Modelling the Environmental Fate of Dioxins and Furans

Released to the Atmosphere During Incineration

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Prepared by:

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MODELLING THE ENVIRONMENTAL FATE OF DIOXINS AND FURANS RELEASED TO THE ATMOSPHERE DURING INCINERATION

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Table of Contents

Executive Summary	
Introduction	4
Chemical Properties	4
Incineration Emissions	9
The RAIDAR model	
Results	14
Discussion	
References	

Executive Summary

In this study a screening-level mass balance model is applied to estimate the environmental distribution and fate, including bioaccumulation of dioxins and furans inadvertently generated during the combustion of wastes associated with mining, and oil and gas work camps in northern Canada. The scenario addressed comprised one camp of 1000 persons per 100 km² generating 30 kg of waste per person per week. These wastes are disposed of in one of two ways: uncontrolled waste combustion generating 3500 μ g toxic equivalent (TEQ) of dioxins and furans per tonne of waste, and controlled waste incineration generating 9.5 μ g TEQ of dioxins and furans per tonne of waste. The model assumes that the dioxins and furans are emitted to the atmosphere and experience an environmental fate dependent on their physical chemical partitioning and reactivity properties. To simulate the fate of the complex mixture it was treated as consisting of 17 compounds, each with defined properties and toxic equivalent values. The total TEQ was then calculated for the sum of all compounds.

The results show that the emitted dioxins and furans are deposited on the surrounding landscape and enter the local food web from soil, water, and vegetation. Screening level estimates are made of the concentration and TEQ of the substances in a range of biota. Because these concentrations are proportional to the emission rate and the two case studies assume a ratio of emission rates of 3500/9.5 or 368, the concentration in the "worse" case simulations are a factor of 368 higher than those in the "better" case. The bioaccumulation food web component of the model predicts higher concentrations in terrestrial carnivores and avian scavengers, and especially for the more highly chlorinated substances. The largest contributor to the TEQ burden in wildlife is from 1,2,3,7,8-Pentachloro-DD (59.2%), 2,3,4,7,8-Pentachloro-DF (19.6%), and 2,3,7,8-Tetrachloro-DD (14.6%).

It is concluded that extensive uncontrolled burning of wastes could result in substantial accumulations of dioxins and furans in the local ecosystem, some of which will persist for some 8.5 years with exposure levels approaching those considered to be of toxicological concern. The use of controlled incineration will substantially reduce the expected contamination levels and correspondingly reduce the likely exposure and effects.

Introduction

Dioxins and furans are a set of over 200 congeners produced unintentionally by human activities, including waste incineration, chemical manufacturing, petroleum refining, fuel combustion in vehicles, wood burning, and electric power generation. Since the introduction of increased regulation, pulp and papermills are no longer the major source of these substances and waste incineration is now being scrutinized (Williams, 2005).

In the north incineration at large remote work camps is a growing concern. Northern incineration is unregulated and is becoming a more pressing issue with the increase in mining and oil and gas activities. In particular, the Mackenzie Gas Project, if approved, is proposing more than 30 remote camps all of which will incinerate camp waste on site. The incineration technology used varies greatly and these camps have the potential to be a significant source of dioxins and furans.

These substances are known to be toxic to fish and wildlife affecting both the survival and reproductive success of fish, birds and mammals. In this study the exposure levels of wildlife to contaminants from the incineration of camp waste are estimated using mass balance modelling.

Toxic equivalents (TEQ) provide a convenient method for combining the adverse toxic effects of the components of a mixture. Here the toxic equivalent factors (TEFs) for the various dioxin and furan congeners, as given in Table 1a, are used to produce concentrations with the toxic equivalent of 2,3,7,8-TCDD.

Chemical Properties

The partitioning properties of dioxins and furans vary with the number and position of the chlorines present. With more chlorines present degradation tends to be slower and partitioning to lipids tends to increase. Here octanol is used as a surrogate for lipids in biota and for organic carbon in environmental media. This is convenient because the partition coefficients of chemicals between water and octanol and between air and octanol are commonly measured properties. The differences in chemical partitioning range over orders of magnitude as shown in

Table 1 (a-c). Figure 1 is a chemical space plot of all the substances and shows their partitioning properties and increasing affinity for octanol. Here it is assumed that there is no metabolic degradation of any of the substances, although it is known that metabolism occurs, albeit slowly. Metabolism, which is both congener and organism dependent, is not well quantified. Including metabolic conversions of the chemicals can be expected to reduce bioaccumulation and biomagnification and thus concentrations in the organisms, i.e., the assumption of no metabolism is a protectively conservative assumption. For convenience, an identifying code has been assigned to each dioxin and furan congener as shown in Table1a. These codes are used throughout this report.

