Bull. Environ. Contam. Toxicol. (1992) 48:789–794

Environmental Contamination and Toxicology

Polychlorinated Dibenzo-*p*-dioxins (PCDDs) and Dibenzofurans (PCDFs) in Mainstream and Sidestream Cigarette Smoke

Göran Löfroth[1] and Yngve Zebühr[2]

[1]Environmental Health Unit, Nordic School of Public Health, POB 12133, S-402 42 Gothenburg, Sweden and [2]Department of Analytical Chemistry and Department of Zoology, University of Stockholm, S-106 91 Stockholm, Sweden

Widespread interest in polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) appeared after the disclosure that the 2,3,7,8-tetrachlorodibenzo-p-dioxin can be present in commercial chlorophenol derivatives (Courtney et al. 1970) and the detection of PCDFs in commercial polychlorinated biphenyls (Vos et al. 1970). Formation of PCDDs and PCDFs have since been detected in a range of processes involving carbonaceous materials, chlorine and heat such as waste incineration (Olie et al. 1977), leaded gasoline combustion (Marklund et al. 1987), pulp and paper production (Kuehl et al. 1987) as well as in model experiments with the combustion of hydrocarbons in the presence of hydrogen chloride (Eklund et al. 1988; De Fre and Rymen 1988). Due to the fact that tobacco contains substantial amounts of chlorine (Jenkins et al. 1985; Martin 1988) and an early observation of some PCDDs in tobacco smoke (Bumb et al. 1980), we decided to analyze PCDDs and PCDFs in mainstream and sidestream cigarette smoke. Due to the high costs, the study was limited to one common Swedish commercial cigarette brand. Since the initiation of this study, two reports on PCDDs and PCDFs in cigarette smoke, with widely different results, have appeared (Muto and Takizawa 1989; Ball et al. 1990).

MATERIALS AND METHODS

The cigarettes were smoked in the standardized manner with one 2 s and 35 mL puff per minute until the indicated butt length was reached. The mainstream smoke was collected on glass fiber filters (35 mm diameter; Stora Filter Products, Sweden) followed by two polyetherurethane (PUF) plugs (18 mm diameter, 30 mm length and 25 kg/m^3 density). The sidestream smoke, emitted into a 190 L acrylic plastic box, was likewise collected on glass fiber filters (90 mm diameter) followed by two PUF plugs with a flow rate of about 10 m^3/h. The glass fiber filters were changed after each cigarette for mainstream smoke and after every second one for sidestream smoke. The PUF plugs were maintained for the entire sample consisting of 20 cigarettes. A blank sample with no smoking was col-

Send reprint requests to G. Löfroth at the above address.

lected in the same manner as the sidestream smoke sample. The filters and the PUF plugs were kept sealed at -20 °C until they were analyzed. Filters and PUF plugs were combined in the analysis. The extraction of samples, HPLC fractionation and GC/MS analysis for PCDDs and PCDFs were performed after addition of ^{13}C-labelled internal standards as described earlier by Zebühr et al. (1989) for ambient air samples.

The cigarette brand is nominally labelled as giving 17 mg carbon monoxide, 21 mg tar and 1.6 mg nicotine in mainstream smoke. Each cigarette weighed about 1 g, incl. the filter. The total amount of tobacco smoked for the sample was 13.5 g, i.e. 0.675 g per cigarette. The average particle collection on filters was 17.3 mg per cigarette for mainstream and 14.1 mg for sidestream.

The International Equivalency Factor (I-TEF) values (Kutz et al. 1990) have been used to compute the International Toxicity Equivalents (I-TEQ). The current I-TEF values are zero for most of the isomers, but non-zero for isomers containing chlorine in all of the 2,3,7 and 8 positions. The rational for the use of I-TEF has been reviewed by Safe (1990).

RESULTS AND DISCUSSION

The analytical results are summarized in Table 1 in which the amounts of isomers with non-zero I-TEF values and the total quantity of congeners are given. Using the current I-TEF values, it can be calculated that the mainstream smoke from 20 cigarettes contained about 18 pg I-TEQ (i.e. about 1 pg/cigarette) and sidestream smoke about 39 pg (i.e. about 2 pg/cigarette). It can be further estimated that no particular isomer contributed more than 20 percent to the total I-TEQ. Most components were below the detection level (0.3-1.3 pg) in the parallelly analyzed blank sample with the exception of 6.8 pg 1234678-hepta-CDD, 4.0 pg 1234678-hepta-CDF and 7.3 pg octa-CDD giving an I-TEQ for the blank sample of <1.9 pg. The recovery of the added ^{13}C-labelled internal standards was for all samples in the range 69-116 percent.

