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Dioxin Levels in Mainstream Smoke from Cigarettes with Different TPM Deliveries*

by

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SUMMARY

The presence of dioxin-like compounds, such as chlorinated dibenzodioxins, chlorinated dibenzofurans and chlorinated biphenyls, in mainstream cigarette smoke has been investigated for seven cigarette brands covering a range of 'tar' deliveries from 1 mg to 14 mg. Adjusted per milligram of total particulate matter (TPM), ultra-light cigarettes had the highest concentrations of toxic equivalents (TEQ) of 10 fg/mg TPM. As the 'tar' delivery increased, lower concentration values were found in lights and full-flavor cigarettes. Calculated on the basis of a pack of twenty cigarettes, mainstream smoke from the ultra-lights and lights products produced values around 200 fg TEQ, and the full-flavor brand produced 575 fg TEQ per pack. Levels of TEQ from dioxin-like compounds in the tobacco section of four cigarette brands did not show significant differences and were similar to previous literature findings. [Beitr. Tabakforsch. Int. 21 (2004) 205–209]

ZUSAMMENFASSUNG

Das Vorkommen von Dioxin-ähnlichen Verbindungen, wie z.B. chlorierte Dibenzodioxine, chlorierte Dibenzofurane und chlorierte Biphenyle, wurde im Hauptstromrauch von sieben Zigarettenmarken mit einem Kondensatgehalt von 1 mg bis 14 mg untersucht. Bezogen auf ein Milligramm Gesamtpartikelmasse (TPM = total particulate matter) wiesen „Ultra-Light" Zigaretten mit 10 fg/mg TPM die höchsten Konzentrationen an toxischen Äquivalenten (TEQ) auf. Bei zunehmendem Kondensatgehalt wurden in „Light" und „Full-Flavour" Zigaretten niedrigere TEQ Werte gemessen. Bezogen auf eine Packung mit zwanzig Zigaretten liegen die Werte im Hauptstromrauch von „Ultra-Light" und „Light" Zigaretten bei ungefähr 200 fg TEQ und im Rauch von „Full-Flavour" Zigaretten bei 575 fg TEQ pro Packung. Die TEQ Mengen von Dioxin-ähnlichen Verbindungen im Tabak von vier Zigarettenmarken wiesen keine signifikanten Unterschiede auf und stimmten mit bereits publizierten Daten überein. [Beitr. Tabakforsch. Int. 21 (2004) 205–209]

RESUME

La présence de composés de type dioxine, tels que les dibenzodioxines chlorées, les dibenzofuranes chlorés et les biphényls chlorés, dans la fumée principale de cigarette a été dosée dans sept marques de cigarettes ayant des teneurs en goudron de 1 mg à 14 mg. Ajusté par milligramme de matière particulaire totale (MPT), les cigarettes ultra-légères ont montré les valeurs les plus importantes en équivalents toxiques (EQT) de 10 fg/mg de MPT. Si le taux de goudron est plus élevé, les valeurs d'EQT des cigarettes légères et plein arôme sont plus faibles. Calculé par rapport à un paquet de vingt cigarettes, les valeurs d'EQT de la fumée principale des cigarettes légères et ultra-légères sont d'environ de 200 fg d'EQT, et pour les cigarettes plein arôme de 575 fg d'EQT par paquet. Les valeurs d'EQT des composés de type dioxine dans le tabac de quatre marques de cigarettes ne sont pas significativement différentes et correspondent aux résultats rapportés dans la littérature. [Beitr. Tabakforsch. Int. 21 (2004) 205–209]

INTRODUCTION

Cigarette smokers are presented with a large selection of tobacco products that offer ultra-low delivery of nicotine and 'tar' to the full-flavor amounts found in many American-style cigarettes. American-style cigarettes are a blend of flue-cured, burley and Oriental tobaccos and often include reconstituted tobacco. Cigarette design changes can

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Table 1. Descriptions of cigarettes and 'tar' amounts as listed on the pack. All cigarettes were king size (KS) except those from Brand A which were 100's.

Cigarette identification	Cigarette description	'Tar' (mg) [a]	Country of manufacture
Brand A	1 mg	1	USA
Brand B	1 mg	1	not listed
Brand C	1 mg	1	USA
Brand D	ultra-light	5	USA
Brand E	ultra-light	6	not listed
Brand F	light	10	not listed
Brand G	full-flavor	14	not listed

[a] 'Tar' = TPM – nicotine – water.

lower the amounts of nicotine and 'tar', but it has been determined that other compounds in smoke do not decrease proportionately with nicotine (1). The generation of smoke components can occur through distillation/vaporization/entrainment or via pyrosynthesis.

