A SIMPLE MODEL TO PREDICT PCDD/F CONCENTRATIONS IN VEGETATION AND SOIL

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Introduction

Pollutants released to the environment are distributed into various environmental compartments (e.g. water, soil and biota). The knowledge of pollutant fate and transport is essential in order to assess the potential impact on the environment. Compartment multimedia models have become useful screening tools for determining multimedia pollutant exposure as well as for risk assessment[1].

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) are well-known environmental pollutants. PCDD/Fs enter the atmosphere primarily as combustion by-products from incineration, metal production, automobile emissions, as well as a number of industrial activities. Atmospheric transport and subsequent deposition of PCDD/Fs are the processes primarily responsible for the ubiquitous presence of these organic contaminants in the biosphere. Because these compounds are semivolatile and hydrophobic, they accumulate in organic rich media as soils, sediment and biota.

On the other hand, PCDD/Fs are a group of chemicals that have been treated traditionally as a single compound, 2,3,7,8-tetrachloro-dibenzo-p-dioxin (2,3,7,8-TCDD). However, the environmental fate and transport of individual PCDD/F congeners varies substantially. Taking this into account, the aim of this study was to develop a model for vegetation and another for soils, which were able to predict the levels of the 17 individual 2,3,7,8-congeners. In order to validate these models, the results were compared with those obtained from a monitoring program carried out in the vicinity of a municipal solid waste incinerator (MWSI) placed in Montcada (Barcelona, Spain).

Methods and Materials

Accumulation of PCDD/Fs in vegetation occurs by two main pathways: uptake from soil and direct deposition. Because of the liphophilic character of PCDD/Fs, apparently, accumulation from soils is a minor pathway. Therefore, direct deposition (gas and particle-phase dry and wet) from the atmosphere is the predominant source of PCDD/Fs to vegetation (Table 1).

With respect to the soil model, the contaminant mass fraction in surface soil is estimated using a simple accumulation model in which PCDD/Fs are assumed to deposit, mix and remain within a fixed soil depth. Background soil concentration, direct particle deposition (dry and wet) and uptake by root onto the plant are the pathways that contribute to soil accumulation (Table 2).

In order to validate our model, the predicted results were compared with data obtained in a monitoring program performed in the vicinity of an old MSWI between 1996 and 1998[5,6]. The levels of PCDD/Fs in soils and vegetation were analyzed in 24 samples in 1996, 1997 and 1998. Median values of PCDD/F levels in soil and vegetation were used to validate the models. The meteorological and geographical parameters that were needed in our models were those corresponding to this area.

Data on PCDD/F levels in soils from 1996 were used as background soil concentrations in the model, whereas the concentrations of PCDD/Fs in vegetation and soil during 1998 were used to validate both, soil and vegetation models.

Table 1. Summary of the algorithm to calculate vegetation concentrations

VEGETATION CONCENTRATION, C_{abv}	
$C_{abv} = C_{va} + C_{ddp} + C_{wdp} + C_{ur}$	
C_{abv}: concentration in above-ground vegetation, expressed on a dry weight basis, ppm C_{va}: concentration due to vapor-phase absorption or airborne contaminants[2,4], ppm C_{ddp}: concentration due to dry deposition of contaminated particulate onto plant matter[3,4], ppm C_{wdp}: concentration due to wet deposition of contaminated particulate onto plant matter[3,4], ppm C_{ur}: concentration due to uptake by root onto plant matter[4], ppm	
$C_{va} = \frac{B_{vpa} C_v VG_{ag}}{d_a}$	C_{va}: concentration due to vapour-phase absorption, ppm B_{vpa}: mass-based air-to-leaf biotransfer factor, unitless C_v: vapor-phase concentration of contaminant in air, ng/m^3 VG_{ag}: empirical correction factor d_a: density of air, kg/m^3
$C_{ddp} = \frac{D_d I_j}{K_P Y_j}\left(1 - e^{-K_P T_P}\right)$	C_{ddp}: concentration due to dry particle deposition, ppm D_d: dry particle deposition flux, ng/m^2/y I_j: fraction intercepted by crop during deposition, unitless K_P: first-order weathering vegetation dissipation constant, 1/y Y_j: dry matter yield of crop j, kg/m^2 T_p: length of the growing period of the plant, y
$C_{wdp} = \frac{D_w R_w I_j}{K_P Y_j}\left(1 - e^{-K_P T_P}\right)$	C_{wdp}: concentration due to wet particle deposition, ppm D_w: wet particle deposition flux, ng/m^2 y R_w: fraction of particles retained after rainfall, unitless
$C_{ur} = C_{sa} BCF$	C_{ur}: concentration due to uptake by root onto plant matter, ppm C_{sa}: contaminant mass fraction in the soil, ng/kg BCF: root uptake factor, unitless