Bumb et al. (1980) performed dioxin analysis on mainstream smoke collected on a simple silica column and detected hexa-, hepta- and octa-CDDs just at or slightly above the detection limit. Muto and Takizawa (1989) have used low resolution mass spectrometry for the analysis of PCDDs in tobacco smoke obtained by a continuous smoking process in which all the cigarette tobacco gave rise to mainstream smoke. They reported that hepta-CDD was the most abundant congener being more than 90 percent of the total amount of PCDDs.

Ball et al. (1990) have screened ten German cigarette brands for PCDDs and PCDFs in mainstream smoke obtained by the regular standardized smoking procedure. They reported an average amount of all congeners to about 10 pg per cigarette corresponding to about 0.1 pg I-TEQ. These values are about ten times less than those obtained in the present study, 75 pg and 1 pg I-TEQ per cigarette for mainstream smoke. Apart from this difference in amounts, the con-

Table 1. PCDDs and PCDFs in cigarette smoke.

Component[a]	Isomer	I-TEF[b]	Mainstream	Sidestream
			pg per 20 cigarettes	
TCDD	2378	1	0.56	1.4
	all	-	12.1	13.4
PeCDD	12378	0.5	3.0	6.3
	all	-	21.4	42.7
HxCDD	123478	0.1	2.0	3.8
	123678	0.1	6.8	12
	123789	0.1	5.0	11
	all	-	50.4	104
HpCDD	1234678	0.01	121	245
	all	-	246	426
OCDD	12345678	0.001	441	776
Σ PCDDs			770	1360
TCDF	2348[c]/2378	0.1	24	41
	all	-	90	115
PeCDF	12348[c]/12378	0.05	6.7	16
	23478	0.5	6.8	12
	all	-	64.6	127
HxCDF	123479[c]/123478	0.1	26	77
	123678	0.1	9.5	25
	123789	0.1	2.7	7.8
	234678	0.1	4.1	10
	all	-	106	258
HpCDF	1234678	0.01	200	470
	1234789	0.01	51	100
	all	-	396	956
OCDF	12345678	0.001	65	214
Σ PCDFs			720	1670
Σ PCDDs+PCDFs			1490	3030

a) T, tetra; Pe, penta; Hx, hexa; Hp, hepta; O, octa.
b) International Toxicity Equivalency Factor, Kutz et al. (1990).
c) These isomers have zero I-TEF-values but are not separated in the analysis.

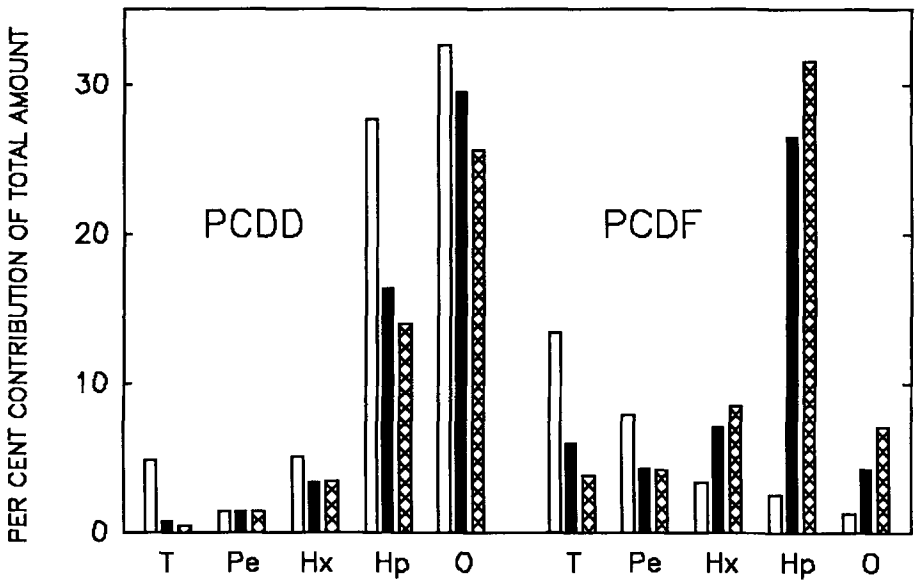

Figure 1. The congener profile, given as percent of the total amount of PCDDs and PCDFs, for mainstream smoke reported by Ball et al. (open bar), mainstream smoke in the present study (filled bar) and sidestream smoke in the present study (hatched bar).

gener profile reported by Ball et al. (1990) and the congener profiles of mainstream and sidestream smoke obtained in the present study are relatively similar (Figure 1).

