Field Evaluation of a Freshwater Aquatic Food Chain Model for PCBs

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Abstract
A mathematical model of the transfer of PCBs through the freshwater aquatic food chain is described. The model predicts concentrations of selected individual PCB congeners in forage fish and pike, given source terms of atmospheric deposition and watershed soil concentrations. The efficacy of the model has been evaluated using data from a field study conducted in the R. Severn near Birmingham, UK. Results demonstrate overall model predictions of individual PCB concentrations in both forage fish and pike underestimate measured concentrations by factors of between *ca* 1.2 and 25 for individual congeners. Closer scrutiny reveals that the principal cause of this underestimation are the algorithms used to predict PCB levels in suspended sediment.

Introduction

The consumption of fish constitutes an important pathway of human exposure to SOCs like PCBs, and as a result, there have been many attempts to predict their transfer through freshwater aquatic food chains[1,2]. This paper describes the algorithms used to predict the transfer of selected PCB congeners through the freshwater aquatic environment, using source terms of atmospheric deposition and watershed soil concentrations to predict levels in edible fish. The validity of the model is assessed by comparison of predicted concentrations of PCBs in forage fish and pike, with those determined in a field study conducted in the R. Severn, near Birmingham, UK.

Experimental Methods

Field Study

<u>Sampling protocols</u>

Samples were taken from the R. Severn at Stourport-on-Severn, Worcestershire, a semi-rural location *ca* 20 km from the centre of Birmingham. All fish samples were obtained *via* electric fishing conducted between April and August 1996. In all, 5 composite samples (each consisting of edible fillets from 6 fish) were analysed for pike, whilst between 2 and 6 whole fish were homogenised to provide 1 composite sample for each of four forage species, *viz:* Minnow, Gudgeon, Bullhead, and Ruffe. A total of 6 bulk atmospheric deposition samples were collected at monthly intervals between July and December 1996. The sampling apparatus consisted of a glass vessel connected to an inverted frisbee. Samples of watershed soil were taken to a depth of 5 cm from 4 sites, and homogenised to provide a sample representative of the area. Finally, 4 samples of river water were taken between July and December 1996; each sample was analysed separately for both "freely-dissolved" PCB, and that sorbed to suspended material - defined as that retained by a 1 μm diameter pore size glass fibre filter.

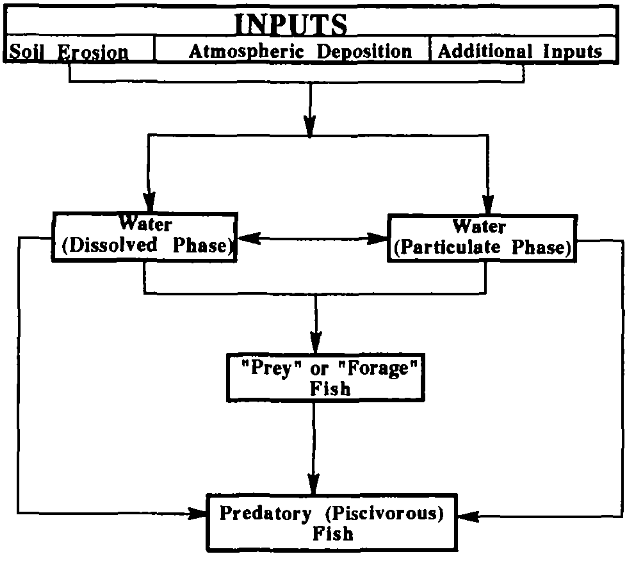
<u>Sample Purification and Analysis</u>

PCB analyses were conducted using well-validated containment-enrichment, GC/MS procedures reported elsewhere[3]. Recoveries of quantitation standards added to check PCB losses during both sampling and analysis ranged between 45 and 90% for all samples. The organic carbon content of soil, bottom sediment, and suspended sediment was determined using a Leco Multiphase Carbon Determinator RC-412, with TSS loadings of water samples determined gravimetrically.

Algorithms used in mathematical model

Figure 1 illustrates the basic model structure. The algorithms used in the model are given overleaf:

Figure 1: Basic Structure of Freshwater Aquatic Food Chain Model



Input-to-suspended sediment algorithms (adapted from[4])
The algorithms and input data used are:

$$C_{ssed} = \frac{[(1 \times 10^6 * (CS_{ws} * X_e * WA_t * E * SD) + L_{dep} + AI) * \tau]}{\dfrac{V_{fx}}{Kd_{ssed}} + (f_s * ER_w) + \dfrac{OC_{sed} * (1 - f_s) * ER_w}{OC_{ssed}}}$$

where: C_{ssed} is predicted PCB concentration in suspended sediment at steady state (ng kg^{-1})

CS_{ws} is contaminant concentration in watershed soil (mg kg^{-1}) - see Table 1.

