BLACK CARBON-INCLUSIVE FUGACITY MODELLING TOOL FOR ESTIMATING THE AQUATIC FATE OF PCDD/Fs IN THE GRENLAND FJORDS IN NORWAY

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Introduction

For many years, it has been reasoned that amorphous organic matter is almost entirely responsible for the sorbing capacity of sediments[1] for hydrophobic compounds and that the solid–water distribution coefficient, K_d (L_W/kg_{dw}), can be estimated from

$$K_d = f_{POC} K_{POC} \qquad\qquad (1)$$

where f_{POC} is the mass fraction of organic carbon in dried soil or sediment and K_{POC} (L_W/kg_{OC}) is the organic carbon normalized solid–water partition coefficient. It has further been shown that K_{POC} is closely related to the octanol–water partition coefficient (K_{OW})[2,3]. This approach for describing solid-water distribution is widely used in fate modelling[4]. There is, however, increasing evidence to suggest that the existing organic-matter (OM) partitioning model paradigm is not sufficient to explain the sorption of hydrophobic organics to sediments and aquatic particulate matter. The presence of strongly sorbing pyrogenically-derived materials, such as unburned coal, kerogen, cenosphere, soot and charcoal (the remnants of incomplete combustion, commonly termed "black carbon" or BC), in sediment particles has been shown to lead to enhanced sorption of hydrophobic organic compounds.[5]

In this paper we use a previously developed aquatic fate model (DIG-modelling tool)[6] to simulate the fate of PCCD/Fs in the Grenland Fjords in Norway. We investigate the ability of the model to simulate the particulate-phase concentration of PCDD/Fs in various parts of the fjord by both (I) an organic matter partitioning model, and (II) a BC-inclusive model. The simulated results are validated by observations from three intensive field studies. We know from previous work that the distribution of PCDD/Fs in the fjord is strongly related to the fraction of BC[7] in the solids, but this is the first attempt to mechanistically model the fate of PCDD/Fs sorbed to BC using a multimedia model.

Materials and Methods

Selected compounds

Analytical data for model comparison are available for 7 PCDD congeners and 10 PCDF congeners from three separate campaigns that intensively sampled the water column and bottom sediments in December 1998, June–July 1999 and May 2000, respectively[7]. In this paper, the results of two compounds have been selected for presentation, namely: 2378-tetrachlorodibenzo-p-dioxin (TCDD) and octachlorodibenzofuran (OCDF). These compounds were selected based on their different physical-chemical properties and because of their presence in relatively high concentrations, providing much data for model evaluation.

DIG-modelling tool

The DIG model is a multimedia box model based on the fugacity principle, which was developed to describe for the long-term fate (1950-2050) of PCDD/Fs in the marine environment of the Grenland Fjords in Norway[6]. The Grenland Fjords (Fig. 1) are five jointed fjords in the south of Norway (59° 5' N, 9° 38' E). In the innermost fjord, the Frierfjord, a magnesium production plant began operating in 1951 and closed in 2002. Large amounts of PCDD/Fs and other chlorinated organic pollutants were formed as by-products during the chlorination of magnesium oxide to yield water-free magnesium chloride. The long-term release of PCDD/Fs (especially) to the fjord has left a legacy of contaminated sediments. As a result concentrations in biota in the fjord exceed the EU recommended dietary limit of 4 ng/kg wet weight (sum of PCCD/Fs in 2378-TCDD toxic equivalents). The model used here (Fig. 1) is parameterised exactly as in ref. 6, except with regard to how the distribution between water and suspended particulates and water and bottom sediment, and the flow of particulate material are

