CONVERTING TEQ IN FISH FROM ONE TEF SCHEME TO ANOTHER

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Introduction

Toxic Equivalency Factors (TEFs) have evolved for dioxins/dioxin-like compounds over the last two and half decades. Since various TEF schemes differ by number of congeners considered and TEF values assigned to each congener, for a set of measured dioxins and dioxin-like compounds, the reported TEQ can be affected by the selection of a TEF scheme. The TEQ approach is so widely accepted that virtually all dioxin results are now expressed in this form. Therefore, it is difficult to compare past and current TEQs that are reported using different TEFs without explicitly mentioning the underlying congener concentrations. Using what likely is the largest dioxin/furan (PCDD/F) and dioxin-like polychlorinated biphenyl (dl-PCB or DLP) fish database, here we present regression models that can facilitate conversion of a fish TEQ from an old to a newer TEF scheme.

Materials and methods

Dataset

The fish dataset collected by Ontario Ministry of the Environment (OMOE, Canada) include measurements of 29 congeners of dioxins/furans and dl-PCBs in about 1473 samples of 38 fish species collected from 203 locations across Ontario over the last 10 years. Although the samples mainly included adult predatory fish, forage/juvenile fish were also collected periodically. The samples varied over a large range – size: 3.4-120 cm length, 100-14300 g weight; Sex: 51:49 male to female ratio; contaminant levels: <0.001-424 pg TEQ/g wet wt (based on TEF_{WHO-05}; non-detects = ½ detection limit). This illustrates a variety of contaminant sources such as point discharge, atmospheric input or combination of them for these aquatic systems. A large portion of the dataset comprised of skinless, boneless dorsal fillet measurements; however, the dataset also included composites of several adult and juvenile fish (5% and 10%, respectively), gutted and headless composites (1%), and skin-on fillets (1%).

Extraction and analysis

The samples were analyzed for PCDD/Fs and dl-PCBs using OMOE method DFPCB-E3418 [1], Homogenized fish tissue (5 g) was fortified with known amounts of $^{13}C_{12}$-labeled surrogates for 2,3,7,8-substituted PCDD/Fs and dl-PCBs, and digested with hydrochloric acid over night. Digested samples were extracted with hexane and cleaned using a three stage (silica/alumina/carbon) column cleanup procedure. The PCDD/Fs and non-*ortho* dl-PCBs (PCB-77, -81, -126, -169) were in the planar fraction and the mono-*ortho* (MO) PCBs were in the non-planar fraction. Both fractions were analyzed using a Micromass Autospec at a resolving power of 10,000 coupled to a Hewlett-Packard HP6890 gas chromatograph (GC) on a 40 m DB-5 column (0.18 mm i.d., 0.18 µm film thickness). SIM was used to monitor both the native and $^{13}C_{12}$-labeled (surrogate) compounds. Extracts were analyzed in the splitless mode with He carrier gas at a linear velocity of 0.8 cm/s. The injector temperature and transfer line temperature were maintained at 280 °C and 300 °C, respectively. The temperature program for MO Fraction was: 150 °C for 1 min; 150 °C to 200 °C at 5 °C per min; 200 °C to 227 °C at 1 °C per min; 227 °C to 250 °C at 10 °C per min; 250 °C to 300 °C at 15 °C per min; 300 °C for 3 min. The temperature program for planar fraction was: 140 °C for 1 min; 140 °C to 200 °C at 52 °C per min; 200 °C to 235 °C at 2.9 °C per min; 235 °C to 267°C at 3 °C per min; 267 °C to 300 °C at 7 °C per min; 300 °C for 7 min. All PCDD/F and dl-PCB data were corrected for surrogate standard recoveries.

TEF schemes

The most acceptable TEF scheme during the early 1990s was proposed by a North Atlantic Treaty Organization (NATO) working group in 1989 [2]. This scheme was developed by scientific experts from several countries and is known as NATO-TEF or International-TEF (I-TEF). This scheme ($TEF_{NATO-I-89}$) more or less replaced previously developed TEF schemes notably $TEF_{Eadon-82}$ (USA [3]), $TEF_{Ontario-84}$ (Canada [4]), $TEF_{Germany-85}$ [5], $TEF_{California-86}$ [6] $TEF_{USEPA-87}$ [7], and $TEF_{Nordic-88}$ [8]. More recently, the World Health Organization (WHO) suggested modified TEFs in 1994 (TEF_{WHO-94}), 1998 (TEF_{WHO-98}) and 2005 (TEF_{WHO-05}) [9-11].

Statistical analysis

The TEQ values were calculated using measured 17 PCDD/F and 12 dl-PCB concentrations and TEFs from various schemes with mammalian TEFs for TEF_{WHO-98} and TEF_{WHO-05}. The regression models were prepared using SPSS®.