CAS	Chemical Name	ID Code	Molar Mass,
			g/mol
262-12-4	Dibenzo-p-dioxin	D	184.191
39227-54-8	2-Chloro-DD	D1	218.636
33857-26-0	2,7-Dichloro-DD	D2	253.081
30746-58-8	1,2,3,4-Tetrachloro-DD	D4a	321.971
1746-01-6	2,3,7,8-Tetrachloro-DD	D4b	321.971
39227-61-7	1,2,3,4,7-Pentachloro-DD	D5a	356.416
40321-76-4	1,2,3,7,8-Pentachloro-DD	D5b	356.416
39227-26-8	1,2,3,4,7,8-Hexachloro-DD	D6a	390.861
57653-85-7	1,2,3,6,7,8-Hexachloro-DD	D6b	390.861
19408-74-3	1,2,3,7,8,9-Hexachloro-DD	D6c	390.861
35822-46-9	1,2,3,4,6,7,8-Heptachloro-DD	D7	425.308
3268-87-9	Octachloro-DD	D8	459.751
132-64-9	Dibenzofuran	F	168.191
5409-83-6	2,8-Dichloro-DF	F2	237.082
51207-31-9	2,3,7,8-Tetrachloro-DF	F3	305.978
57117-41-6	1,2,3,7,8-Pentachloro-DF	F5a	340.418
57117-31-4	2,3,4,7,8-Pentachloro-DF	F5b	340.418
70658-26-9	1,2,3,4,7,8-Hexachloro-DF	F6a	374.863
57117-44-9	1,2,3,6,7,8-Hexachloro-DF	F6b	374.863
72918-21-9	1,2,3,7,8,9-Hexachloro-DF	F6c	374.863
60851-34-5	2,3,4,6,7,8-Hexachloro-DF	F6d	374.863
67462-39-4	1,2,3,4,6,7,8-Heptachloro-DF	F7a	409.308
55673-89-7	1,2,3,4,7,8,9-Heptachloro-DF	F7b	409.308
39001-02-0	Octachloro-DF	F8	443.753
35693-99-3	2,2',5,5'-Tetrachlorobiphenyl	PCB-52	291.988
50-32-8	Benzo(a)pyrene	Bap	252.309
118-74-1	Hexachlorobenzene	HCB	284.782

Table 1a: The selected chemicals (Mackay et al, 2006).

Table 1b: Partitioning properties of the selected chemicals at 25°C (based on Mackay et al, 2006). K_{OW} is the octanol-water partition coefficient, K_{OA} is the octanol-air partition coefficient, and K_{AW} is the air-water partition coefficient.

