CONGENER SPECIFIC EVALUATION OF HUMAN TOXICITY POTENTIALS FOR PCDD/Fs, CO-PCBs AND HCB WITH FISH INTAKE

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Introduction

Toxic Equivalency Factor (TEF) indicates the toxicity of a compound relative to TCDD based on either administered dose (for humans) or tissue concentration (for fish and birds). TEF concept is widely accepted as a method to evaluate the complex mixtures of PCDD/Fs and dioxin-like PCBs for many matrices including both biotic and abiotic compartments, although the biological meaning is obscure in the latter case. A better way to evaluate the risks associated with these compounds in abiotic media is to include the source-to-dose relationships by modeling the congener specific fate and exposure. In the field of Life Cycle Assessment (LCA), Human Toxicity Potential (HTP)[1,2] is gaining momentum as a tool to characterize the potential harm of a compound released to the environment. HTP includes both inherent toxicity and source-to-dose relationships for chemical emissions. HTPs for 330 substances[1] and 181 substances[2] are available in the literature, but in both cases HTPs for dioxin-like compounds are not congener specific, i.e., 2,3,7,8-TCDD surrogate approach is used. Apart from HTP methods, many models[3,4] that predict the congener specific intake of PCDD/Fs and Co-PCBs are available. These efforts focused on, among others, the air-grass-cattle-milk/beef exposure pathway, reflecting its importance in Europe and U.S. On the other hand, in Japan, fish intake constitutes 60-80% of the total daily intake of TEQs,[5,6] which implies the importance of modeling the exposure pathways that lead to fish concentrations. This paper presents congener specific HTPs for dioxin-like compounds following a unit emission to air, water and soil in Japan.

Methods

HTPs for 90 combinations of 30 substances (7 PCDDs, 10 PCDFs, 12 Co-PCBs and HCB) and 3 emission media (air, water and soil) were calculated by the following method. First, a multimedia environmental fate model was developed and used to calculate steady state concentrations of the target substances in the environment (air, water, soil and sediment) and food (fish, leafy vegetables and milk/meat). Next, Predicted Daily Intakes (PDIs) for the 90 combinations were calculated by multiplying daily intakes and the media/food concentrations. The PDIs were divided by the PDI for a reference combination (2,3,7,8-TCDD emitted to air) to obtain Environmental Fate and Exposure Factors (EFEFs). Finally, EFEFs were multiplied by TEFs to obtain HTPs.

The environmental fate model used in this study is a Mackay type multimedia model with two geographical scales (Japan and moderate zone). The PDIs for the two scales were aggregated based on population. Exposure routes considered are 1) inhalation, 2) soil ingestion, 3) fish, 4) leafy vegetables and 5) milk/meat. Congener specific parameters are shown in Table 1.

Results and Discussion

Media concentrations following a unit emission to air, water and soil are shown in Figure 1.

RISK ASSESSMENT

As shown in Fig.1(a), concentrations in air due to air emissions became lower as the number of chlorines increased. This is because a deposition (elimination) from air is more efficient in particle-bound phase than in gas phase. The soil under the air receives this deposition fluxes, thus those congeners with more chlorines are more abundant in the soil. On the other hand, concentrations in leafy vegetables show a different profile from that in the soil, reflecting the lower contribution from wet depositions to the vegetations. The concentrations in air were within a factor of 7 for all compounds and 2.5 except HCB. The range of concentrations in vegetations was 1 order of magnitude. In milk, the range became as wide as 3 orders.

Concerning emissions to water (Fig.1(b)), more than 2 orders of difference in fish concentrations were predicted, while the predicted water concentrations were within a factor of 3 (about 0.5 order). BCF is clearly the key parameter in determining the fish concentration. The BCFs adopted in this paper are logarithmic means of the ratios between water concentrations and fish concentrations derived from 368 field measurements by Environmental Agency of Japan (1999). Recognized uncertainties in these BCFs are: 1) difference in rates of detection among congeners, 2) lack of differentiation between fish species, and 3) exclusion of sediment-to-fish routes. Concerning the last factor, the ratios of sediment concentration over water concentration in terms of fugacity are higher for Co-PCBs than for PCDD/Fs due to the past pollution of PCBs in Japan. This could have resulted in an overestimate of BCFs for Co-PCBs.

Figure1(c) shows that the determinant of soil concentrations following emissions to the soil is the degradation half-life in the soil. Water concentrations caused by the soil emissions were estimated to be 1/100-1/200 of those by water emissions and in the same order as those by air emissions.

Figure 2 shows the measured and modeled contribution to daily intakes from 5 exposure routes. As seen in Figure 2(c), not soil ingestions but fish intakes are the most important pathways for lower chlorinated PCDD/Fs and all Co-PCBs in soils. This result suggests the need to revise the environmental standard in Japan for dioxins (PCDD/Fs + Co-PCBs) in soils, because the current standard is based solely on soil ingestions.