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) were detected in cigarette smoke by BUMB *et al.* in 1980 (2). Four subsequent published reports have examined PCDDs and PCDFs in cigarette smoke by using glass filter pads or glass filters with a sorbent downstream (3–6). Chemical constituents in mainstream smoke are often categorized as vapor-phase components or particulate phase components, based on collection using a Cambridge filter pad. Compared to typical vapor-phase smoke components, PCDDs and PCDFs are relatively nonvolatile and are associated with the particulate phase in cigarette smoke. The motivation to assess levels of dioxins in cigarette smoke stemmed from their widely known environmental presence and public health concerns.

Many public health agencies accept the 1998 recommendation from the World Health Organization (WHO) on the tolerable daily intake (TDI) of dioxin-like compounds (7). The 1998 TDI from WHO was set to be between 1 and 4 pg/kg-body weight, and the TDI applied to all dioxin-like compounds through the use of toxic equivalency factors (TEFs) to calculate a total toxic equivalent. A WHO committee has updated dioxin exposure calculations based on a provisional tolerable monthly intake (8). The latest WHO TEFs for PCDDs, PCDFs, and polychlorinated biphenyls (PCBs) were established by VAN DEN BERG *et al.* in a report published in 1998 (9).

TEQs from TCDDs and TCDFs determined for mainstream cigarette smoke have varied considerably. In a 1982 report by CRUMMET, the TEQ value was less than 0.1 pg/cigarette (3). Starting in 1989, three almost contemporaneous reports listed mainstream smoke TEQ values of 0.06, 1.0 and 3.65 pg/cigarette (4–6). In MUTO and TAKIZAWA's work (4) that reported the highest TEQ, the cigarettes were smoked continuously until 10 mm from the filter, and the PCDD and PCDF congener profiles were different than the profiles from BALL (5) and LÖFROTH (6). Both the BALL and LÖFROTH studies used similar smoking protocols that were intended to approximate human smoking. Using BALL's result of 0.06 pg/cigarette and MUTO's results of 3.65 pg/cigarette to compare the TDI contribution of smoking a pack of twenty cigarettes per day by a 60-kg adult, the BALL result would suggest that smoking contributes less than 2% to the TDI, but MUTO's result indicates that the smoker might exceed the TDI when the TEQ from dietary sources is included.

Over the past two decades, there have been many significant changes related to dioxin exposure and to cigarette manufacturing and consumption that would suggest a need to reexamine dioxin levels in mainstream cigarette smoke. It is plausible that the TEQ in cigarette smoke derives from dioxin-containing residue left on tobacco leaves throughout the growing and harvesting season (10). This source of dioxins should decrease with the global environmental decrease in dioxin levels as determined in a number of studies (11). Since the early 1980's most, if not all, major cigarette companies have switched to paper vendors who use total chlorine free processes in their cigarette paper manufacturing. In addition, recent studies indicate that dioxin-like compounds found in cigarette smoke do not significantly contribute to the risk of cancer (12,13).

With changes in public policy and consumer demand, cigarette manufacturers offered more choices in nicotine/'tar' delivery such as ultra-lights, lights, medium, or full-flavor styles. The modifications in cigarette design to produce lower delivery products altered mainstream smoke composition (14). The objectives of this present study were to determine if the TEQ in mainstream smoke changed with TPM and to examine if dioxin levels on tobacco leaf might influence dioxin levels in smoke for the various cigarette styles.

EXPERIMENTAL

Cigarette descriptions

Seven American-style cigarette brands (A to G) were used in the study. One brand could not be imported into the USA, and arrangements were made with a third party to handle the preparation of samples from this cigarette brand. All cigarettes were obtained in the autumn of 2003, and the manufacturing dates were estimated to be no more than six months prior to collection. Table 1 contains descriptions of the samples. The cigarettes used in this study contained charcoal in the filter section.

Collection of mainstream TPM and analytical method

Prior to smoking, all cigarettes were conditioned according to ISO guidelines (15). For the analysis of mainstream smoke condensate, the cigarettes were smoked on an RM-20 CSR rotary smoking machine (Borgwaldt, Hamburg, Germany) using International Organization for Standardization (ISO) recommendations (16). The smoke condensate was collected on 92 mm Cambridge pads (Whatman, Maidstone, UK). Enough cigarettes of each type were smoked to obtain about 0.2 g of TPM per Cambridge pad. Three Cambridge pads were then pooled to form a sample having approximately 0.6 g of TPM. All samples were prepared in duplicate. The samples were stored in a refrigerator and shipped in a cooler with ice for analysis at Triangle Laboratories, Durham, North Carolina, USA, a National Environmental Laboratory Accreditation Program (NELAP) certified laboratory for dioxin analysis.

