Are Dioxins and Furans Predominantly Anthropogenic?

Claude Fortin and David Caldbick. Commercial Chemicals Evaluation Branch, Environment Canada. Ottawa, Ontario Canada. K1A 0H3

Abstract

This paper presents a scientific rationale demonstrating that polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are predominantly anthropogenic. The weight of available evidence on the release and resulting environmental concentrations of PCDDs and PCDFs indicates that the concentrations of PCDDs and PCDFs measured in the environment result largely from human activity.

Introduction

The Toxic Substances Management Policy (TSMP) outlines the Canadian government's approach to the management of toxic substances [1]. The policy presents a management framework based on two key objectives: virtual elimination from the environment of toxic substances that are persistent, bioaccumulative, and primarily the result of human activity (Track 1), and life-cycle management of other toxic substances and substances of concern to prevent or minimise their release into the environment (Track 2). Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) were assessed against the criteria for selection of Track 1 substances under the Canadian Toxic Substances Management Policy (TSMP).

The analysis presented in this paper is based on a review of scientific information covering both specific congeners and the class of substances usually referred to as polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDDs and PCDFs). Both the number of chlorine atoms and their positions determine the physical and chemical properties, and therefore the fate and toxicity of a given congener. There are 75 PCDD and 135 PCDF congeners for a total of 210. The most studied congener is 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. The range of selected values for certain physical and chemical properties of PCDDs and PCDFs are presented in Tables 1a and 1b.

Assessment: Are dioxins and furans predominantly anthropogenic?

For a substance to be "predominantly anthropogenic", as defined in th TSMP, its concentration in the environment has to result largely from human activity [1]. Since quantitative data describing the relative importance of anthropogenic and natural sources of a given substance are not always available, a predetermined numerical parameter has not been specified in the TSMP for this criterion. Assessments are based on expert judgement using the weight of available evidence.

The relative importance of natural versus anthropogenic sources of PCDDs and PCDFs is a subject of debate in the scientific literature. The arguments presented in that debate are usually based on either monitoring data documenting the spatial or temporal variations in the concentrations of PCDDs and PCDFs in environmental media, or estimates of releases from various sources. The following presents the evidence available for both approaches.

Trends in the concentrations of PCDDs and PCDFs in space and time

Concentrations of PCDDs and PCDFs in sediment, soil and preserved tissue can be followed over time. The information available to compare the concentrations of PCDDs and PCDFs in various media over time and space are summarised in Table 2.

The data consistently show that PCDD and PCDF concentrations have greatly increased since the beginning of the century. These findings have been reported for sediments in North America and Europe, and from archived soil and plant samples in Britain (References in Table 2). Various authors have attributed this phenomenon to an increase in the release of these substances to the environment due to the production, use and release of chlorinated organic compounds and the incineration of solid wastes.

The analysis of preserved human tissue also suggests that the concentrations of PCDDs and PCDFs result from relatively recent phenomena. Tissues from mummified remains of Chilean Indians from approximately 2800 years ago contained no PCDDs or PCDFs above the analytical background level (typically < 5 parts per trillion) [12]. In discussing their results, the authors stated that the maximum level measured in their study was lower by a factor of at least 20 than the lowest value found in humans from industrialised countries. Taking into account that the samples date from a time when cooking was done over open fires (therefore resulting in high exposure to wood smoke), the authors concluded that PCDDs and PCDFs "originating in fires burning clean fuels probably do not significantly contribute to the body burden of these materials in modern humans". These authors state that the distribution of fatty acids in the samples suggests "minimal bacterial degradation of the PCDDs and PCDFs they were analysing.

The concentrations of PCDDs and PCDFs were measured in tissue from two Inuit women whose corpses had been preserved for more than 400 years [13, 20]. Concentrations measured were much lower than those found in modern individuals. Despite the poor ventilation in igloos, and the use of oil for cooking and heating which resulted in high exposure to products of incomplete

combustion, the authors concluded that the tissue from these women provided an integrated picture of the potential for exposure to, and accumulation of, PCDDs and PCDFs. The possibility of chemical degradation of PCDDs and PCDFs over time was discussed and the authors concluded that degradation of these compounds is not substantial [20].