Table 2 shows the calculated EFEFs. It is clear that the difference in source-to-dose relationships among the dioxin-like compounds drastically affects the risks associated with their emissions.

References

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Table 1. Congener specific model parameters

Chemical name	P_L	H	log Kow	log Koc	Kva	log BCFfish j)		COR	Degradation half life [hr]			
	[Pa]	[Pa-m^3/mol]	-	-	[m^3/g-dry]	ave.	N	-	air	water	soil	sediment
2378TCDD	8.19E-4 a)	1.62 d)	6.96 d)	5.74 g)	52 h)	2.79	14	0.35 l)	290 o)	2,900 q)	17,000 c)	55,000 c)
12378P5CDD	2.21E-4 a)	1.48 d)	7.50 d)	6.18 g)	43 h)	3.26	40	0.24 l)	450 o)	4,500 q)	17,000 c)	55,000 c)
123478H6CDD	6.26E-5 a)	1.45 d)	7.94 d)	6.53 g)	29 h)	3.06	6	0.15 l)	1,000 o)	10,000 q)	55,000 c)	55,000 c)
123678H6CDD	5.98E-5 a)	1.45 d)	7.98 d)	6.56 g)	29 h)	2.89	32	0.18 l)	690 o)	6,900 q)	55,000 c)	55,000 c)
123789H6CDD	5.46E-5 a)	0.832 d)	8.02 d)	6.60 g)	29 h)	2.83	13	0.13 l)	690 o)	6,900 q)	55,000 c)	55,000 c)
1234678H7CDD	1.56E-5 a)	0.832 d)	8.40 d)	6.90 g)	16 h)	2.31	225	0.033 l)	1,600 o)	16,000 q)	55,000 c)	55,000 c)
O8CDD	4.20E-6 a)	0.513 d)	8.75 d)	7.19 g)	13 h)	1.75	264	0.0039 l)	4,000 o)	40,000 q)	55,000 c)	55,000 c)
2378T4CDF	1.12E-3 a)	2.69 d)	6.46 d)	5.33 g)	27 h)	3.58	57	0.0005 l)	480 o)	4,800 q)	17,000 c)	55,000 c)
12378P5CDF	3.72E-4 a)	1.91 d)	6.99 d)	5.76 g)	28 h)	2.94	77	0.0005 l)	770 o)	7,700 q)	17,000 c)	55,000 c)
23478P5CDF	2.91E-4 a)	2.57 d)	7.11 d)	5.86 g)	28 h)	3.26	99	0.17 l)	820 o)	8,200 q)	17,000 c)	55,000 c)
123478H6CDF	1.01E-4 a)	1.91 d)	7.53 d)	6.20 g)	21 h)	2.99	16	0.14 l)	1,900 o)	19,000 q)	17,000 c)	55,000 c)
123678H6CDF	9.68E-5 a)	1.91 d)	7.57 d)	6.23 g)	21 h)	2.85	15	0.15 l)	1,400 o)	14,000 q)	17,000 c)	55,000 c)
123789H6CDF	6.64E-5 a)	0.955 d)	7.76 d)	6.39 g)	21 h)	2.53	0 k)	0.0005 l)	1,300 o)	13,000 q)	17,000 c)	55,000 c)
234678H6CDF	7.76E-5 a)	1.78 d)	7.65 d)	6.30 g)	21 h)	2.69	37	0.089 l)	1,500 o)	15,000 q)	17,000 c)	55,000 c)
1234678H7CDF	2.92E-5 a)	1.41 d)	8.01 d)	6.59 g)	16 h)	2.47	111	0.035 l)	3,400 o)	34,000 q)	17,000 c)	55,000 c)
1234789H7CDF	1.65E-5 a)	1.00 d)	8.23 d)	6.77 g)	16 h)	2.48	9	0.043 l)	3,000 o)	30,000 q)	17,000 c)	55,000 c)
O8CDF	5.78E-6 a)	0.776 d)	8.60 d)	7.07 g)	15 h)	2.58	42	0.0033 l)	8,000 o)	80,000 q)	55,000 c)	55,000 c)
33'44'-T4CB (#77)	1.41E-3 b)	10.4 e)	6.14 f)	5.63 f)	22 i)	4.00	338	0.012 m)	350 o)	3,500 q)	55,000 c)	55,000 c)
344'5-T4CB (#81)	1.41E-3 b)	14.5 e)	6.14 f)	5.59 f)	19 i)	4.18	194	0.10 n)	350 o)	3,500 q)	55,000 c)	55,000 c)
33'44'5-P5CB (#126)	2.45E-4 b)	8.29 e)	6.60 f)	5.95 f)	44 i)	4.25	150	0.35 m)	520 o)	5,200 q)	55,000 c)	55,000 c)
33'44'55'-H6CB (#169)	4.24E-5 b)	6.60 e)	7.06 f)	6.23 f)	70 i)	4.09	18	0.31 m)	760 o)	7,600 q)	55,000 c)	55,000 c)
233'44'-P5CB (#105)	5.51E-4 b)	10.1 e)	6.39 f)	5.83 f)	31 i)	4.63	350	0.40 n)	680 o)	6,800 q)	55,000 c)	55,000 c)
2344'5-P5CB (#114)	5.51E-4 b)	14.5 e)	6.39 f)	5.77 f)	26 i)	4.61	276	0.80 n)	530 o)	5,300 q)	55,000 c)	55,000 c)
23'44'5-P5CB (#118)	4.10E-4 b)	12.7 e)	6.46 f)	5.73 f)	31 i)	4.73	348	0.80 n)	420 o)	4,200 q)	55,000 c)	55,000 c)
2'344'5-P5CB (#123)	4.10E-4 b)	17.6 e)	6.46 f)	5.73 f)	26 i)	4.57	244	0.20 n)	420 o)	4,200 q)	55,000 c)	55,000 c)
233'44'5-H6CB (#156)	9.54E-5 b)	8.97 e)	6.84 f)	6.10 f)	59 i)	4.74	332	0.80 n)	1,100 o)	11,000 q)	55,000 c)	55,000 c)
233'44'5'-H6CB (#157)	9.54E-5 b)	8.56 e)	6.84 f)	6.12 f)	60 i)	4.63	251	0.40 n)	950 o)	9,500 q)	55,000 c)	55,000 c)
23'44'55'-H6CB (#167)	7.10E-5 b)	11.1 e)	6.92 f)	6.02 f)	59 i)	4.75	295	0.80 n)	950 o)	9,500 q)	55,000 c)	55,000 c)
233'44'55'-H7CB (#189)	1.65E-5 b)	6.74 e)	7.30 f)	6.37 f)	70 i)	4.33	114	0.80 n)	1,600 o)	16,000 q)	55,000 c)	55,000 c)
Hexachlorobenzene	2.45E-1 c)	131. c)	5.50 c)	4.92 c)	4.2h)	3.89	- c)	0.80 n)	16,000 p)	160,000 q)	55,000 c)	55,000 c)