Table 2. Dioxin-like WHO TEQ levels from the tobacco section with paper from four brands of cigarettes. Duplicate samples were sent for each analysis, given as Rep 1 and Rep 2. To calculate the total TEQ in a box of cigarettes, a tobacco plus cigarette paper weight of 0.7 g was used.

Cigarettes		Total WHO TEQ (pg/g)	Total WHO TEQ pg in 1 pack
Brand A	Rep 1	0.82	11.5
	Rep 2	0.76	10.6
Brand E	Rep 1	0.65	9.1
	Rep 2	0.58	8.1
Brand F	Rep 1	0.50	7.0
	Rep 2	0.61	8.6
Brand G	Rep 1	0.64	8.9
	Rep 2	0.70	9.8

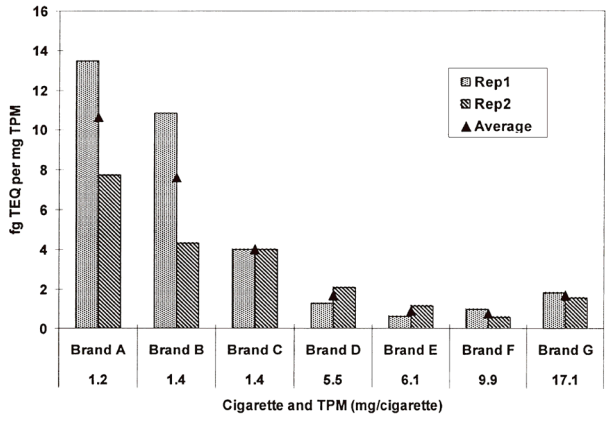

Figure 1. Femtograms of TEQ (PCDDs/PCDFs + PCBs) per mg TPM in mainstream smoke of seven cigarette brands. The TPM per cigarette is listed below the cigarette identification. Two samples (Rep 1 and Rep 2) were analyzed for each brand. The average of Rep 1 and Rep 2 is indicated as ▲.

Analysis for dioxins was performed at Triangle Laboratories according to procedures in Environmental Protection Agency (EPA) Method 8290. Additional analyses for polychlorinated biphenyls (PCBs) using Triangle Laboratories' enhanced procedures for EPA Method 1668A were performed. For the PCB analyses an additional set of samples was sent. Sample reports for PCDDs, PCDFs and PCBs included WHO TEFs. A WHO TEQ for each sample was calculated using the detectable values.

RESULTS AND DISCUSSION

Dioxin and PCB TEQ levels from cigarette components

Research groups have found dioxin-like compounds on tobacco leaf from many production sources, and ten years have past since the latest published report in this regard (10). To monitor recent tobacco TEQ levels, the tobacco section of cigarettes was removed from the filter section and sent with the accompanying cigarette paper for analysis. Approximately 18 g of tobacco and cigarette paper were sent for testing from four brands. The total WHO-TEQ (including PCDDs, PCDFs, and PCBs) values for each sample is summarized in Table 2. To relate the TEQ to a one pack-a-day smoker, we used a tobacco + cigarette paper weight of 0.7 g to calculate a total TEQ for a pack (box of twenty) of cigarettes. The results in Table 2 indicate that the four brands contained similar total TEQ values of dioxin-like compounds. The PCB contribution to the total TEQ was generally between 15 and 20 percent. It is interesting to note that the TEQs for a pack of cigarettes from Table 2 were very similar to the total TEQ from several tobacco leaf samples as determined by MATSUEDA (10).

When samples of cigarette paper, taken directly from a bobbin, and the filter section of Brand A were also sent for analysis, there were no detectable levels for the dioxin-like analytes. Thus, this work confirms that dioxin-like compounds in cigarettes are found only on the tobacco leaves.

Dioxins and PCBs in mainstream cigarette smoke

Modifying a cigarette design to lower the delivery of nicotine or 'tar' has been shown to change the smoke chemistry in a modestly predictable manner (14). Studies on toxicity vs. cigarette TPM have not been definitive, but it appeared that lower delivery cigarettes may produce TPM with slightly higher toxicity (14). To answer the question of dioxins and cigarette delivery, mainstream smoke from seven brands of cigarettes covering a range of TPM were examined for dioxin-like compounds. While PCBs were included in the present analysis, a systematic study of PCB recovery on the Cambridge pad has not been reported. Charcoal is known to strongly retain PCBs, and if a small percent of PCBs was partitioned in the vapor phase, the charcoal filters may reduce PCB levels. It is assumed in this report that PCBs partition between vapor phase and particulate phase similarly to naphthalene and aminobiphenyls which were collected on a Cambridge pad, as reported earlier (17,18).