Concentrations of PCDDs and PCDFs from urban or industrialised sites are generally higher than those from rural or non-industrialised zones. For example, concentrations of PCDDs and PCDFs are lower in the sediment of Siskiwit Lake, which is located on Isle Royale, near the northern shore of Lake Superior, than those measured in the lake Michigan and Erie [5]. In addition, concentrations of PCDDs and PCDFs in sediment from Lake Huron were highest in samples collected near urban areas and lowest in those from the open lake [3].

For atmospheric concentrations, the results of a monitoring program for the City of Detroit incinerator indicate that the mean concentrations of PCDDs and PCDFs (expressed in terms of 2,3,7,8-TCDD toxic equivalent [TEQ]) at a remote site (Walpole Island) were approximately three times lower than those measured either directly downwind from the Detroit incinerator or at a site influenced by other incinerators [10]. Recent (1994/95) measurements from a Canadian ambient air sampling program show that mean concentrations of PCDD (expressed in terms of 2,3,7,8,-TCDD toxic equivalent) range from 8 to 14 fg/m^3 at rural remote sites and from 90 to 260 fg/m^3 at urban sites [10].

The results of several authors show that the ambient air concentrations of PCDDs and PCDFs at various sites in the United States, Germany, and the Netherlands were consistently higher near industrial sites or near municipal waste incinerators than those measured in suburban or rural areas [11].

The concentrations of PCDDs and PCDFs in adipose tissue and milk samples from people living industrialised countries, such as Japan and the United States were found t be higher than those from less industrialised countries such as India and Vietnam [18,19]. The results from Vietnam show that the concentrations of PCDDs and PCDFs in individuals living in areas sprayed with Agent Orange, a defoliant heavily contaminated by PCDDs and PCDFs, were much higher than those living elsewhere in the country [18].

Estimates of releases of PCDDs and PCDFs

Several studies estimating the relative importance of sources of PCDDs and PCDFs have been published recently [21, 22, 23]. These studies identify municipal and medical waste incinerators as the most significant anthropogenic sources of PCDDs and PCDFs. Only two authors attempted to compare the relative contribution of anthropogenic and natural sources of PCDDs and PCDFs. In the United States, the atmospheric releases of PCDDs and PCDFs from forest and agricultural fires were approximately one tenth of the releases from anthropogenic sources [21], while forest fires were the largest single source of emissions of PCDDs and PCDFs in Canada [23]. This conclusion was based on the assumption that concentrations of dioxins in particulates from

residential wood combustion chimneys provided the most useful basis to estimate the releases of PCDDs and PCDFs from forest fires. That assumption has since been challenged. The U.S. EPA considered that using chimney soot as a surrogate to estimate the release of PCDDs from forest fires will result in overestimating these releases because "dioxin (PCDD) levels in soot are likely to be much higher than what is actually emitted on particulates due to accumulation in chimneys" [24].

The generation and release of PCDDs and PCDFs in combustion processes can be affected by the presence of PCDDs and PCDFs in feedstocks, the presence of chlorinated precursors in fuels and feed stock, and *de novo* synthesis from unrelated carbon and inorganic chlorine [25]. Although low levels of PCDDs and PCDFs have been measured from forest fires, these may not necessarily be associated with natural sources. These authors suggest that the PCDDs and PCDFs could be either resuspended from previous deposits or be formed during the combustion process from anthropogenic chlorinated substances previously deposited [26].

Other factors to take into account when estimating the relative importance of anthropogenic and natural sources of PCDDs and PCDFs include the fact that, in general forest fire control programs have reduced the annual combustion of forest and agriculture biomass while anthropogenic sources (e.g., incineration and combustion for energy generation purposes) have increased [21]. Other authors also suggest that current emission inventories of PCDDs and PCDFs underestimate the amounts of these substances released from diesel fuel combustion and from recycling of scrap iron suggesting that the relative importance of natural sources is probably overestimated [27, 16, 28].

Conclusion

The monitoring record clearly and consistently indicates that although natural sources can contribute to a background level of PCDDs and PCDFs, they cannot account for: 1) the large increase in the concentrations measured in various environmental media since the beginning of the century, nor 2) the higher concentrations measured in various media in industrialised as opposed to non-industrialised areas.

On the basis of the information reviewed, it is concluded that the main contemporary sources of PCDDs and PCDFs are anthropogenic. Therefore, the concentrations of these substances measured in the environment result predominantly from human activities.