The formation of PCDDs and PCDFs during smoking is likely dependent on the smoking process and the tobacco chlorine concentration. The difference in amounts reported by Ball et al. (1990) and the present study cannot be due to dissimilar smoking processes and it is unlikely that the chlorine concentration is very much different between common German and Swedish cigarettes. A cause for the divergence might be sought in the sample collection. Whereas Ball et al. (1990) smoked 20 cigarettes at a time in three successive batches with a relatively large collection device, the present study was performed with one cigarette at a time with very short teflon tubings between cigarette, filter and XAD plugs in order to minimize losses.

Tobacco smoke contains PCDDs and PCDFs. Irrespective of the exact amount, their presence in mainstream smoke is an additional burden of xenobiotic compounds to the smoker. Their presence in sidestream smoke contaminates the space around the smoker. It is interesting to note that Bumb et al. (1980) detected high levels of dioxins in dust taken from a home electrostatic precipitator which was located in a smoker's home (Lamparski and Nestrick, personal communication).

Acknowledgment. This work has partly been supported by a grant from the Swedish Council for Building Research.

REFERENCES

Ball M, Päpke O, Lis A (1990) Polychlordibenzodioxine und Polychlordibenzofurane in Cigarettenrauch. Beitr Tabaksforsch Int 14:393-402

Bumb RR, Crummet WB, Cutie SS, Gledhill JR, Hummel RH, Kagel RO, Lamparski LL, Luoma EV, Miller DL, Nestrick TJ, Shadoff LA, Stehl RH, Woods JS (1980) Trace chemistries of fire: A source of chlorinated dioxins. Science 210:385-390

Courtney KD, Gaylor DW, Hogan MD, Falk HL, Bates RR, Mitchell I (1970) Teratogenic evaluation of 2,4,5-T. Science 168:864-866

De Fre R, Rymen T (1988) PCDD and PCDF formation from hydrocarbon combustion in the presence of hydrogen chloride. Chemosphere 19:331-336

Eklund G, Pedersen JR, Strömberg B (1988) Methane, hydrogen chloride and oxygen form a wide range of chlorinated organic species in the temperature range 400 C-950 C. Chemosphere 17:575-586

Jenkins Jr RW, Goldey C, Williamson TG (1985) Neutron activation analysis in tobacco and cigarette smoke studies: 2R1 cigarette composition, smoke transferance and butt filtration. Beitr Tabaksforsch Int 13:59-65

Kuehl DW, Butterworth BC, DeVita WM, Sauer CP (1987) Environmental contamination by polychlorinated dibenzo-p-dioxins and dibenzofurans associated with pulp and paper mill discharge. Biomed Environ Mass Spect 14:443-447

Kutz FW, Barnes DG, Bretthauer EW, Bottimore DP, Greim H (1990) The international toxicity equivalency factor (I-TEF) method for estimating risks associated with exposures to complex mixtures of dioxins and related compounds. Toxicol Environ Chem 26:99-109

Marklund S, Rappe C, Tysklind M, Egebäck KE (1987) Identification of polychlorinated dibenzofurans and dioxins in exhausts from cars run on leaded gasoline. Chemosphere 16:29-36

Martin JM (1988) Analysis of selected elements in tobacco by wavelength dispersive X-ray fluorescence spectrometry. J Assoc Off Anal Chem 71:1038-1041

Muto H, Takizawa Y (1989) Dioxins in cigarette smoke. Arch Environ Health 44:171-174

Olie K, Vermeulen PL, Hutzinger O (1977) Chlorodibenzo-p-dioxins and chlorodibenzofurans are trace components of fly ash and flue gas of some municipal incinerators in the Netherlands. Chemosphere 6:455-459

Safe S (1990) Polychlorinated biphenyls (PCBs), dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), and related compounds: Environmental and mechanistic considerations which support the development of toxic equivalency factors (TEFs). Crit Rev Toxicol 21:51-88

Zebühr Y, Näf C, Broman D, Lexen K, Colmsjö A, Östman C (1989) Sampling techniques and clean up procedures for some complex environmental samples with respect to PCDDs and PCDFs and other organic contaminants. Chemosphere 19:39-44

Vos JG, Koeman JH, van der Maas HL, ten Noever de Brauw MC, de Vos RH (1970) Identification and toxicological evaluation of chlorinated dibenzofurans and chlorinated naphthalene in two commercial polychlorinated biphenyls. Fd Cosm Toxicol 8:625-633

Received November 7, 1991; accepted December 15, 1991.