X_e is unit soil loss (kg m^{-2} yr^{-1}), assumed to be 1.68[5]

WA_t is area of the watershed (m^2), 4.35*10^6 for the River Severn

E is enrichment ratio, assumed to be 5.0

SD is sediment delivery ratio, calculated as below

L_{dep} is direct load to the water body due to deposition (mg yr^{-1}), calculated as below

AI represents additional inputs (mg yr^{-1}) to the aquatic system - *e.g.* direct industrial or sewage effluent discharge. Assumed here in the absence of reliable data to be zero, but may be significant.

τ is overall residence time of PCBs in aquatic system (years). Assumed here to be 1.

V_{fx} is annual volumetric flow of the water body (L yr^{-1}), say 1.0*10^{11} for the R. Severn

Kd_{ssed} is the suspended sediment-water partition coefficient (L kg^{-1}), derived as shown below

f_s is the fraction of the eroded soil which remains suspended, calculated as below

ER_w is total watershed soil erosion (kg yr^{-1}), calculated as below

OC_{sed} is fraction of organic carbon in bottom sediment, measured at 0.014
OC_{ssed} is fraction of organic carbon in suspended sediment, measured at 0.116

Kd_{ssed}, SD, L_{dep}, f_s and ER_w are calculated thus:

$$Kd_{ssed} = K_{oc} * OC_{ssed}$$

and $K_{oc} = K_{ow} * 0.41$

$$SD = (3.28 * DL)^{-0.22}$$

$$L_{dep} = DEP_{tot} * WA_w$$

$$f_s = \frac{T_{ss} * V_{fx} * 10^{-6}}{WA_t * X_e * SD}$$

$$ER_w = WA_t * X_e * SD$$

where

DL is average distance to water body (m), assumed to be 100
DEP_{tot} is average bulk deposition flux in location of water body (mg m^{-2} yr^{-1}) - see Table 1
WA_w is water body area (m^2), $1.00*10^6$ for the R. Severn
T_{ss} is total suspended solids loading (mg L^{-1}), assumed here to be 2.5, based on field data

Suspended sediment -to-dissolved-phase water algorithm [4])
The algorithm and input data used are:

$$c = C_{ssed} / Kd_{ssed}$$

where c is dissolved contaminant concentration in water (ng l^{-1})
and Kd_{ssed} and C_{ssed} are as described above

Algorithms to predict levels of PCBs in fish (adapted from [1]))
The algorithms and input data used are:

$$C_i = [(k_{ui} * c) + \sum_{j=1}^{n} \alpha * C_{ij} * v_j] / k'$$

where C_i is wet weight contaminant concentration in fish species i at steady state (ng kg^{-1})
k_{ui} is rate of freely-dissolved contaminant uptake by species i (ml H_2O g $species^{-1}$ d^{-1}) - derived as below
c is dissolved contaminant concentration in water (ng l^{-1})
α is efficiency with which ingested contaminant is absorbed by species i (g chemical absorbed g

chemical ingested^{-1}). Determined on a congener-specific basis as described below.
C_{ij} is daily consumption of species j by species i (g species j g species i^{-1} d^{-1}). Determined on a species-specific basis as described below.
$k' = k_d + g_i$
k_d is contaminant depuration rate (g contaminant lost g chemical present in species i^{-1} d^{-1}). Determined on a contaminant-specific basis as described below. Assumed to be species-independent.
g_i is growth rate of species i (g organism gained g organism^{-1} d^{-1}). Determined on a species-specific basis as described below.
v_j is wet weight contaminant concentration in species j (ng kg^{-1})

$k_{ui} = 1000 * (W_i^{-\gamma}) * \alpha$

where W_i is wet weight of fish species i (g), assumed here to be 100 and 2000 for forage fish and pike respectively
$\gamma = 0.25$ (the mean of the range of 0.2 - 0.3 cited in[2])
and α is determined on a contaminant-specific basis according to the following algorithms for organisms of W_i > 10 - 100 g[2]
For Log K_{ow} = 3 - 6, $\alpha = 0.5$
For Log K_{ow} = 6 - 10, Log $\alpha = 1.2 - 0.25 *$ Log K_{ow}

C_{ij} for pike is assumed to be 0.034 with respect to their consumption of forage fish. We have assumed that the sole "food" of forage fish is suspended sediment - a not unreasonable assumption, given that our analytical methodology measures PCBs in suspended material, which will inevitably include phytoplankton *etc.*. A similar term is included for pike, to account for uptake of contaminant associated with suspended material. On this basis therefore:

C_{ij} (for consumption of suspended material) = $k_{ui}/\alpha * TSS * 1 \times 10^{-6}$

where: k_{ui} = rate of freely-dissolved contaminant uptake by fish
TSS = total suspended solids concentration of water (mg l^{-1}). The 1×10^{-6} term converts to kg l^{-1}
k_d = 0.0344 for trichlorobiphenyls; 0.011 for tetrachlorobiphenyls; 0.012 for pentachlorobiphenyls; and 0.00398 for hexachlorobiphenyls and heptachlorobiphenyls. All values as cited in[2].
g_i = 9.16×10^{-3} for forage fish (the mean of 5 values cited in[6] for mysis and alewife), and 0.01 for pike[7])

Results and Discussion
Predictions of PCB concentrations in abiotic matrices
Table 1 lists measured PCB concentrations in a variety of abiotic matrices in the R. Severn, and compares them with concentrations predicted using the algorithms described above. Evidently, the algorithms employed significantly underestimate measured values of both C_{ssed} and c.