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Table 1a Summary of Selected Physical and Chemical Properties for Groups of Dioxin Congeners [2].

Congener group	Molecular weight (g/mol)	Vapour pressure (Pa 10^{-3})	Water solubility (mg/m^3)	Log K_{ow}
M_1CDD	218.5	73-75	295-417	4.75-5.00
D_2CDD	253.0	2.47-9.24	3.75-16.7	5.60-5.75
T_3CDD	287.5	~1.07	~8.41	~6.35
T_4CDD	322.0	0.00284-0.275	0.0193-0.55	6.60-7.10
P_5CDD	356.4	~0.00423	~0.118	~7.40
H_6CDD	391.0	~0.00145	~0.00442	~7.80
H_7CDD	425.2	~0.000177	~0.0024	~8.00
O_8CDD	460.0	0.000953	0.000074	8.20

Table 1b Summary of Selected Physical and Chemical Properties for Groups of Furan Congeners [2].

Congener group	Molecular weight (g/mol)	Vapour pressure (Pa 10^{-3})	Water solubility (ng/m^3)	Log K_{ow}
D_2CDF	237.1	~14.6	~14.5	~5.44
T_4CDF	306.0	~0.199	~0.419	~6.1
P_5CDF	340.4	~0.0172	~0.236	~6.5
H_6CDF	374.8	0.0031-0.0036	0.0177-0.0083	~7.0
H_7CDF	409.3	0.00054-0.00057	~0.00135	~7.4
O_8CDF	443.8	0.000101	0.00116	8.0

Table 2 **Comparison of the Concentration of PCDDs and PCDFs found in various Environmental media over time and space.**

A) Temporal trends

Sediment (ng/kg)

Congeners			**Reference**
	Lake Huron (approx. 1940)	Lake Huron (1975)	3) data presented for samples offering best time resolution according to the authors
H_7CDD	< 100	≈ 300	
H_7CDF	< 100	≈ 300	
O_8CDD	< 100	≈ 1300	
	Georgia Strait (1955)	Georgia Strait (1970)	4)
O_8CDD	≈ 100	≈ 380	
2,3,7,8-TCDF	≈ 2	≈ 10	
	Howe Sound (1955)	Howe Sound (1970)	4)
O_8CDD	≈ 105	≈ 450	
2,3,7,8-TCDF	≈ 3	≈ 8	
	Siskiwit Lake (1935)	Siskiwit Lake (1982)	5)
T_4CDF	<0.4	15	
$\sum H_7CDD$	8.2	70	
$\sum H_7CDF$	1.6	20.2	
O_8CDD	54	560	
	Baltic Sea (1938)	Baltic Sea (1985)	6)
$\sum T_4CDF$	27.7	186.0	
$\sum T_4CDD$	5.9	34.3	
$\sum P_5CDF$	20.0	180.0	
$\sum P_5CDD$	6.7	66.6	
$\sum H_6CDF$	20.3	164.4	
$\sum H_6CDD$	11.7	134.9	
$\sum H_7CDF$	19.6	129.9	
$\sum H_7CDD$	8.8	212.0	
O_8CDF	35.5	73.0	
O_8CDD	11.9	273.0	
PCDD (75% OCDD)	Green Lake, N.Y. (1920)	Green Lake, N.Y. (1980)	7) values estimated from

	< 50	≈ 900	graphic presented by the authors

Soil (ng/kg)

Congeners	Rural England (1893)	Rural England (1986)	**Reference**
∑TCDF	3.2	10.4	8)
∑TCDD	0.3	1.8	
∑P_5CDF	3.5	11.2	
∑P_5CDD	0.9	3.9	
∑H_6CDF	3.9	9.9	
∑H_6CDD	2.2	9.0	
∑H_7CDF	1.9	6.4	
∑H_7CDD	3.2	13.0	
OCDF	1.1	4.9	
OCDD	11.0	25.0	
∑PCDD/F	31	95	

Plants (ng/kg)

Congeners	Rural England 1891-1900	Rural England 1960-1970	**Reference**
∑TCDF	2.4	3.9	8)
∑TCDD	0.6	1.4	
∑P_5CDF	3.1	3.9	
∑P_5CDD	1.2	3.0	
∑H_6CDF	1.0	3.8	
∑H_6CDD	1.4	7.1	
∑H_7CDF	0.5	8.4	
∑H_7CDD	0.9	21.0	
OCDF	0.3	5.0	
OCDD	0.8	39.0	
∑PCDD/F	12	96.5	