Water Solubility,	Vapour Pressure	log K _{OW}	log K _{OA} ^a	$\log K_{AW}^{a}$
g/m ³	(solid), Pa			
0.865	0.055	4.3	6.62563	-1.16281
0.295	0.017	5	7.293896	-1.14695
0.00375	0.00012	6.38	8.865835	-1.24292
0.00055	6.4E-06	6.6	9.420611	-1.41031
1.93E-05	2E-07	6.8	9.670955	-1.43548
0.000118	8.8E-08	7.4	11.36969	-1.98484
9.82E-05	5.8E-08	7.5	11.57097	-2.03549
0.000006	5.1E-09	7.8	11.6728	-1.9364
0.000006	4.8E-09	7.9	11.79913	-1.94957
0.000006	6.5E-09	8.02	11.78746	-1.88373
2.4E-06	7.5E-10	8	12.27069	-2.13535
7.4E-08	1.1E-10	8.2	11.75956	-1.77978
4.75	0.4	4.27	6.513076	-1.12154
0.0145	0.00039	5.44	8.02965	-1.29482
0.000419	0.000002	6.53	9.759739	-1.61487
0.0002	0.000001	6.99	10.15326	-1.58163
0.000236	3.5E-07	6.5	10.19108	-1.84554
8.25E-06	3.2E-08	7	10.23168	-1.61584
0.000008	2.9E-08	7.57	10.83106	-1.63053
0.000008	1.44E-08	7.76	11.3251	-1.78255
0.000008	2.6E-08	7.65	10.95849	-1.65424
1.35E-06	4.7E-09	7.4	10.64043	-1.62022
1.3E-06	6.2E-09	8.23	11.33375	-1.55187
1.16E-06	5E-10	8	12.11259	-2.0563
0.03	0.0049	6.1	7.815805	-0.8579
0.0038	7E-07	6.04	10.767	-2.3635
0.005	0.0023	5.5	6.776974	-0.63849
by the model				
	Water Solubility, g/m^3 0.865 0.295 0.00375 0.00055 1.93E-05 0.000118 9.82E-05 0.000006 0.000006 2.4E-06 7.4E-08 4.75 0.0145 0.000419 0.0002 0.000236 8.25E-06 0.000008 0.000008 0.000008 1.35E-06 1.3E-06 1.3E-06 1.3E-06 1.16E-06 0.03 0.003 0.005 by the model	Water Solubility, g/m^3 Vapour Pressure (solid), Pa 0.8650.055 0.02950.2950.0170.003750.000120.000556.4E-061.93E-052E-070.0001188.8E-089.82E-055.8E-080.0000065.1E-090.0000066.5E-092.4E-067.5E-107.4E-081.1E-104.750.40.004190.000020.00020.000010.00020.000010.00023.5E-078.25E-063.2E-080.000082.9E-080.000082.6E-081.35E-064.7E-091.3E-066.2E-091.16E-065E-100.030.00490.00387E-070.0050.0023	Water Solubility, g/m^3 Vapour Pressure (solid), Palog Kow g/m^3 (solid), Pa0.8650.0554.30.2950.01750.003750.000126.380.000556.4E-066.61.93E-052E-076.80.0001188.8E-087.49.82E-055.8E-087.50.0000065.1E-097.80.0000066.5E-098.022.4E-067.5E-1087.4E-081.1E-108.24.750.44.270.01450.000395.440.00020.0000016.990.0002363.5E-076.58.25E-063.2E-0870.0000082.9E-087.570.0000082.9E-087.651.35E-064.7E-097.41.3E-066.2E-098.231.16E-065E-1080.030.00496.10.00387E-076.040.0050.00235.5by the model5.5	Water Solubility, g/m3Vapour Pressure (solid), Pa $\log K_{OW}$ $\log K_{OA}^a$ $g/m3$ (solid), Pa 0.865 0.055 4.3 6.62563 0.295 0.017 5 7.293896 0.00375 0.00012 6.38 8.865835 0.00055 $6.4E-06$ 6.6 9.420611 $1.93E-05$ $2E-07$ 6.8 9.670955 0.000118 $8.8E-08$ 7.4 11.36969 $9.82E-05$ $5.8E-08$ 7.5 11.57097 0.000006 $5.1E-09$ 7.8 11.6728 0.000006 $6.5E-09$ 8.02 11.78746 $2.4E-06$ $7.5E-10$ 8 12.27069 $7.4E-08$ $1.1E-10$ 8.2 11.75956 4.75 0.4 4.27 6.513076 0.00419 0.000002 6.53 9.759739 0.0002 0.000001 6.99 10.15326 0.00008 $2.9E-08$ 7.57 10.83106 0.000008 $2.9E-08$ 7.65 10.95849 $1.35E-06$ $4.7E-09$ 7.4 10.64043 $1.3E-06$ $6.2E-09$ 8.23 11.33375 $1.16E-06$ $5E-10$ 8 12.11259 0.03 0.0049 6.1 7.815805 0.0038 $7E-07$ 6.04 10.767 0.005 0.0023 5.5 6.776974



Figure 1: Chemical partitioning space is defined by the tendency to partition to air, water, or octanol (as a surrogate for lipids and organic carbon). In this plot, chemicals in the upper left tend to partition to air, chemicals in the lower left partition to water, and chemicals in the lower right partition to lipids and organic carbon (i.e., octanol). The dioxins (+) and furans (*) are labelled by the number of chlorines present and tend to partition into the organic matter in soil and sediment and into lipids in organisms. The diagonals indicate lines of constant octanol-air partitioning (K_{OA}). Also shown are coordinates for hexachlorobenzene (HCB), 2,2',5,5'-Tetrachlorobiphenyl (PCB 52), and benzo(a)pyrene (BaP), as reference compounds.

Table 1c: Environmental degradation half-lives of the selected chemicals at 25°C (based on Mackay et al, 2006). It is assumed that there is no metabolic conversion of the chemicals in any of the biota in the food web.

