The Distribution of Polychlorinated Biphenyls (PCBs) in the River Thames Catchment under the Scenarios of Climate Change

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Abstract:

Measurements have shown low levels of PCBs in water but relatively high concentrations in the resident fish of the River Thames (UK). To better understand the distribution and behaviour of PCBs in the Thames river basin and their potential risks, a level III fugacity model was applied to selected PCB congeners (PCB 52, PCB 118 and PCB 153). The modelling results indicated that fish and sediments represent environmental compartments with the highest PCB concentrations; but the greatest mass of PCBs (over 70%) is likely to remain in the soil. As emissions decline, soil could then act as a significant secondary source of PCBs with the river bed-sediment functioning as a long-term reservoir of PCBs. The predicted changes in temperature and rainfall forecast in the UK Climate Projections 2009 (UKCP09) had only a modest influence on PCB fate in the model. The most significant result being a tendency for climate change to enhance the evaporation of PCBs from soil to air in Thames catchment.

Key words: **PCBs**, **Fugacity**, **River Thames**, **Climate Change**, **Fish**

1. Introduction:

Polychlorinated Biphenyls (PCBs) are industrial chemicals whose main application was heat exchange fluids in electrical equipment. An estimated 1.3 million tonnes of PCBs were manufactured globally between 1990 and 1993; and approximately 66,500 tonnes of PCBs were produced in the UK between 1954 and 1977 (Breivik et al., 2002). PCBs are considered to be amongst the most persistent, bio-accumulative, and toxic of organic chemicals listed as Persistent Organic Pollutants (POPs) under the Stockholm Convention. The production and usage of PCBs have been banned and regulated in the UK since 1976 (Creaser C.S. et al., 2007). However, since 1990, emissions of the contaminants continued due to losses from old PCB-containing equipment that is still in use or from their disposal. With the phasing out of the old equipment in recent decades, the emissions of PCBs have dropped significantly in the UK (from 6698 kg/a in 1990 to 906 kg/a in 2009, approximately)(NEAI, 2011). However, due to the persistence of PCBs, they continue to exert their influence on the environment and transfer freely between different environmental compartments. Because of their lipophilicity, PCBs are also likely to bio-accumulate and bio-magnify in aquatic food chains. In Thames fishes, the PCBs levels suggested by recent studies (Jürgens et al., 2015) exceed the unrestricted consumption thresholds (5.9 μg/kg for $\sum$PCBs) which was proposed by the U.S. Environmental Protection Agency. As primary emissions of PCBs are declining, the continuing presence of PCBs in fish from the River Thames is likely to be a function of both their persistence and continuing secondary emissions.

To predict PCBs' potential risks, information on their distribution, transport and ultimate sinks in the catchment is essential. However, addressing temporal and spatial distribution of PCBs by chemical analysis is both a time-consuming and expensive activity. Mass balance models can assist in predicting the transport and distribution of PCBs throughout the environment. Recently, this approach has been successfully employed in lakes and rivers, such as the Great Lakes on the Canada–United States border (Thompson et al., 1999) and the Altamaha River and the Willamette River in the US (Kilic and Aral, 2009). Studies in Europe exist for the western Baltic Sea (Wodarg et al., 2004) and the Venice Lagoon (Dalla Valle et al., 2005). But estimates on the levels of PCBs in the biosphere (fish) were not included in any of these studies.

Given the extraordinary persistence of PCBs, it is worthwhile considering how climate change might exert positive or negative influences on their fate. Previous studies forecasted the possible influence of climate change on PCBs on the European (Paul et al., 2012) and worldwide environments (Lohmann et al., 2007; Macleod et al., 2005). Fate in a marine environment was considered by Lamon et al. (2012b), where the effects of climate induced changes on sea currents, temperature, wind speeds, precipitation on the fate of PCBs revealed temperature as one of the most influential. It was suggested the increase in temperature could enhance the emissions of PCBs from primary and secondary sources and lead to alterations in the rates of partitioning, volatilisation, degradation and reaction (Paul et al., 2012; Teran et al., 2012). Dalla Valle et al. (2007) suggested that future increases in temperature could reduce PCB concentrations in the environment but enhance their potential for long range atmospheric transport (LRAT) from the Venice lagoon (Dalla Valle et al., 2007). The influence of climate change on PCBs at river basin scale has not been extensively studied. There is also a lack of knowledge on the interactions of fish with PCBs and with climate change issues.