Table 2. Summary of the algorithm to calculate soil concentrations

SOIL CONCENTRATION, C_s	
$C_s = C_{bg} + C_{sddp} + C_{swdp} - C_{ur}$	
C_s: concentration in above-ground soil, ppm C_{bg}: background soil concentration[5], ppm C_{sddp}: concentration due to dry particulate deposition[2], ppm C_{swdp}: concentration due to wet particulate deposition[2], ppm C_{ur}: concentration due to the uptake by root onto plant matter, ppm	
$C_{sddp} = \frac{D_d}{K_s d_z \tau}\left(1 - e^{-K_s T}\right)$	C_{sddp}: concentration due to dry particulate deposition, ppm D_d: dry particle deposition flux, ng/m^2 y K_s: first-order of dissipation constant, 1/y T: length of the deposition period, y D_z: soil bulk density, kg/m^3 τ: soil mixing depth, m
$C_{swdp} = \frac{D_w F_w}{K_s d_z \tau}\left(1 - e^{-K_s T}\right)$	C_{swdp}: concentration due to wet particulate deposition, ppm D_w: wet deposition flux, ng/m^2 y F_w: fraction of wet deposition adhering to grass

Results and Discussion

The comparison between the results in soil and vegetation predicted by the models and those found in the monitorized area is shown in Table 3. For almost all individual congeners, PCDD/F concentrations were lower than those predicted. The discrepancies between predicted and experimental data were greater for vegetation than for soils. The greatest discrepancies were found for OCDD, 1,2,3,7,8,9-HxCDF and 2,3,4,6,7,8-HxCDF in both models (soils and vegetation). On the other hand, the most toxic congener (2,3,7,8-TCDD) showed one of the best match of predicted/measured concentration in the soil model. In vegetation, the congeners showing the best match were 2,3,7,8-TCDF and 1,2,3,7,8,9-HxCDD. The I-TEQ predicted for soils and vegetation showed a quite good agreement with resoect to that observed in both models. The relation between the predicted and measured concentrations for each PCDD/F congener is depicted in Figure 1.

Table 3. Comparison of data obtained from the model and those from the monitoring program (results are expressed in ng/kg)

	Vegetation			Soil		
	concen. predicted	concen. observed[5]	ratio predicted /observed	Concen. predicted	concen. observed[5]	Ratio Predicted /observed
2,3,7,8-TCDD	0.02	0.09	0.22	0.17	0.20	0.85
1,2,3,7,8-PeCDD	0.08	0.30	0.27	0.61	0.90	0.68
1,2,3,4,7,8-HxCDD	0.24	0.27	0.89	0.75	1.10	0.68
1,2,3,6,7,8-HxCDD	0.63	0.60	1.05	1.27	2.10	0.60
1,2,3,7,8,9-HxCDD	0.47	0.50	0.94	1.41	1.75	0.81
1,2,3,4,6,7,8-HpCDD	7.88	3.60	2.18	36.80	35.50	1.04
OCDD	111.18	10.50	10.59	190.59	82.50	2.31
2,3,7,8-TCDF	1.09	1.20	0.91	1.86	1.50	1.24
1,2,3,7,8-PeCDF	0.15	0.80	0.19	1.23	1.55	0.79
2,3,4,7,8-PeCDF	0.31	0.70	0.44	1.66	2.50	0.66
1,2,3,4,7,8-HxCDF	1.21	0.80	1.51	2.61	3.80	0.69
1,2,3,6,7,8-HxCDF	0.41	0.71	0.58	1.73	2.65	0.65
1,2,3,7,8,9-HxCDF	0.49	0.05	9.80	0.61	0.20	3.05
2,3,4,6,7,8-HxCDF	0.03	0.90	0.03	3.10	4.50	0.69
1,2,3,4,6,7,8-HpCDF	1.06	2.70	0.39	13.16	22.00	0.60
1,2,3,4,7,8,9-HpCDF	0.85	0.30	2.83	1.76	1.60	1.10
OCDF	2.19	1.35	1.62	27.18	21.00	1.29
I-TEQ	0.90	1.21	0.74	3.44	4.43	0.78