B) Space Comparison:

Sediment (ng/kg)

Congeners	Siskiwit Lake	Lake Huron (43 30'N,81 55'W)	Lake Michigan (43 43'N, 86 38'W)	Lake Erie (42 32'N, 79 45"W)	**Reference**
OCDD	560	310	780	2000	9)

Air

Congeners			**Reference**
O_8CDD (pg/m^3)	Walpole Island-rural 1.1	Windsor-urban 2.8	10)
	Trout Lake Wisconsin-rural	Bloomington, Indiana -suburban	11)
$\sum T_4CDF$ (fg/m^3)	83	340	
$\sum T_4CDD$	0.3	5.3	
$\sum P_5CDF$	67	200	
$\sum P_5CDD$	6.1	51	
$\sum H_6CDF$	31	120	
$\sum H_6CDD$	52	140	
$\sum H_7CDF$	12	93	
$\sum H_7CDD$	93	360	
O_8CDF	6.0	36	
O_8CDD	160	2200	

Tissue (human) (pg/g)

Mummified human remains-Chile (2800 years before present)	Modern human	Reference
2,3,7,8-D nd* 2,3,7,8- F nd O_8CDD 18.2 **	T_4CDD/F 3-10 O_8CDD 400-1000	12)
Mummified human remains- Inuit T_4CDF/D-H_6CDF/D- nd H_7CCDF - 6 ± 6	 T_4CDD 3-10 P_5CDD 10-32 O_8CDD 414-1100	13)

*nd = not detected (theoretical detection limit = 3X noise limited background)

** value for one sample. Other samples generally below analytical background level of 5 pg/g

Atmospheric concentrations (fg/m3) of PCDDs/PCDFs as Reviewed by Edgerton [26].

Site	Type	Total PCDD/PCDF	Reference
Bloomingtom, Indiana (USA)	suburban	2200	14)
Trout Lake, Wisconsin (USA)	rural	510	14)
W. Germany	industrial	8700	15)
W. Germany	industrial	37000	16)
W. Germany	suburban	2900	16)
W. Germany	tunnel	29000	16)
Netherlands	1 km from MWI*	47000	17)
Netherlands	2 km from MWI*	9100	17)

* Municipal Waste Incinerator

Tissue-Adipose (human) (pg/g)

Congeners	Non-industrialised Northern Vietnam (not-sprayed with Agent Orange)	Non-industrialised Southern Vietnam (sprayed with Agent Orange)	Industrialised Canada (1976)	Industrialised Canada (1980)	Industrialised New York 1982-83	**Reference**
2,3,7,8-D	nd	18	6.4	10	7.2	18)
2,3,4,7,8-F	7.2	12	15	18.4	14.3	
1,2,3,7,8-D	nd	9.1	10	13.2	11.1	
1,2,3,7,8/ 1,2,3,6,7,8-F	7.7	33	16	17.3	31.3	
1,2,3,5,7,8-D	5.6	57	8.7	90.5	95.9	
1,2,3,4,6,7,8-D	17	121	135	116	164	
1,2,3,4,6,7,8-F	4.2	17	30	39.4	16.5	
1,2,3,4,5,7,8,9-D	52	900	850	611	707	

Human milk
(pg/g) wet weight

Congeners	United States (New York)	India	Japan	**Reference**
2,3,7,8-F	nd; 0.16	0.13 ; 0.2 ; 0.31	0.10; 0.08	19) (values presented for 2 or 3 samples per country. Results for HpCCDD, HpCCDF, OCDD and OCDF not presented beause of contamination problem acknowledged by the authors)
2,3,7,8-D	0.29; Nd	nd ; nd; nd	0.06; 0.19	
2,3,4,7,8-F	0.36; 0.33	0.06 ; 0.15 ; 0.31	0.74; 0.80	
1,2,3,7,8-D	nd; 0.14	nd ; 0.10 ; nd	0.13; 0.15	
Total HxCDDs	1.81; 1.27	0.46; 0.78; 0.73	1.02; 1.32	
Total HxCDFs	nd; 0.39	0.29; 1.1; 0.48	0.30; 0.27	