Results and Discussion

PCDD/F-TEQ conversion

The regression models that facilitate conversion of PCDD/F-TEQ in fish from one TEF scheme to another are presented in Table 1. The relationship PCDD/F-TEQ_{WHO-05} = 0.925 × PCDD/F-TEQ_{WHO-98} suggests that PCDD/F-TEQ based on the latest TEF_{WHO-05} are about 7.5% lower than that based on TEF_{WHO-98}. Little change is expected when $TEF_{Nordic-88}$ and $TEF_{NATO-I-89}$ based PCDD/F-TEQs are converted to the newer TEF_{WHO-05} scheme. The PCDD/F-TEQs reported using $TEF_{Germany-85}$ and $TEF_{USEPA-87}$ need to be raised by about 36% and 27%, respectively, in order to convert them to PCDD/F-TEQ_{WHO-05}. In contrast, the PCDD/F-TEQs derived from $TEF_{Eadon-82}$, $TEF_{Ontario-84}$, and $TEF_{California-86}$ are required to be lowered by about 20%, 32% and 63%, respectively. These results suggest that according to current toxicological standards, all previous TEF schemes for PCDD/F except $TEF_{Germany-85}$ and $TEF_{USEPA-87}$ were conservative in estimating PCDD/F-TEQ.

DLP-TEQ conversion

Figure 1 shows the relationships among DLP-TEQs calculated using three TEF schemes released in 1994, and revised in 1998 and 2005. All three possible combinations have strong linear relations with the DLP-TEQ_{WHO-94} and DLP-TEQ_{WHO-98} are expected to be almost identical. This is attributed to almost identical TEF values in both schemes except inclusion of PCB-81 in TEF_{WHO-98}, where PCB-81 has negligible (<0.1%) contribution to DLP-TEQ and thereby to Total-TEQ. The DLP-TEQ_{WHO-05} is on average 25% lower than DLP-TEQ_{WHO-94} & DLP-TEQ_{WHO-98}.

Total-TEQ conversion

The only required regression model to convert Total-TEQ from an older TEF scheme to the latest TEF scheme is from TEF_{WHO-98} to TEF_{WHO-05}. As shown in Figure 2, Total-TEQ_{WHO-05} is on average 22% lower than Total-TEQ_{WHO-98}. This finding is in accordance with preliminary estimates of van den Berg et al. [11] who reported on average 17% decrease in Total-TEQ values for trout from the TEF_{WHO-98} to TEF_{WHO-05} scheme.

Contribution to TEQ

The major (>75%) contribution to PCDD/F-TEQ_{WHO-05} is from 2,3,7,8-TCDD (33%), 1,2,3,7,8-PCDD (26%), 2,3,7,8-TCDF (10%), and 2,3,4,7,8-PCDF (9%). The DLP-TEQ_{WHO-05} is dominated by PCB-126 which on average contributes about 88% (range 22-97.5%, 25-75 quartiles 85-89%) [12]. Similarly to DLP-TEQ, Total-TEQ is also dominated by PCB-126, which contributes about 50% and 63% for TEF_{WHO-98} and TEF_{WHO-05}, respectively. This is mainly attributed to on average >70% (range 1-99%, 25-75 quartiles 53-84%) of Total-TEQ resulting from dl-PCBs.

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Table 1: Conversion factors for converting dioxins/furans related Toxic Equivalent (PCDD/F-TEQ) from one TEF scheme to another. The conversion values are presented in form of $PCDD/F\text{-}TEQ_Y = m \times PCDD/F\text{-}TEQ_X$, where Y TEF schemes are shown in rows, X TEF schemes are shown in columns, and m values are shown in bold letter along with standard errors (SE) and R^2 values.