Figure 1 contains a graph of fg TEQ per mg TPM obtained for each brand of cigarette, in ascending order of TPM delivery. Each duplicate analysis was included. From Figure 1, there is a distinct decrease in the concentration of TEQ from dioxin-like compounds as the TPM increases. Assuming that the dioxins were transferred into particulate phase mainstream smoke from tobacco leaf, the decrease of the TEQ concentration was caused by the higher content of compounds such as water and propylene glycol in the TPM of full-flavor cigarettes. Published research supports the assumption of dioxin transfer from tobacco leaf as the primary source while pyrosynthesis of dioxins from chlorinated precursors has a limited role (10). Of the many congeners, 1,2,3,4,6,7,8-heptaCDD, 1,2,3,4,6,7,8,9-octaCDD, 1,2,3,4,7,8-hexaCDF and 2,3,3',4,4'-pentaCB were detected most often in the tobacco and TPM. To indicate the contribution from PCDDs/PCDFs and PCBs to the total TEQ, the results for each brand were averaged and the contributions plotted, as given in Figure 2. The contributions for PCBs varied considerably among the seven brands. There are many factors which could contribute to this variation, such as filter design, paper porosity, cigarette coal temperature, etc.

When calculating the results on a per pack basis, the graph in Figure 3 indicates that the total mainstream TEQ expo-

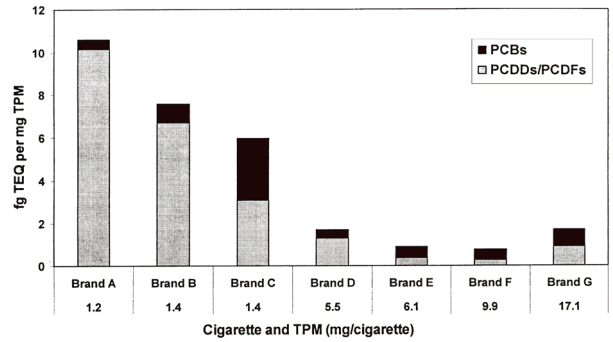

Figure 2. Contribution to the total TEQ from PCDDs/PCDFs and PCBs. The data points for each brand were averaged.

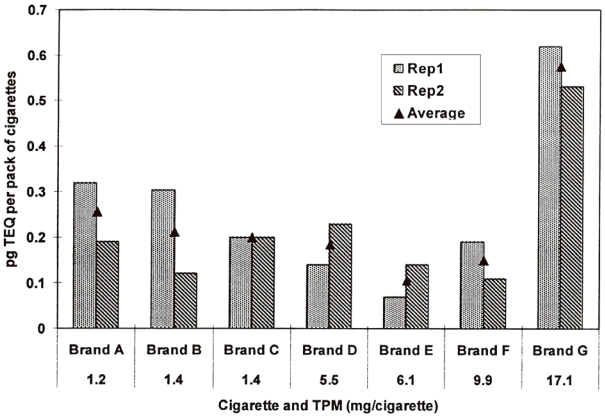

Figure 3. Picograms of TEQ (PCDDs/PCDFs + PCBs) per pack of twenty cigarettes for each brand. Two samples (Rep 1 and Rep 2) were analyzed for each brand. The average of Rep 1 and Rep 2 is indicated as ▲.

sure from a pack of cigarettes is roughly constant for 1 mg, ultra-light and light cigarettes. Only the full-flavor cigarettes had a higher delivery of dioxin-like compounds to the smoker. Since the tobacco sections had almost the same TEQ level, the transfer efficiency of dioxins into mainstream smoke did not vary with the 1 mg, ultra-light and light cigarettes. The full-flavor cigarette, Brand G, delivered twice the amount of dioxins compared to the other styles. Although the data points for Brand G were relatively precise, additional data would be needed to determine whether most full-flavor brands produced higher dioxins in mainstream smoke.

Having indicated distinct TEQ trends from the seven cigarette brands, the above results can also be compared to literature TEQ values of samples obtained using standardized smoking protocols. LÖFROTH and ZEBÜHR used a 21 mg 'tar' cigarette and found 900 fg TEQ of PCDDs and PCDFs per cigarette (6). BALL and coworkers analyzed ten best-selling German cigarettes and found an average 60 fg TEQ from PCDDs and PCDFs in mainstream smoke per cigarette (5). During the time of the BALL study, most of the best-selling cigarette brands were, most likely, full-flavor styles. Our result near 29 fg/cigarette for the TEQ from PCDDs and PCDFs for Brand G (14 mg 'tar') was significantly lower than the two previously mentioned studies on full-flavor cigarettes. If dioxin delivery continues to increase with TPM, then the value obtained for Brand G would not be outside expectations since the other two studies used higher TPM cigarettes that were on the market.

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