described. In this modified DIG-model, adsorption to BC and transport of chemical in association with particulate BC is additionally considered. The modification to mechanistically model sorption to BC is described below.
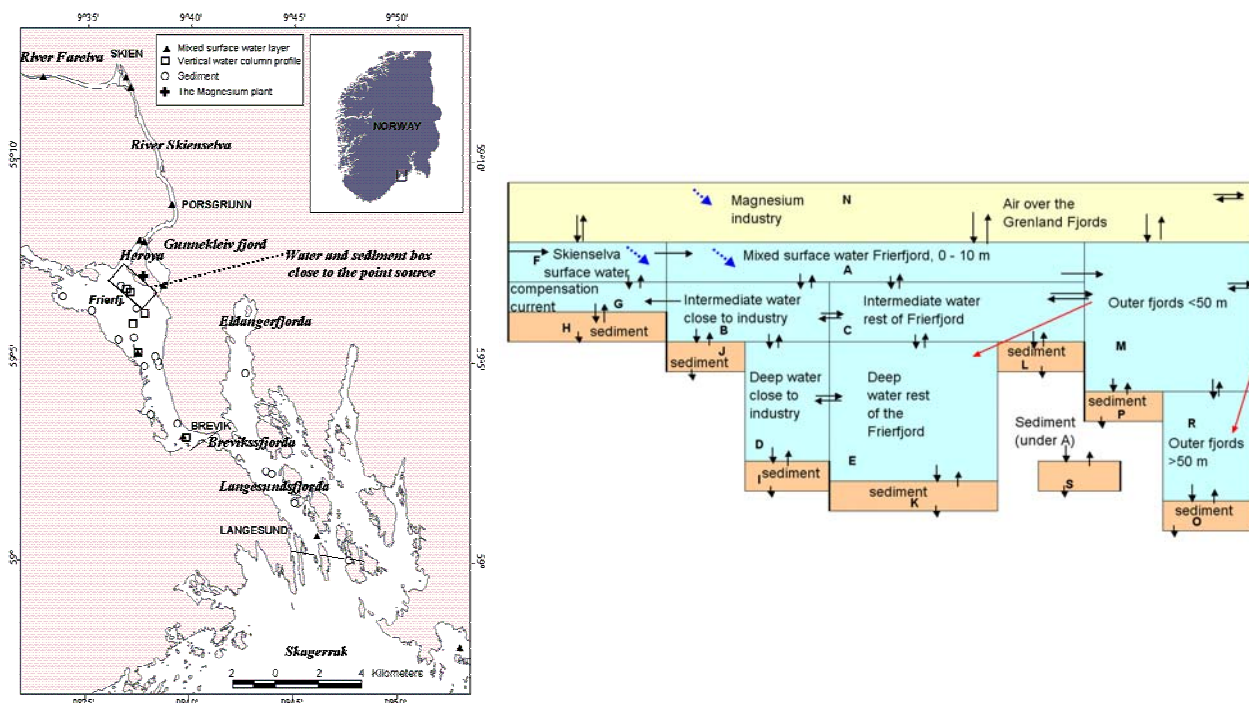

Fig.1. The left-hand side shows the Grenland Fjords area with sampling sites. The right-hand side shows a vertical view of the DIG model compartments. Intermedia transfer routes are shown as solid arrows. Dashed arrows are emission routes to air and surface water

Sorption model

Both Freundlich and Langmuir isotherms have been used to describe the combined sorption into OM (absorption) and onto BC (adsorption)[5]. It is debatable which of these two models provides the best approximation and indeed neither may be ideal. The Freundlich model is represented by equation (2)

$$C_S = f_{POC} K_{POC} C_W + f_{SC} K_{BC} C_W^n \qquad (2)$$

where C_S is the concentration on the solid (mol/kg solid), f_{SC} is the mass fraction soot carbon in the sediment, C_W is the dissolved compound concentration in water (mol/L), K_{BC} is the BC-normalized adsorption coefficient and n is the Freundlich non-linearity parameter. Equation (2) is difficult to apply in practice to the PCDD/Fs because of the lack of congener-specific values for the Freundlich non-linearity parameter (n). The Langmuir model is represented by equation (3)[8]

$$C_S = f_{OC} K_{OC} C_W + f_{BC} \left[\frac{b C_W Q_{max}}{1 + b C_W} \right] \qquad (3)$$

where Q_{max} and b are the maximum site adsorption capacity of the sorbent (mol/kg BC) and the Langmuir site sorption affinity (L/mol), respectively. At low water concentrations equation (3) reduces to[8]

$$C_S = f_{OC} K_{OC} C_W + f_{BC} b Q_{max} C_W \tag{4}$$

where bQ_{max} is equivalent to K_{BC}. This shows that in the Langmuir isotherm, at low sorbent concentrations, where the strongest sorption sites are far from being saturated, the relationship between the concentration on the solid and the water concentration is linear. This is contrary to the Freundlich isotherm where sorption is non-linear at all water concentrations. The Langmuir isotherm seems intuitively to better describe the competitive sorption process. In the Langmuir isotherm, a non-linear relationship only exists when there is competition for adsorption sites. This linear sorption isotherm for BC may be appropriate in systems where pollutant concentrations are very low. Indeed, the sorption isotherm for phenanthrene was recently found to be linear for the concentration range 0-10 ng/L[9]. Therefore, if our reasoning is correct, theoretically-derived K_{BC} values together with estimates of f_{BC} can be used to predict the enhanced sorption of hydrophobic organics to sediments without correcting for non-linearity in aquatic systems where concentrations of planar organic contaminants in water are low and thus there is little competition for sorption sites.