ID Code	Air	Water	Soil	Sediment	Air	Water	Soil	Sediment
	hours	hours	hours	hours	days	days	days	days
D	55	55	1700	5500	2.3	2.3	70.8	229.2
D1	170	170	5500	17000	7.1	7.1	229.2	708.3
D2	170	170	5500	17000	7.1	7.1	229.2	708.3
D4a	170	550	17000	55000	7.1	22.9	708.3	2291.7
D4b	170	550	17000	55000	7.1	22.9	708.3	2291.7
D5a	550	550	17000	55000	22.9	22.9	708.3	2291.7
D5b	550	550	17000	55000	22.9	22.9	708.3	2291.7
D6a	550	1700	55000	55000	22.9	70.8	2291.7	2291.7
D6b	550	1700	55000	55000	22.9	70.8	2291.7	2291.7
D6c	550	1700	55000	55000	22.9	70.8	2291.7	2291.7
D7	550	1700	55000	55000	22.9	70.8	2291.7	2291.7
D8	550	5500	55000	55000	22.9	229.2	2291.7	2291.7
F	55	170	1700	5500	2.29	7.1	70.8	229.2
F2	170	550	5500	17000	7.1	22.9	229.2	708.3
F3	170	550	17000	55000	7.1	22.9	708.3	2291.7
F5a	550	550	17000	55000	22.9	22.9	708.3	2291.7
F5b	550	550	17000	55000	22.9	22.9	708.3	2291.7
F6a	550	1700	17000	55000	22.9	70.8	708.3	2291.7
F6b	550	1700	17000	55000	22.9	70.8	708.3	2291.7
F6c	550	1700	17000	55000	22.9	70.8	708.3	2291.7
F6d	550	1700	17000	55000	22.9	70.8	708.3	2291.7
F7a	550	1700	17000	55000	22.9	70.8	708.3	2291.7
F7b	550	1700	17000	55000	22.9	70.8	708.3	2291.7
F8	550	5500	55000	55000	22.9	229.2	2291.7	2291.7
PCB-52	1700	55000	55000	55000	70.8	229.2	2291.7	2291.7
Bap	170	1700	17000	55000	7.1	70.8	708.3	2291.7
HCB	17000	55000	55000	55000	708.3	2291.7	2291.7	2291.7

Incineration Emissions

For a remote camp of approximately 1000 people, each person producing approximately 30 kg of waste per week (Chandler 2006), it is estimated that 1560 tonnes per year of waste will be incinerated onsite. For low technology combustion with no air pollution control systems it is estimated that 3,500 µg TEQ/ tonnes municipal solid waste (MSW) are produced (UNEP 2005). This total PCDD and PCDF emission rate of 5460 mg TEQ/year is used here to represent a "worse" case scenario. A "better" case scenario is represented by 9.5 µg TEQ/tonnes MSW measured at the Fort Smith medical waste incinerator (Lanfranco 2006; Chandler 2006) or 14.82 mg/year. Not all of the congeners in Table 1 were included in the Fort Smith report.

Table 2: Emissions estimates based on analysis of the Fort Smith incinerator (Lanfranco 2006). Emissions were calculated assuming 1000 camps using "worse" and "better" incineration technologies. The "scaling factors" are calculated as $E_{T, TEQ}$ ($M_i TEF_i$) / TEQ_T where M_i is the analyzed amount for the congener i, M_T is the total analyzed amount, $E_{T, TEQ}$ is the total emission in units of TEQ mg/y, TEF_i is the TEF for congener i, TEQ_T is the sum of the products $M_i TEF_i$. The toxic equivalent concentrations are calculated as $C_{i,TEQ} = C_O *$ (Scaling factor / E_O) where C_O is the concentration due to the unit emission, E_O .

		Analyzed		Scaling	Emissions,	mg TEQ / y
ID Code	TEF	Amount, ng	TEQ, ng	Factors	Worse Case	Better Case
D4b	1	0.0370	0.037	0.404557	2208883	5995.5
D5b	0.5	0.0220	0.011	0.120274	656695	1782.4
D6a	0.1	0.0062	0.00062	0.006779	37014	100.5
D6b	0.1	0.0097	0.00097	0.010606	57908	157.2
D6c	0.1	0.0068	0.00068	0.007435	40596	110.2
D7	0.01	0.0370	0.00037	0.004046	22089	60.0
D8	0.001	0.0460	0.000046	0.000503	2746	7.4
F3	0.1	0.0270	0.0027	0.029522	161189	437.5
F5a	0.05	0.0450	0.00225	0.024601	134324	364.6
F5b	0.5	0.0540	0.027	0.295217	1611887	4375.1
F6a	0.1	0.0300	0.003	0.032802	179099	486.1
F6b	0.1	0.0280	0.0028	0.030615	167159	453.7
F6c	0.1	0.0019	0.00019	0.002077	11343	30.8
F6d	0.1	0.0250	0.0025	0.027335	149249	405.1
F7a	0.01	0.0290	0.00029	0.003171	17313	47.1
F7b	0.01	0.0042	0.000042	0.000459	2507	6.8
F8	0.001	0.0000	0	0	0	0
Total		0.4088	0.091458	1	5460000	14820