PCBs have 209 possible congeners that vary widely in their chemical and toxicological properties (Creaser C.S. et al., 2007; Hope, 2008). About 130 of them were produced commercially. In this paper, three PCB congeners (PCB52, PCB118, and PCB153) were selected for further study as they symbolise the range of PCB properties and also have been detected in the catchment (Jurgens et al., 2015). The selected congeners are among the ICES 7 PCBs which have been recommended by the European Union Community Bureau of Reference for monitoring. PCB118 is also among the group of 'dioxin-like' PCBs that have similar toxic and biological responses to those of dioxins (Kannan et al., 1989; Safe et al., 1985; Webster et al., 2013).

The aims of this study were: 1) To understand the distribution of PCBs throughout the Thames catchment through the use of multi-media fate model 2) Corroborate the model predictions using field measurements or nearest literature reported values for three test PCB congeners (53,118, 253), and finally 3) estimate the extent to which climate change might alter the fate of PCBs in the River Thames Catchment and so affect environmental and human exposure.

2. Materials and methods

2.1. The Thames Catchment

The River Thames is the longest river that sits entirely within England with a total length of 346 km (Fig. 1). It flows through the capital city London to the North Sea. The catchment covers an area of approximately 10,000 square kilometres, which comprises less than 10% of the area of England and Wales. However, it includes the most heavily urbanised area which houses nearly a quarter of the population of England and Wales (supporting about 14 million people) (Crossman et al., 2013). There are 352 sewage treatment plants in the Thames Region of which discharge into River Thames (Williams et al., 2009). The bedrock of Thames is mainly high permeable chalk, although there are also some reaches of low permeability clays

(Crossman et al., 2013). The climate in the river Thames catchment is close to a typical temperate maritime climate, with modest rainfall (716.9 mm mean annual precipitation between 2000 and 2008), warm summers and mild winters (average 17°C in summer and 5.56°C in winter between 2000 and 2008) (Crossman et al., 2013). The discharge in the river Thames varies significantly with seasons, with relatively high flows in winter and lower flows in summer (Crossman et al., 2013). On average, the flow ranges from around 1.5m^3/s at the source at Cricklade, to about 37.5m^3/s at Caversham and up to 65.5m^3/s at Teddington (Jin. et al., 2010; Johnson, 2010). Jin et al. (2012) have divided the Thames system into 22 reaches and sub-catchments (Fig. 1), and have applied the INCA model to predict their vulnerability to climate change. It is suggested that climate change could affect the river flows and could exacerbate water quality problems (Nitrogen, Phosphorus) of Thames (Jin et al., 2012).