Figures 2a and 2b show how each pathway contribute to the total PCDD/F concentrations. For vegetation, the most notable pathway is the vapour-phase absorption by the plant followed by the uptake by roots (Figure 2a). It coul be expected taking into account the liphophilic character of PCDD/Fs. On the other hand, the most important pathway for the levels of PCDD/Fs in soil is the background soil concentration itself (Figure 2b). Soils reflect cumulative PCDD/F deposition during rather long periods of time. Consequently, as soil background levels represent accumulation during

long periods of time, these levels will be usually higher than the deposition for a relatively short period of time (three years).

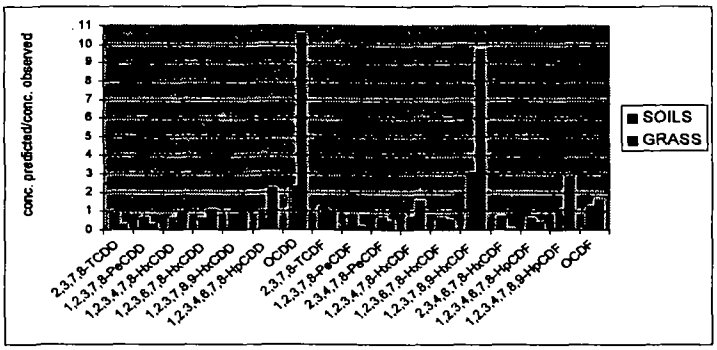
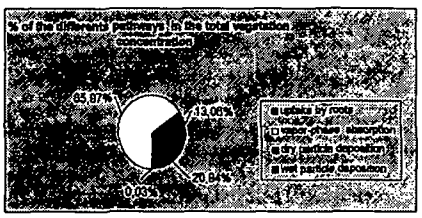
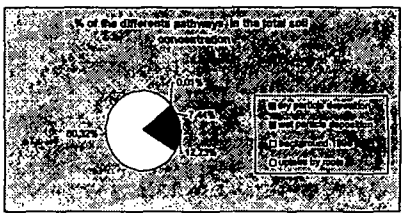


Figure 1. Ratio of predicted and measured concentrations for each PCDD/F congener





Figures 2a and 2b. Contribution of each pathway to PCDD/F levels in vegetation and soil

Conclusions

1) The current models predict the soil and vegetation levels in a good agreement with the measured levels.

2) The most important pathway contributing to accumulation of PCDD/Fs in vegetation is the vapour-phase absorption.

3) The most important pathway contributing to accumulation of PCDD/Fs in soil is the background concentration itself.

References

1. Ryan P.A. and Cohen Y. (1986) Chemosphere 15, 21.
2. Lorber M., Cleverly D., Schaum J., Phllips L., Schweer G. and Leighton T. (1994) Sci. Total Environ. 156, 39.
3. Zemba S.G., Green LC., Crouch E.A.C. and Lester R.R. (1996) J. Hazard. Mater. 47, 229.
4. Harrad S. and Smith D.J.T. (1997) Chemosphere 34, 1723.
5. Domingo J.L., Schuhmacher M., Granero S., Llobet J.M. and de Kok H.A.M. (1999) Arch. Environ. Contam. Toxicol. 36, 377.
6. Domingo J.L., Schuhmacher M., Meneses M., Granero S., Llobet J.M. and de Kok H.A.M. (1999) J. Environ. Sci. Health A34,165.