The RAIDAR model

The RAIDAR model (Arnot et al 2006) was used to estimate how emissions of the selected substances to air are likely to become distributed in the environment and local wildlife. This model assumes that the emissions have been ongoing for sufficient time such that a steady-state condition has been achieved, i.e., there is no change with time and all emissions are now balanced by losses from the system. This represents the maximum achievable concentrations for the modelled environment and is thus protectively conservative. The time required to reach this steady-state level can be calculated from the model outputs.

The modelled area is 10^{11} m² or 10^5 km², i.e., approximately a tenth of the area of the Northwest Territories. Hot-spots are not modelled. Each environmental medium is assumed to be a "well-mixed" box with average conditions. The modelled environment and food web are evaluative in nature and not specific to any particular region. The environment is similar to that in the EQC model (Mackay et al 1996) that has been widely used in chemical fate evaluation. A complete list of environment and food web properties are given in Table 3.

An area of 100 km², i.e., 10 km \times 10 km, might better represent the case of a remote northern camp, however, the model would require extensive modification to address this smaller area. To approximate this case, the modelled area was considered to contain 1000 camps evenly spaced over the total area. If desired these areas and camp numbers can be adjusted. Essentially, the model thus addresses a situation in which there is 1 camp of 1000 persons for every 100 km² i.e. 10 km \times 10 km area. The emission rate from this camp is assumed to be a "worse" case of 5460 mg TEQ per year and a "better" case of 14.82 mg/year. Scaling these rates by a factor of 1000 to the entire area of 10⁵ km² results in emissions of a "worse" case of 5460000 mg/year and a "better" case of 14820 mg/year. These rates are used to scale the model results from the unit emissions.

	Area	Depth	n V	olume	Vo	lume	Density	
	m²	m	F	raction	m³		kg/m³	
Air	10^{11}	1000)	-		10^{14}	1.18	
Air Vapour	-	-		-		10^{14}	1.18	
Aerosol	-	-		2×10 ⁻¹¹	4	2000	2400	
Water	10^{10}	20		-	2	$\times 10^{11}$	1000	
Water	-	-		-	2	$\times 10^{11}$	1000	
Susp.Particles	-	-	(0.000005	5 10	00000	1500	
Fish	-	-	(0.000001	1 20	00000	-	
Soil	9×10^{10}	0.2		-	1.8	8×10^{10}	1500	
Pore Air	-	-		0.2	3.0	5×10^{9}	1.18	
Pore Water	-	-		0.3	5.	4×10^{9}	1000	
Solids	-	-		0.5	9	$\times 10^{9}$	2400	
Sediment	10^{10}	0.05		-	5	$\times 10^8$	1280	
Pore Water	-	-		0.8	4	$\times 10^8$	1000	
Solids	-	-		0.2		10^{8}	2400	
Coastal Water	0	0		-		0		
Org Carbon Fraction	σ/σ			Advecti	on Res	idence '	Time	
Susp Particles	02						h	d
Soil solids	0.02			Air			100	4.2
Sediment solids	0.02			Water			100000	4167
Biotic Linid (g/g ww)	0.01			Soil			-	-
Diotic Lipic (5/5 ww)	0.05			Sedime	nt		50000	2083
				Coastal	Water		100	4.2
Air Temperature		25	°C					
Water Temperature		10	°C					
Wind Speed	1	4.4	km/h					
Oxygen Saturation (W	Vater)	90	%					
Water pH	,	7						
Transport Velocities		m/	Ъ	m/v				
Air side air-water MT	Ϋ́C	111/	11 4	5 III/ y	13800			
Water side air water N			0.05	, .	138			
Poin roto	VIIC	(0.00)	430			
Aarosol deposition vo	locity	(1.0001		0.870 87600			
Soil air phase diffusio	n MTC		0.02))	175.2			
Soil water phase diffu	ni MTC	0	0.02		175.2			
Soll water phase unitu		0.	10000		12000			
Soli air boundary laye		() 4	+3800			
Sediment-water wirt		(J.0001 510-	7 0	0.870			
Sediment deposition v		•	3×10^{-2}	0.0 7 0.00	00438			
Sealment resuspensio	ii velocity	0	2×10 00007	- 0.00	0 429			
Soil water runoff rate		0.	10-5) 8 07	0.438			
Soll solids runoff rate			10	8.76	5×10°			
Scavenging ratio (unit	tless)	2	00000)				

Table 3: Environmental properties of the generic region.