Two versions of the DIG-model were generated in which sorption was estimated by either: (I) an organic matter partitioning model (equation 1) and $K_{POC} = 0.41\ K_{OW}$[2], or (II) a BC-inclusive model, without competitive adsorption, based on equation (4). The fractions of OC and BC in the suspended particulates and bottom sediment for the different compartments in the model have been previously measured[7].

K_{BC} values were estimated from thermodynamic calculations as described in ref. 10. Using melting temperatures from Iorish et al.[11], and subcooled liquid solubilities from Govers and Krop[12], this gave log K_{BC} values of 10.3 and 12.2 for 2378-TCDD and OCDF, respectively. An alternative approach to estimating K_{BC} is to use the relationship for planar sorbates derived by Xia and Ball[13] is

$$Log K_{BC} = 1.6 \log K_{OW} - 1.4 \tag{5}$$

Using K_{OW} values from ref. 12 in equation (5) gives K_{BC} values of 9.7 and 12.4 for 2378-TCDD and OCDF, respectively. The two different estimation approaches provide K_{BC} values, which are similar. We believe this strong comparison provides confidence in both the estimation methods and values obtained from thermodynamic calculations. Because of space limitations, it is not possible to list all model input parameters and equations. A full listing of model equations can be found in ref. 6.

Results and Discussion

Model simulations were carried out for the two target PCDD/F congeners for the period from 1950 to 2050. Here we test the performance of the two sorption models by comparing model results to field measurements taken from three field campaigns undertaken between 1989 and 2001. To quantitatively compare model predictions with observations, model bias (MB) was calculated as C_P/C_O, where C_P is predicted concentration and C_O is median observed concentration. It indicates systematic overestimation (if MB > 1.0) or underestimation (if MB < 1.0). The evaluation of the model is focused on the particulate fraction, since this contains the largest amounts of the PCDD/Fs, and hence tells the most about the accuracy of the mass-balance results.

Table 1 shows that the organic matter-partitioning model under-predicts concentrations in the particulates in the water column by a factor of 28 to 71. It performs better for the sediments, but still under-predicts observations by a factor of 2.3 to 25. The BC-inclusive model performs better, under-predicting water column particulate concentrations by about a factor of 4 and over-predicting sediment concentrations by a factor of 1.4 to 5. Therefore, model predictions for the BC-inclusive model were always within a factor of 5 of observations, which is very respectable for models of this type.

In dilute, relatively unpolluted, and OM-poor systems (e.g. marine systems) such as the Grenland Fjords, BC is hypothesised to be an important sorbent for planar compounds.[9] The BC-inclusive model represented by equation 4, which assumes no competitive sorption, would appear to offer a mechanistic explanation for the enhanced sorption of PCDD/Fs to particulates in this particular system. In more polluted systems, competitive

sorption would be expected unless the system is sufficiently polluted that adsorption sites become fully saturated. Further field-testing of BC-inclusive models is needed to test these various hypotheses.

Table 1. Model bias for the comparison of model predictions with observations for the particulate phase for different model boxes (Fig. 1) for the organic matter partitioning (OMP) model and BC-inclusive model.

	Box	2378-TCDD		OCDF	
		OMP	**BC**	**OMP**	**BC**
W A T E R	F	0.0036	0.01	0.13	0.21
	A	0.040	0.24	0.00044	0.039
	B	0.019	0.71	0.033	0.33
	C	0.014	0.22	0.0023	0.073
	D	0.0030	0.20	0.065	0.69
	E	0.014	0.18	0.059	0.40
	M	0.13	0.43	0.040	0.12
	Median	**0.014**	**0.22**	**0.036**	**0.27**
S E D I M E N T	H	0.13	0.21	0.83	0.99
	I	0.00044	0.039	0.023	1.5
	J	0.033	0.33	0.15	1.3
	K	0.0023	0.07	0.015	0.38
	L	0.065	0.69	0.63	5.8
	O	0.059	0.40	0.32	2.1
	P	0.040	0.12	0.42	1.4
	R	0.0043	0.41	1.7	190
	S	0.13	0.21	0.83	0.99
	Median	**0.04**	**5.2**	**0.44**	**1.44**

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