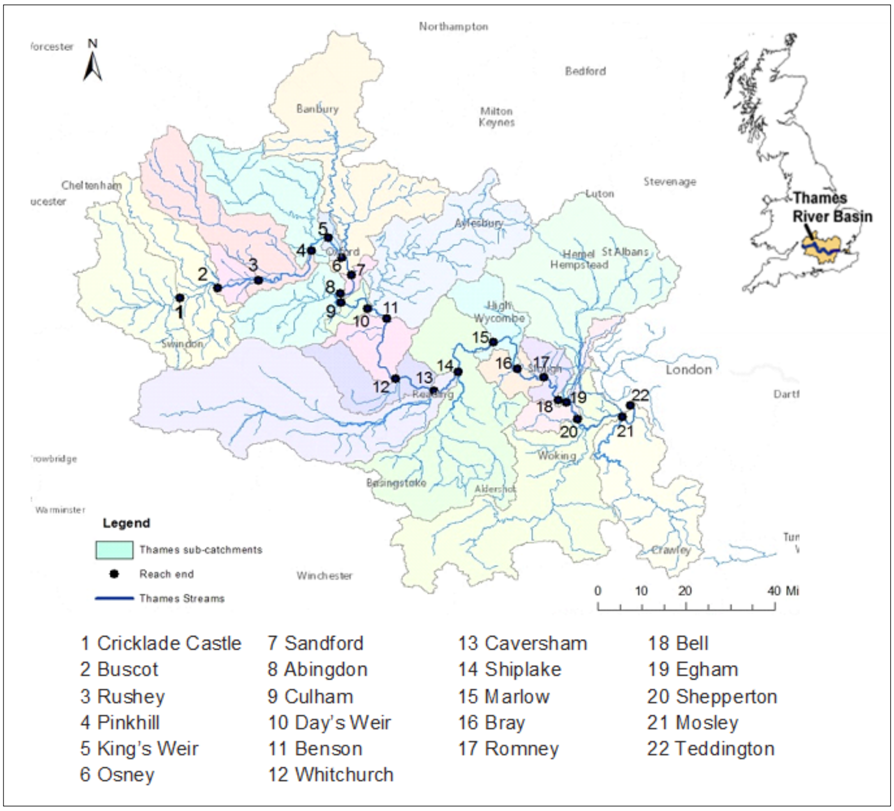

Fig.1. Location map of the non-tidal river Thames catchment showing the major tributaries and sub-catchments (Crossman et al., 2013)

2.2. The Level III Fugacity Model

The fugacity model is a multi-media mass balance model that employs the concept of fugacity as a thermodynamic equilibrium criterion and treats partitioning of chemicals between different environmental compartments (Mackay, 2001). There are basically four levels of fugacity models. A level III fugacity model has been applied in this study. The level III model provides a more realistic description of the chemicals' fate including emissions, advective inflows, degradation, advective losses and intermedia exchange processes, as shown in Supporting Information in Fig. SI1. The four bulk environmental compartments considered in the level III fugacity model are air, soil, water and sediment. These compartments contain varying proportions of sub-catchments (e.g. air, water, solid and biota). The model runs in steady-state conditions and assumes that equilibrium exists within (i.e. between sub-compartments), but not between bulk compartments. The rates of intermedia transport and transformation are calculated using the constant D (Table. SI1). More detailed information on level III fugacity model are provided elsewhere (Mackay, 2001; MacLeod et al., 2002).

2.3. Model Set-up

In this study, of four bulk compartments (air, soil, water, and sediment) a sub-compartment in water (fish) was included. Whilst a fish compartment may only account for a small part of the overall pool, concentrations could be high and of environmental significance (Jürgens et al., 2015).

Table 1. Physico-chemical parameters of the selected PCBs

	PCB-52	PCB-118	PCB-153
[a] Molar mass	292.0	326.4	360.9
[a] Melting point (°C)	87	109	103
[b] Solid vapour pressure (Pa)	0.000745	0.0000196	0.0000122
[b] Solid water solubility (g/m^3)	0.00957	0.000650	0.000301
[c] ΔH_{vap} (kJ/mol)	81	89	91
[d] Ea (kJ/mol)	7	10	12
[a] Log K_{ow}	6.1	7.1	7.4
[e] Half-life in air (day)	60	120	2396
[e] Half-life in Water (day)	1196	2396	4792
[e] Half-life in Soil (day)	3500	2396	6583
[e] Half-life in Sediment (day)	3500	2396	6583

[a] Mackay et al. (1992);

[b] Dalla Valle et al. (2007); Paasivirta et al. (1999);

[c] Enthalpy of vaporization (Bamford et al., 2000; Kong et al., 2013);

[d] Activation energy for degradation of PCBs in air (Kong et al., 2013);

[e] Sinkkonen and Paasivirta (2000); Sweetman et al. (2002)

The level III fugacity model for the river Thames relies on two major sets of parameters: the physic-chemical properties of the selected chemicals (Table 1) and environmental properties of the study area (Table 2). The values for vapour pressure, water solubility and half-lives have been adjusted for the annual average temperature of the river Thames catchment (11.07 °C). Detailed information on the environmental and landscape properties of the river Thames catchment was obtained from Meteorological Office in England and Wales, Environment Agency, or from similar environments taken from literature and adjusted for the study area as deemed appropriate. More input environmental parameters used in the modelling are provided in Supporting Information in Table SI2.