The model contains a generic food web, this was modified slightly to better reflect a northern ecosystem and is shown in Figure 2. In this food web, the lower trophic level organisms (foliage, roots, plankton, and invertebrates) are assumed to be at equilibrium with their environment. This simplification is often sufficient as a first approximation since the uptake and loss processes are relatively fast and the organisms are often short-lived. By assuming equilibrium, these biota can be modelled with very few properties, namely the mass fractions of lipid, non-lipid organic matter, and water. Higher trophic level organisms are modelled assuming the steady-state condition has been achieved. For these organisms, additional properties are required to estimate chemical uptake and loss rates as shown in Table 4.



Figure 2: The foodweb in the RADIAR model, modified to better reflect the northern ecosystem (based on Arnot et al 2006).

Table 4: Food web properties.

Organism Size and Composition. All biota are assumed to contain 20% of non-lipid organic matter (NLOM) and to have lipid with a density of 900 $\rm kg/m^3$

		Mass	Density	Lipid Fraction	Water Content
		kg	kg/m³	g/g	g/g
1	Foliage vegetation	-	1000	0.01	0.79
2	Root vegetation	-	1000	0.01	0.79
3	Plankton	-	1000	0.01	0.79
4	Benthic invertebrate	-	1000	0.05	0.75
5	Pelagic-benthic fish	0.1	1000	0.05	0.75
6	Piscivorous fish	2.2	1000	0.2	0.6
7	Aquatic mammal	1000	1000	0.35	0.45
8	Terrestrial invertebrate	-	1000	0.02	0.78
9	Terrestrial herbivore	120	1000	0.1	0.7
10	Terrestrial carnivore	80	1000	0.2	0.6
11	Avian omnivore	0.25	1000	0.05	0.75
12	Avian scavenger	4.5	1000	0.1	0.7

Aquatic Feeding Matrix

-	Consumer			
	5	6	7	12
	Pelagic-benthic	Piscivorous	Aquatic	Avian
sumed	fish	fish	mammal	scavenger
Plankton	0.5			
Benthic invertebrate	0.5		0.3	
Pelagic-benthic fish		1	0.4	0.4
Piscivorous fish			0.3	0.15
Aquatic mammal				0.02
Terrestrial invertebrate				0.2
Terrestrial herbivore				0.18
Avian omnivore				0.05
Total Diet	1	1	1	1
	sumed Plankton Benthic invertebrate Pelagic-benthic fish Piscivorous fish Aquatic mammal Terrestrial invertebrate Terrestrial herbivore Avian omnivore Total Diet	Consumer 5 Pelagic-benthic sumed fish Plankton 0.5 Benthic invertebrate 0.5 Pelagic-benthic fish Piscivorous fish Aquatic mammal Terrestrial invertebrate Terrestrial herbivore Avian omnivore Total Diet 1	Consumer56Pelagic-benthicPiscivoroussumedfishfishPlankton0.51Pelagic-benthic fish1Piscivorous fish1Aquatic mammal1Terrestrial invertebrate1Terrestrial herbivore1Avian omnivore1Total Diet1	Consumer567Pelagic-benthicPiscivorousAquaticsumedfishfishmammalPlankton0.50.3Benthic invertebrate0.50.3Pelagic-benthic fish10.4Piscivorous fish0.3Aquatic mammal0.3Terrestrial invertebrate0.3Terrestrial herbivore11Avian omnivore11Total Diet11

Terrestrial Feeding Matrix

	e	Consumer			
		9	10	11	12
		Terrestrial	Terrestrial	Avian	Avian
Cor	nsumed	herbivore	carnivore	omnivore	scavenger
1	Foliage vegetation	0.8		0.4	
2	Root vegetation	0.2		0.05	
5	Pelagic-benthic fish				0.4
6	Piscivorous fish				0.15
7	Aquatic mammal				0.02
8	Terrestrial invertebrate			0.55	0.2
9	Terrestrial herbivore		1		0.18
11	Avian omnivore				0.05
12	Avian scavenger				
	Total Diet	1	1	1	1

Air Respiration

		Parameter	Parameter	Activity	
		А	В	Factor	Rate m ³ /h
5	Pelagic-benthic fish	0.98	0.65	0	0.000873
6	Piscivorous fish	0.98	0.65	0	0.006507
7	Aquatic mammal	0.55	0.8	1.5	8.63461
9	Terrestrial herbivore	0.55	0.8	1.5	1.583389
10	Terrestrial carnivore	0.55	0.8	1.5	1.144761
11	Avian omnivore	0.4	0.77	2.5	0.014329
12	Avian scavenger	0.4	0.77	2.5	0.132667

Water Consumption and Excretion. All organisms that drink water are assumed to excrete it at the same rate, i.e., a urination factor of 1.