Table 1: Measured and Predicted Concentrations of PCBs in Abiotic Matrices from the R. Severn

PCB #	DEP_{tot} ($ng/m^2/yr$)	Watershed Soil (ng/kg)	Measured C_{ssed} (ng/kg)	Predicted C_{ssed} (ng/kg)	Measured c (ng/l)	Predicted c (ng/l)
28	6430	124	17400	2030	0.191	0.068
52	8100	84.7	14700	4200	0.125	0.070
101	7380	148	17100	6830	0.105	0.057
105	505	54.1	22200	812	0.011	0.007
118	3070	146	23400	3500	0.077	0.029
138	8550	268	16100	16700	0.083	0.035
153	2680	225	29100	6800	0.063	0.018
180	8350	180	14000	16100	0.023	0.027

DEP_{tot}, watershed soil concentrations, C_{ssed} and c values are averages of 6, 4, 4 and 4 measurements respectively.

Predictions of PCB concentrations in forage fish and pike using predicted levels in abiotic matrices as source terms

Average wet weight PCB concentrations measured in both forage fish (average of 4 species) and pike from the R. Severn, are listed in Table 2, alongside predicted concentrations obtained using the predicted C_{ssed} and c values given in Table 1. Clearly, the underestimation of measured values evident in Table 1, has been "carried over", thus resulting in similar discrepancies between measured and predicted PCB concentrations in fish.

Table 2: Measured and Predicted Wet Weight Concentrations of PCBs in Fish from the R. Severn. Predicted Values Obtained using Predicted C_{ssed} and c Concentrations as Source Terms

PCB #	Measured Forage Fish (ng/kg)	Predicted Forage Fish (ng/kg)	Measured Pike (ng/kg)	Predicted Pike (ng/kg)
28	883	263	1030	223
52	2460	598	870	730
101	3360	441	1590	472
105	875	52.5	1430	56.2
118	2210	226	3600	242
138	4250	521	4320	598
153	3880	251	2750	294
180	1920	429	6650	469

Predictions of PCB concentrations in forage fish and pike using measured levels in abiotic matrices as source terms

Table 3 compares average wet weight PCB concentrations measured in both forage fish (average of 4 species) and pike from the R. Severn, with predicted concentrations obtained using the measured C_{ssed} and c values listed in Table 1. It is clear that for all congeners bar # 180, a much closer correlation is obtained than when the predicted values were employed as source term data. This clearly suggests that the principal source of error in the overall model lies with the algorithms used to predict C_{ssed} and c values.

Possible sources of error

Given the "screening-level" sophistication of the algorithms used, and the relatively limited scope of the field validation exercise, there are numerous possible causes of the underestimation of C_{ssed} and c values. The principal ones are considered to be:

- that the overall residence time in the R. Severn for all PCBs may be greater than the 1 year assumed here. The assumed value is comparable to the range of values reported for the Great Lakes[8], but it is highly likely that residence times will be both location- and congener-specific.
- that the assumption that PCB contamination of the R. Severn is at steady state may be wrong.
- that the assumption that additional PCB inputs to the R. Severn are zero is unlikely to be true. A possible additional source which may exert a significant impact, is the sewage works at Bridgnorth, *ca* 25 km upstream.
- that measured values of both DEP_{tot} and watershed soil concentrations may be unrepresentative of the watershed area. In more urbanised locations, values of both input sources may well be greater. However, measurements of DEP_{tot} at a sampling site close to the centre of Birmingham[9] are not significantly different to those detected at Stourport-on-Severn over the same period, and we therefore consider the DEP_{tot} data used here to be reasonably representative of the area covered by the R. Severn.

Table 3: Measured and Predicted Wet Weight Concentrations of PCBs in Fish from the R. Severn. Predicted Values Obtained using Measured C_{ssed} and c Concentrations as Source Terms

PCB #	Measured Forage Fish (ng/kg)	Predicted Forage Fish (ng/kg)	Measured Pike (ng/kg)	Predicted Pike (ng/kg)
28	883	851	1030	1380
52	2460	1200	870	1870
101	3360	879	1590	1040
105	875	396	1430	896
118	2210	806	3600	1180
138	4250	836	4320	796
153	3880	975	2750	1190
180	1920	371	6650	406

The above considerations could clearly account for much of the discrepancy between predicted and measured concentrations of PCBs. We are currently attempting to obtain reliable estimates of additional PCB inputs, as well as a more representative estimate of watershed soil concentrations of PCBs. In summary, this work suggests that if all inputs to a river system are known, then the algorithms described here are likely to provide a useful "screening-level" predictive tool.

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