Table 2. Environmental Properties of River Thames Catchment

Parameter	Value	Data Sources
Temperature (°C)	11.07	Meteorological Office
Total catchment area (m^2)	1.00E+10	Crossman et al. (2013)
Water surface area (m^2)	1.96E+07	Crossman et al. (2013)
Depth of river (m)	3	—
Organic carbon in soil (g/g)	0.02	Hiederer. and Kochy. (2012)
Organic carbon in sediment (g/g)	0.1	Sweetman et al. (2002)
Lipid in fish (g/g)	0.05	Experiment data
Residence time in air (annual average) (h)	8.5	—
Residence time in water (annual average) (h)	324	Johnson, Acreman et al. (2009)
Rain rate (m/h)	1.03E-04	Sweetman et al. (2002)

2.4. Model Evaluation

To evaluate the performance of the fugacity level III modelling, a range of measured data of PCBs in different environmental compartments was needed. However, only a limited number of observed datasets were available (Table 4). Although hundreds of water samples in the River Thames have been examined by the Environment Agency , very few of them exceed the detection limit of 0.001μg/L. To the best of our knowledge, no PCB congener-specific measurement of sediment in River Thames has been carried out in recent years. The pollutant levels of PCBs in soil were tested in the UK Soil and Herbage Pollutant Survey (UKSHS) Project (Creaser C.S. et al., 2007). However, only average values for rural and urban areas of England were reported (Creaser C.S. et al., 2007). The observed air concentrations of the studied PCBs have been collected from the results of Toxic Organic Micro-Pollutants (TOMPS) program (Schuster et al., 2010). The PCBs values in Thames fish were collected both from previous work (Jürgens et al., 2015; Yamaguchi et al., 2003) and in an analysis of fish samples collected from the Thames as part of the CEH (Centre of Ecology and Hydrology) Fish Archive Project.

2.5. Examining fate over time and the influence of climate change

2.5.1. Emissions over time

The emission values of PCBs are critical parameters that drive the model and should therefore, be as accurate as possible. However, these data are often unavailable and difficult to estimate. In this study, an average value of gaseous PCBs emissions for the 2000s have been estimated using data from the National Atmospheric Emissions Inventory (NEAI) PCB emissions reports (NEAI, 2011). The major emissions of PCBs to River Thames water are from the treated sewage wastewater effluents. The information related to PCBs values in the sewage works outflows in Thames catchment for recent years is not available. However, Bogdal et al. (2010) have analysed average PCBs values in the effluents from the largest wastewater treatment work in Lake Thun catchment, Switzerland. The estimations of PCBs emissions to Thames water were made by extrapolating the reported PCBs concentrations to all sewage works discharging to River Thames. The emission rates of PCBs are temperature dependant. In this study, the effects of temperature on the emissions of PCBs were not considered. But the emissions were assumed to decrease with a function of time, which is calculated according to the following equation (Eq. 1) (Dalla Valle et al., 2005):

$$\mathrm{E(t)} = E(2008)e^{[-0.4(t-2008)]} \qquad (1)$$

where E is the total emission rates and t is the year (2008< t <2100).