		Drinking	Drinking	Drinking/Urnination
		Parameter A, L/d	Parameter B	Rate m ³ /h
7	Aquatic mammal	0.01	0.9	0.000209
9	Terrestrial herbivore	0.09	0.9	0.000279
10	Terrestrial carnivore	0.09	0.9	0.000194
11	Avian omnivore	0.06	0.7	9.47×10 ⁻⁷
12	Avian scavenger	0.06	0.7	7.16×10 ⁻⁶

Feeding

		Max.	Feeding		Feeding	Growth	Diet Et	fficiency
		BMF	Parameter	ſ	Rate	Rate	Parame	eter
		Q	A, kg/d	В	m³/m³.h	1/h	А	В
5	Pelagic-benthic fish	4	0.02	0.85	2.14×10^{-7}	2.14×10 ⁻⁹ 9	2	-8
6	Piscivorous fish	8	0.02	0.85	2.97×10^{-6}	2.97×10^{-8}	2	-8
7	Aquatic mammal	120	0.02	0.8	0.000837	8.37×10^{-6}	1.05	-10
9	Terrestrial herbivore	4	0.08	0.72	0.000419	4.19×10^{-6}	1.05	-10
10	Terrestrial carnivore	120	0.02	0.8	0.000111	1.11×10^{-6}	1.05	-10
11	Avian omnivore	10	0.05	0.85	2.56×10^{-6}	2.56×10^{-8}	1.05	-10
12	Avian scavenger	60	0.05	0.85	2.99×10^{-5}	2.99×10^{-7}	1.05	-10

Results

Initially unit emissions to the model environment of a broad range of PCDD and PCDF congeners and the selected comparison chemicals are assumed. Figure 3 shows the relative concentrations of D4b (2,3,7,8-Tetrachloro-DD) in all of the environmental media and biota. The affinity of D4b (2,3,7,8-Tetrachloro-DD) for organic matter and lipids is evident by examination of these relative concentrations. The high concentration associated with the foliage is due to atmospheric deposition. In each of the aquatic (blue bars) and terrestrial (green bars) food webs the organism trophic level is reflected in the relative concentration. If metabolism were included, this effect is expected to be less pronounced.



Figure 3a: The relative concentrations of D4b (2,3,7,8-Tetrachloro-DD) in all of the environmental media (black bars) and aquatic (blue bars) and terrestrial (green bars) biota. The avian scavenger is indicated in teal as a reminder that its diet includes both aquatic and terrestrial food sources.



Figure 3b: The fugacities of D4b (2,3,7,8-Tetrachloro-DD) in all of the environmental media (black bars) and aquatic (blue bars) and terrestrial (green bars) biota. The avian scavenger is indicated in teal as a reminder that its diet includes both aquatic and terrestrial food sources.

Figure 4 shows the relative concentrations of the substances in the terrestrial carnivore with the three reference substances on the far right. Results are congener specific but it can be seen that the concentrations are lower in the environmental media and range over many orders of magnitude with the terrestrial carnivore showing the highest set of concentrations. The pattern of increasing concentration with increasing chlorine number occurs as expected and applies to all media.



Figure 4a: The relative concentrations of all the chemicals in the terrestrial carnivore.



Figure 4b: The relative fugacities of all the chemicals in the terrestrial carnivore.

The persistence, or longevity, of each congener in the environment can be estimated as the amount present in the system at steady-state divided by the total removal rate. This is the average time that any one molecule of the chemical will spend in the system before it is degraded, buried in the sediment, or flows out in the air or water. A useful feature of this value is that it does not depend on the emission rate. The persistence of the dioxins and furans range from a few days for D1 to 8.5 years for the higher chlorinated dioxins and furans.

Using the emissions in Table 2 concentrations of each congener were calculated and scaled to the toxic equivalent of D4b (2,3,7,8-TCDD) using toxic equivalent factors (CEPA 1993; Lanfranco, 2006). The sum of these concentrations are given in Figure 5.



Figure 5: Estimated TEQ concentrations of dioxins and furans in the environment and the ecosystem resulting from MSW incineration at a remote camp. The green squares represent the "better" case, yellow diamonds represent the "worse" case.