P_L: subcooled liquid vapor pressure. H: Henry's law constant at 25. Kva: vegetation-air (bulk) partition coefficient. BCFfish: bioconcentration factors for fish. COR: carryover rate for cow's milk. a: Eitzer&Hites(1988) ES&T. 22(11)1362. Donnelly et.al.(1987) J. chromatogr. 392,51. Hale et.al.(1985) Anal. chem. 57, 640. b: Hawker(1989) ES&T. 23(10)1250. c: Mackay(1992)Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals, Lewis Publ. d: Govers et.al.(1998) Chemosphere. 37(9-12)2139 e: Dunnivant&Elzerman(1992) ES&T. 26(8)1567 f: Hansen et.al.(1999) Chemosphere. 39(13)2209. g: Estimated by log Koc = 0.81 log Kow + 0.1 h: Calculated from field measurement data in Bohme et.al.(1999) ES&T. 33(11)1805. i: Estimated by regression with Koa using data in Bohme et.al.(1999) ES&T. 33(11)1805. j: Calculated from field measurement of water and fish concentrations. Environmental Agency of Japan(1999) ref. 7) k: Congener data was not available, thus homologue data was used. l: Fries et.al.(1999) ES&T. 33(8)1165. m: Slob et.al.(1995) Chemosphere. 31(8)3827. n: Estimated from fat/feed ratio and COR in Thomas et.al.(1999) ES&T. 33(1)104. o: Calculated from gas phase OH radical reaction constant by Atkinson et.al.(1997) WASP. 115(1-4)219 and OH radical concentration by Prinn et.al.(2001) Science. 292(5523)1882. p: Brubaker&Hites(1998) ES&T. 32(6)766. q: Estimated by (half life in water) = 10 x (half life in air)

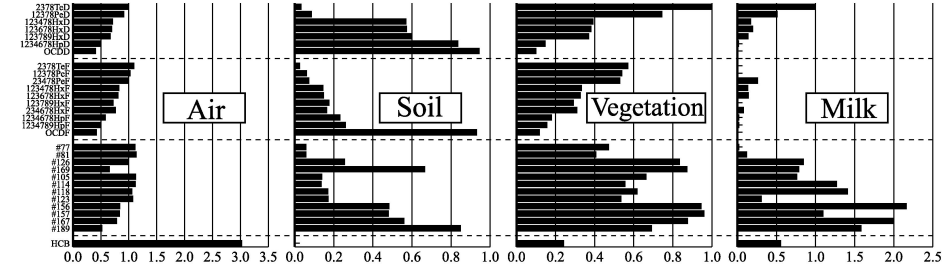

Figure 1. Relative concentration of chemicals in environmental media and foods caused by a unit emission of chemicals to (a) air, (b) water and (c) soil. TCDD emitted to air is the reference for concentrations in air, vegetation and milk. TCDD emitted to soil is the reference for concentrations in soil. TCDD emitted to water is the reference for concentrations in water and fish.