2.5.2. Change in climate with time

In order to estimate the influence of climate change issues on the fate of PCBs in the river Thames catchment, two different scenarios (A and B) were tested. Scenario A assumes the climate to be constant in the period of simulation. In Scenario B, the outcomes of UKCP09 and its medium emission scenario (IPCC SRES A1B) dataset were used. UKCP09 is the latest regional climate model for the UK that provides probabilistic projections for a number of variables (temperature, rainfall, etc.) under three future emission scenarios (Low, Medium and High emissions). For each scenario, the full UKCP09 sampled data consists of 10,000 variants, which capture all the possible combinations, for each 25 km grid square and aggregated region (Murphy et al., 2009). From a random sample of 100 variants, Jin. et al. (2010) illustrated the ranges of temperature and precipitation projections under medium emission scenario at 2020s and 2080s for the Thames catchment. The river flows were simulated with The Integrated Nitrogen Catchment Model (INCA) by using driving data derived from the random samples of UKCP09 database (Jin. et al., 2010). In this study, the average temperature, precipitation rate and river flows in the 2020s and 2080s were obtained from Jin, Whitehead's predictions (Table 3). These suggest some reduction in river flow with warmer temperatures and higher evaporation rates playing an important role (Jin et al., 2012). The current temperature and precipitation rate were supplied by the meteorological office and the mean observed flow from the Environment Agency. The water residence time were estimated from the mean flow and from available values for Thames estimated by Johnson et al. (2009) with a general relationship developed by Round et al. (1998) (Table 3). The future changes in wind speed and snow and ice cover were not addressed. Therefore, these factors were assumed to be constant in the simulation of Scenario B.

Table 3. Different scenarios examined in modelling long-term fate of PCBs in the River Thames Catchment

		Temperature (°C)	Rain rate (mm/day)	Mean Flow (m^3/s)	Water Residence Time (h)*
Scenario A	2000s	11.07	1.86	65.0	324
	2020s	11.07	1.86	65.0	324
	2080s	11.07	1.86	65.0	324
		Temperature (°C)	Rain rate (mm/day)	Mean Flow (m^3/s)	Water Residence Time (h)*
Scenario B	2000s	11.07	1.86	65.0	324
	2020s	11.5	2.03	59.0	333
	2080s	13.6	2.03	58.8	334

* annual average

Temperature can be a dominant driver in determining the fate of chemicals in the environment (Lamon et al., 2012a). The physicochemical properties that are strongly influenced by temperature include vapour pressure (P_s), Henry's law constant (H), partition coefficients (K_{ow}), and water solubility (S_s, S_l). The variations of these parameters according to temperature have been calculated by using the log-linear relationship equations (Supporting Information, Eqs. SI1-SI5) reported by Paasivirta et al. (1999) and Dalla Valle et al. (2007). In addition, the degradation rates of PCBs in the catchment environment will also be influenced by changes in temperature. The variations of degradation rates were calculated according to the Arrhenius equation (Supporting Information, Eq. SI6) (Dalla Valle et al., 2007; Macdonald et al., 2005).

3. Results and discussion

3.1. Comparison of predicted values against observed data

The predicted values were compared with observed concentrations of PCBs in different environmental compartments to evaluate the performance of the model. There have been few reported detections of PCBs in the river water column in the Thames (LOD 0.001μg/L) by the UK Environment Agency. However, this model would predict that water concentrations of PCB 52, 118 and 153 would be 0.00012-0.00025 μg/L which would be well below that detection limit (Table 4). Schuster et al. (2010) have presented the measured values of PCBs in ambient air of six sites in England (London, Manchester, Middlesbrough, Hazelrigg, High Muffles and Stoke Ferry). In this study, the predicted air concentrations were compared to the average values for London and Stoke Ferry, which is within or close to Thames catchment. The estimates for PCB 118 and PCB 153 were in good agreement with the observed values. But the model estimates of PCB 52 in air exceeded the observed values by a factor of 4.0

(Table 4). The lower than expected measured air concentrations of PCB 52 might be attributed to lower emissions than PCB 118 and PCB 153. The observed soil concentrations were collected from the UK Soil and Herbage Pollutant Survey (UKSHS) Project (Creaser C.S. et al., 2007). As urban area covers only about 17% of river Thames catchment (Jin. et al., 2010), the model estimates of soil concentrations were compared to the average values for rural areas of England. The predicted value for PCB 52 agreed well with the average measured values for soil in rural areas (Table 4), whilst the values for PCBs 118 and 153 fell within the expected range although about half the measured average.