Y	**WHO-05**	**0.799** ± 0.005 *0.944*	**0.684** ± 0.007 *0.863*	**1.356** ± 0.009 *0.933*	**0.371** ± 0.005 *0.775*	**1.273** ± 0.006 *0.970*	**1.036** ± 0.002 *0.995*	**1.031** ± 0.002 *0.995*	**0.925** ± 0.001 *0.999*	1
	WHO-98	**0.865** ± 0.005 *0.949*	**0.742** ± 0.007 *0.869*	**1.454** ± 0.011 *0.920*	**0.404** ± 0.005 *0.789*	**1.369** ± 0.007 *0.961*	**1.118** ± 0.002 *0.993*	**1.113** ± 0.002 *0.993*	1	**1.079** ± 0.001 *0.999*
	NATO-I-89	**0.775** ± 0.005 *0.948*	**0.668** ± 0.006 *0.879*	**1.328** ± 0.007 *0.956*	**0.360** ± 0.005 *0.782*	**1.240** ± 0.004 *0.983*	**1.005** ± 0.000 *0.999*	1	**0.893** ± 0.002 *0.993*	**0.965** ± 0.002 *0.995*
	Nordic-88	**0.770** ± 0.005 *0.946*	**0.664** ± 0.006 *0.878*	**1.321** ± 0.007 *0.957*	**0.358** ± 0.005 *0.780*	**1.234** ± 0.004 *0.984*	1	**0.995** ± 0.000 *0.999*	**0.888** ± 0.002 *0.993*	**0.960** ± 0.002 *0.995*
	EPA-87/89	**0.610** ± 0.005 *0.920*	**0.528** ± 0.006 *0.857*	**1.081** ± 0.003 *0.991*	**0.280** ± 0.004 *0.737*	1	**0.797** ± 0.003 *0.984*	**0.793** ± 0.003 *0.983*	**0.702** ± 0.004 *0.961*	**0.762** ± 0.003 *0.970*
	California-86	**1.887** ± 0.013 *0.933*	**1.725** ± 0.008 *0.972*	**2.789** ± 0.048 *0.699*	1	**2.637** ± 0.041 *0.737*	**2.180** ± 0.030 *0.780*	**2.172** ± 0.030 *0.782*	**1.954** ± 0.026 *0.789*	**2.092** ± 0.029 *0.775*
	German-85	**0.551** ± 0.005 *0.885*	**0.479** ± 0.006 *0.834*	1	**0.251** ± 0.004 *0.699*	**0.917** ± 0.002 *0.991*	**0.724** ± 0.004 *0.957*	**0.720** ± 0.004 *0.956*	**0.633** ± 0.005 *0.920*	**0.688** ± 0.005 *0.933*
	Ontario-84	**1.103** ± 0.004 *0.976*	1	**1.741** ± 0.020 *0.834*	**0.563** ± 0.002 *0.972*	**1.625** ± 0.017 *0.857*	**1.322** ± 0.013 *0.878*	**1.316** ± 0.013 *0.879*	**1.172** ± 0.012 *0.869*	**1.261** ± 0.013 *0.863*
	Eadon-82	1	**0.885** ± 0.004 *0.976*	**1.605** ± 0.015 *0.885*	**0.494** ± 0.003 *0.933*	**1.508** ± 0.012 *0.920*	**1.229** ± 0.008 *0.946*	**1.224** ± 0.007 *0.948*	**1.097** ± 0.007 *0.949*	**1.182** ± 0.007 *0.944*
	m ± SE R^2 Legend ↑	**Eadon-82**	**Ontario-84**	**German-85**	**California-86**	**EPA-87**	**Nordic-88**	**NATO-I-89**	**WHO-98**	**WHO-05**
		X								

Figure 1. Toxic equivalent concentrations of dl-PCB for TEF_{WHO-98} and TEF_{WHO-05} (i.e., DLP-TEQ_{WHO-98} and DLP-TEQ_{WHO-05}) as a function of DLP-TEQ_{WHO-94} and DLP-TEQ_{WHO-98}.

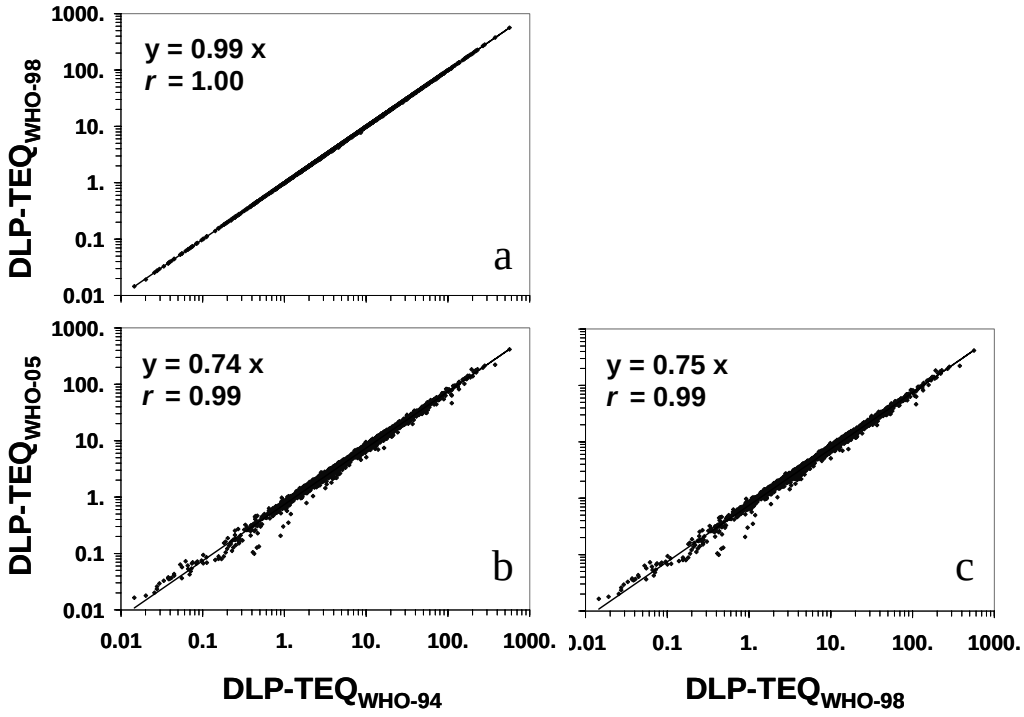

Figure 2. Toxic equivalent concentrations of mixtures of dioxins, furans and dl-PCBs for TEF_{WHO-05} (Total-TEQ_{WHO-05}) as a function of Total-TEQ_{WHO-98}.