*	35	<10*	90	<70*	80	<70*	8	<10*	0.3
	Wood Wool	<10*	96	<10*	120	<70*	110	<70*	65	<10*	1.2
(Pure)		<10*	38	<10*	84	<70*	82	<70*	8	<10*	0.4
2,4,6-Trichloro-	Birch leaves	-	2100	-	5	-	1	-	3	-	6
Pentachloro-	Birch leaves	-	5	-	14	-	56	-	172	-	710

* Signifies the amount in the original formulation

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Table 4.19. Production of CDDs and CDBFs after 0.6 to 1.00 second Pyrolysis in Air of 2-Butoxyethyl-2,4,5-trichlorophenoxyacetate (Ahlim, et al. 1977)

Temperature (°C)	CDBF/CDD amounts (mg/kg)											
	Tetra		Penta		Hexa		Hepta		Octa		Total	
	CDBF	CDD	CDBF	CDD	CDBF	CDD	CDBF	CDD	CDBF	CDD	CDBF	CDD
25	0.13	0.018	0.008	0.007	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.36	0.040
100	1.0	2.5	0.5	<0.5	<0.4	<0.5	2.1	<0.5	<0.4	<0.5	4.6	4.5
500	0.4	2.2	1.5	<0.5	2.0	1.3	<0.7	<0.5	<0.7	<0.5	5.3	5.0
625	0.2	0.4	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	1.4	1.6
675	8.0	2.3	7.1	<0.5	2.8	<0.5	<0.7	<0.5	<0.7	<0.5	19.3	4.3
800	2.1	0.5	3.0	<0.3	3.3	<0.3	2.4	<0.3	2.3	<0.8	13.1	1.9

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coal/municipal refuse electricity plant have been reported to contain PCBs (ppb levels), chlorophenols, and hexachlorobenzene (approximately 5 pph). Only 20 percent of the PCB fraction could be identified, and although CDDs or CDBFs were not sought, it is likely they were present (Vick, et al. 1978).

Concern has been expressed over the formation of CDDs during the cooking of food. Liver, steak, and hamburger from female Holsteins were examined, but only raw liver contained significant amounts of CDDs; levels decreased when the liver was cooked. Variation from sample to sample was high so that no firm conclusions could be reached (Zabik and Zabik, 1980). The situation is rather different for the CDBFs, especially if the tissues contain PCBs. The CDBFs should be formed from PCBs during cooking, via the mechanisms cited in Section 4.4.1.2.2, and verification of this is important. Cooking appears to decrease PCB levels in various foods (e.g., poultry and milk) as well as PBB levels in poultry (Zabik, et al. 1978). The decline appears to be related to the amount of fat rendered in the cooking process, although a complete mass balance should be made using GC/MS.

Another source of CDBF exposure is electrical fires where PCBs are used in insulation. A fire in Toronto, Canada in 1978, released PCBs into the air. Tetra-CDBFs were detected (isomer unknown) in the soot (Ministry of the Environment, Province of Ontario, Canada, 1978). Risk of exposure to CDBFs is high for firemen fighting electrical fires and this possibility should be investigated. Other occupational exposures involving PCBs that

should also be investigated include: chemical plants handling or manufacturing halogenated aromatics: factories making or repairing transformers or capacitors, using casting waxes, or having heat-exchange systems; and during incineration of halogenated aromatics.

4.4.2.8 Other Modes of Formation of Halo-DBFs in the Environment

The thermal route is not an important natural mode of environmental production of halo DBFs.