(c) soil

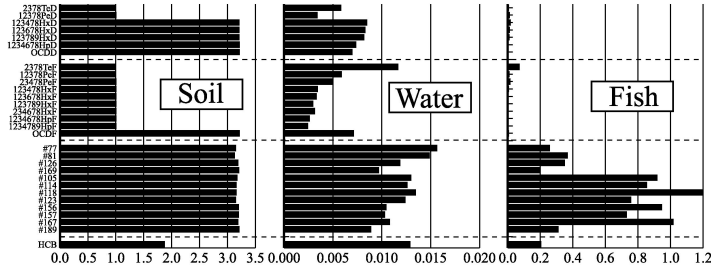

Figure 1(continued). Relative concentration of chemicals in environmental media and foods caused by a unit emission of chemicals to (a) air, (b) water and (c) soil.

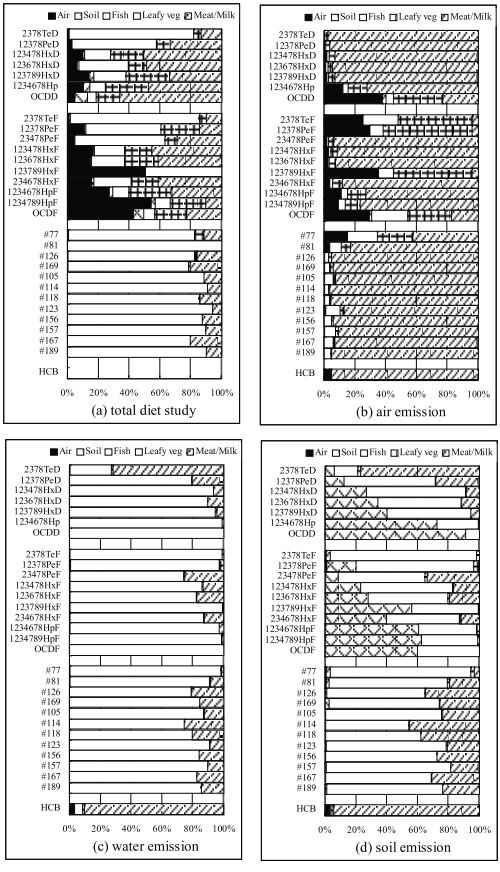

Figure 2. Measured and modeled contribution to daily intakes from inhalation, soil ingestion, fish, vegetables and milk/meat. (a): measured data from ref. 5-7
(b)-(d): model estimate following emission to each compartment.

Table 2. Environmental Fate and Exposure Factors*

Substance name	Emission to		
	air	water	soil
2378TCDD	1.0	0.13	0.0013
12378P5CDD	0.51	0.091	0.00060
123478H6CDD	0.16	0.041	0.00089
123678H6CDD	0.19	0.028	0.00069
123789H6CDD	0.13	0.023	0.00059
1234678H7CDD	0.016	0.0061	0.00033
O8CDD	0.0040	0.0016	0.00026
2378T4CDF	0.023	0.33	0.0027
12378P5CDF	0.018	0.055	0.00040
23478P5CDF	0.28	0.13	0.00092
123478H6CDF	0.14	0.046	0.00032
123678H6CDF	0.14	0.034	0.00027
123789H6CDF	0.0088	0.012	0.00013
234678H6CDF	0.082	0.021	0.00019
1234678H7CDF	0.021	0.010	0.00012
1234789H7CDF	0.021	0.0095	0.00012
O8CDF	0.0054	0.011	0.00040
33'44'-T4CB (#77)	0.041	0.49	0.010
344'5-T4CB (#81)	0.15	0.72	0.017
33'44'5-P5CB (#126)	0.89	0.93	0.019
33'44'55'-H6CB (#169)	0.74	0.53	0.0097
233'44'-P5CB (#105)	0.91	2.1	0.043
2344'5-P5CB (#114)	1.4	2.2	0.055
23'44'5-P5CB (#118)	1.5	2.9	0.068
2'344'5-P5CB (#123)	0.37	1.6	0.035
233'44'5-H6CB (#156)	2.2	2.5	0.047
233'44'5'-H6CB (#157)	1.2	1.8	0.032
23'44'55'-H6CB (#167)	2.0	2.6	0.053
233'44'55'-H7CB (#189)	1.4	0.85	0.015
Hexachlorobenzene	3.8	3.7	1.6

* HTP = EFEF x TEF