While the toxicity of dioxins and furans is widely accepted, there is little definitive data indicating safe and toxic levels. An additional complication is the observed variation in toxicity between organisms. For comparison, it has been recommended that a tolerable daily intake (TDI) for humans be set at 1 to 4 pg/kg of body weight (DEFRA 2002;). If we consider the case of a 70 kg human, this implies 70 to 280 pg per day. From Figure 5, the 2.2 kg piscivorous fish (modelled on a salmonid) will contain $1000 - 3.78 \times 10^5$ pg TEQ of dioxins and furans. For a person eating the two or three 125mL servings of meat per day recommended by the Canadian Food Guide (2007) this results in a dose of 0.05 (assuming two servings of fish in the "better" case emission scenario and a TDI of 4 pg/kg) to 116 (assuming three servings, the "worse" case emission, and a TDI of 1 pg/kg) times the TDI from this source. This is a simple order-of-magnitude calculation but provides a context for considering the concentrations in Figure 5.

The no-observed effect level for D4b (2,3,7,8-Tetrachloro-DD) for chronic exposure in rats is 1 ng/kg of body weight per day (CEPA 1993). Using a calculation similar to the one above for

humans by assuming that the rat has a diet and size similar to the avian omnivore in the model and eats its body weight each day. Under these assumptions the rat would receive a daily dose of 0.8 - 290 times the NOEL under the "better" and "worse" case emission scenarios.



Figure 6: Estimated TEQ concentrations of dioxins and furans in an environment modified to better reflect the NWT (but still at a temperature of 25°C) and the ecosystem resulting from MSW incineration at a remote camp. The green squares represent the "better" case, yellow diamonds represent the "worse" case.

Discussion

Using the existing RAIDAR model the environmental fate and bio-uptake was estimated for a set of dioxins and furans. A generic environment and unit emissions showed that each congener will partition differently but following the general patterns of increased concentrations with increasing chlorine number and increased uptake in higher trophic level organsims. Two emission scenarios were considered to represent a typical northern mining camp; first, a "worse" case scenario to simulate emissions from the barrel burning of camp waste; and second, a "better" case scenario to simulate emissions from incineration equipment capable of meeting the Canada-wide emission standards. Model results suggest that in the "better" case, concentrations are likely to be below the levels where effects are observed. However, in the "worse" case emission scenario, levels of dioxins and furans may be problematic.

This evaluation should be considered to be preliminary due to the many simplifying assumptions.

One important assumptions is that of no metabolism. This assumption is protectively conservative, if a substance is metabolised at any point in the food web, bioaccumulation and biomagnification will be reduced.

Another important assumption in this modelling exercise that should be considered in future work is the model environment temperature of 25°C. At lower temperatures the dioxins and furans can be expected to degrade more slowly due to decreased photolyis and microbial activity, for example. They will also partition more strongly to the soil and sediment where degradation is generally slower than in the air and water. These effects will both tend to increase the concentrations in the environmental media and persistence of the dioxins and furans in the environment making them available for uptake by biota for a longer period. Thus, we expect that concentrations are under-estimated by the model assumption of a constant temperature of 25°C. The factor by which concentrations are underestimated has not been determined in this project, but based on previous experience it is probably of the order of a factor of 10.

The model does not include snow. If a system with constant winter temperatures is considered so that the model's steady-state assumption is not violated, the higher efficiency of snow scavenging should be considered. It has been suggested that snow is approximately 5 times more efficient than rain at scavenging particles out of the air (Wania et al 1999). For dioxins and furans that will tend to partition to the particles, this could be an important transport mechanism moving chemical to environmental media where it will degrade more slowly.

In the northern context, the steady-state assumption does not describe the potentially important seasonal effects. It is possible that chemical may be sequestered in snow during the winter months and that during snowmelt the concentration in snowmelt waters entering the aquatic ecosystem may be very high. This is of even greater concern because snowmelt occurs at a time when many aquatic organisms may be more sensitive due to their lifecycles.

The application of this screening level model shows convincingly that these substances will accumulate in the environment, they will bioaccumulate, especially to higher trophic levels and there will be resulting human and ecosystem expsoure. Exposure will be proportional to the emission rate thus determining that rate is very important. The key quantity is the emission rate per 100 km². Future modelling efforts should involve some estimate of the effects of lower temperatures, snow, and snowmelt.

It may also be useful to seek a degree of validation for the model by applying it to a similar situation in which monitoring data are available. One candidate study is that of PCB dispersion in the Swan HIIIs as reported by Blais et al (2003).

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