Perhaps the most important potential source of environmental contamination is the photochemical production of halo-DBFs from polyhalogenated biphenyls. Hutzinger (1972) observed 0.2 percent 2-chloro-DBF production after seven days of ultraviolet irradiation (310 nm) of aqueous solutions of 2,5,2'5'-tetrachloro- and 2,5-dichloro-biphenyls (5mg/liter). These products were confirmed by Crosby and Moilanen (1973). However, Hutzinger (1972b) found no CDBFs after some aqueous PCB samples (167 mg/liter) were exposed to sunlight for more than two months. This discrepancy may have been caused by concentration effects. Also, 2,4,6,2',4',6'-hexachloro-biphenyl irradiated in methanol did produce some CDBFs; however, the latter were not quantitated (Andersson, et al. 1972). These photochemical products mimic the formation of CDBFs in alkaline solutions of 2,2'-dihydroxybiphenyl in water (Cullinane, et al. 1934; Zahn and Schimmelschmidt, 1940; Case and Schock, 1943). This behavior might imply the necessity of an orthohydroxy-PCB as a reaction intermediate or perhaps the condition that the excited state is more alkaline than the ground

state. There is also a wavelength dependence of the yield of the products. Irradiation at 254 nm (mercury arc) decomposes the CDBF products, but only slowly at 310 nm or at the wavelengths encountered at sea level for sunlight, or for a solar simulator. Triplet sensitizers, for (example, 4,4'-dichlorobenzophenone) may induce faster decompositon as observed in methanolic solution for the photodecomposition of 2,8-di-CDBF (Crosby and Moilanen, 1973). Thus, the presence of other compounds is also important.

The absence of CDBFs on irradiating aqueous PCBs with high energy gamma rays from ^{60}Co (up to 10 Mrad) is thus understandable since high energies degrade any CDBFs formed. The irradiated solutions were also less toxic to striped shrimp than than were the original solutions. Similarly, PCBs were destroyed by Fenton's reagent which produces hydroxyl radicals (Sunada, 1972).

Crosby, et al. (1973) also detected octa-CDD after the ultraviolet irradiation of some chlorophenols, but CDBFs were not sought. Chlorinated o-phenoxyphenols (predioxins) which are common impurities (1 to 5 percent) in chlorophenols also produce CDDs after ultraviolet irradiation (Nilsson, et al. 1974) but again, CDBFs were not sought specifically. The possibility that toxic tetra- and penta-CDBFs could be formed by the reductive dechlorination of higher CDBFs in organic solvents was suggested by Plimmer, et al. 1971, 1973. This topic is discussed in more detail in Section 4.5.3.

Another source of CDBFs through photodecomposition is from the chlorinated diphenyl ethers, which are often present at levels

of 100 ppm in commercial chlorophenols. Irradiation of 1000-ppm solutions in methanol, ethanol, or n-hexane with light of 248 to 579 nm caused cyclization in diphenyl ethers containing at least one ortho-chlorine. Reductive dehalogenation was enhanced in hexane. Although no yields were explicitly given, the degradation was characterized by an induction period and then decomposition obeying a first order kinetic law (Norstrom, et al. 1976, 1977; Choudhry, et al. 1977).

4.4.3 Occurrence of Dibenzofuran and Its Simple Derivatives.

Dibenzofuran and its alkyl derivatives have been found in coal tar (Kruber, et al. 1932, 1936, 1938, 1940, 1943; Forney, et al. 1974; Rusin and Kulczycka, 1975) from which they were first isolated, flue dust samples from hard-coal coking plants where dibenzofuran made up between 0.04 and 0.42 percent of the dust (Masek, 1976), grate ash from combusted coal (Lee, et al. 1977), in oxidized bituminous coal (Hayatsu, et al. 1975), the flyash and stack emissions from combustion of coal plus municipal refuse (Vick, et al. 1978), and in process water from coal conversion (Schmidt, et al. 1974). They have also been found in petroleum distillates (400-700°C) and made up between 0.5 and 0.7 percent, mostly as the dihydro derivatives (Snyder, 1969), flame soots (Crittenden and Long, 1978), incinerator flyash (Eiceman, et al. 1979), tobacco smoke (Hoffmann and Mazzola, 1970; Lee, et al. 1976), marijuana cigarette smoke at 1 ng/100 cigarettes (Lee, et al. 1976), volatiles but not oils of cotton plants (Hedin, et al. 1975) and "Katsuobushi" dried bonito used as a food flavoring agent in Japan (Nishibori and Kasahara, 1978). Very few

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