The predicted sediment concentrations of PCBs in Thames was 9-13 μg/kg. Unfortunately, there appears to be no recent congener-specific monitoring data for PCBs in the sediment of the Thames catchment. The most relevant data that exists is only for PCB as Aroclo-1248 in salt marsh sediment of Two Tree Island at Thames estuary with a mean value of 34.4 μg/kg was reported (1990-1995) (Scrimshaw and Lester, 2001). Much lower values have been reported for the same congeners in River Willamette (located in northwestern Oregon, US) and Lake Thun (situated in the Bernese Oberland, Swizerland) (Bogdal et al., 2010; Hope, 2008) but these are very rural areas (>90%). For the three studied PCBs in Thames fish, the predicted concentrations (2.64-3.71 μg/kg) were in good agreement with their observed values (Table 4). The sum concentration of the three modelled PCBs in fish tissue was predicted to be 9.51 μg/kg in 2000-2010, which would exceed the U.S. EPA unrestricted consumption thresholds (5.9 μg/kg) for $\sum PCBs$. PCB 118 belongs to a group of 'dioxin like' PCBs. The estimated value of PCB 118 in the fish compartment (3.04 μg/kg) would translate to 0.0001 μg/kg toxic 2,3,7,8-TCDD equivalents (Van den Berg et al., 2006). The newly established EU Environmental Quality Standard for dioxin and dioxin-like compounds is 0.0065 μg/kg (European Union, 2013). The levels of PCBs in Thames fish will be linked to the PCBs in surrounding water and sediment via the food chain (Mackay, 2001). The modelled bioconcentration factors (BCFs, Supporting Information Eq. SI7) for the studied PCBs ranged from 15,020 to 21,640, which were much higher than the Canadian criteria for very bioaccumulative (BCF ≥5000) (Gobas et al., 2009). The biota-sediment accumulation factors (BSAFs, Supporting Information Eq. SI8) were calculated to be around 0.6, which were a bit lower than measured data from some laboratory and field studies (0.5-2.8) (Nowell et al., 1999; Weisbrod et al., 2007). While there is a small tendency for the model to underestimate the concentrations of PCBs in soil, the results for the Thames catchment could be considered acceptable since they fall within an order of magnitude from the observed data for each of the four compartments (Hope, 2008). Whether the differences are attributable to underestimated loadings of PCBs or an overestimated degradation rate constant in soil is not clear.

Table 4. Comparison between estimated and measured concentrations of selected PCBs.

Media	PCB 52		PCB 118		PCB 153	
	Observed (min-max, average)	Estimated	Observed (min-max, average)	Estimated	Observed (min-max, average)	Estimated
[f] Air (pg/m^3)	2000-2008, n=50 0.01-71, 14.77	59.0	2000-2008, n=50 0.2-56, 5.46	5.44	2000-2008, n=50 0.02-37, 7.15	7.90
[g] Soil (ng/kg)	2001-2002; England; n = 183 Rural: 0.1-505, 28.6 Urban:7.1-322,75.2	36.6	2001-2002; England; n = 183 Rural: 2.12-6350, 129 Urban: 58.6-3220, 436	80.1	2001-2002; England; n = 183 Rural:24.8-782, 336 Urban: 153-9310, 906	163
[h] Water (µg/L)	2000-2006, n= 181 <0.001	0.000247	2000-2006, n=179 <0.001	0.000149	2000-2006, n=179 <0.001	0.000122
[i] Fish (µg/kg)	2007-2012, n=47 0.16-15.90, 3.17	3.71	2007-2012, n=47 0.15-12.35,2.67	3.16	2007-2012, n=29 0.10-9.52, 2.37	2.64
[j] Sediment (µg/kg)	-	13.2	-	11.3	-	9.43

[f] (Schuster et al., 2010);

[g] (Creaser C.S. et al., 2007);

[h] Environment Agency WIMS database;

[i] CEH fish achieve project;

[j] Data only for PCB as Aroclo-1248 at Thames estuary with a mean value of 34.4 µg/kg.

3.2. Sensitivity and Uncertainty Analysis

To identify the most important factor influencing the fate of the PCBs , a sensitivity analysis was performed. The model was run repeatedly with a simple ±20% variation of an individual input parameter. The sensitivity was calculated by apportioning the relative deviation of the output values to the variance in the input parameter (Valle et al., 2007; Webster et al., 1998) (Eq. 2):

$$S(X_i) = \frac{\partial Y}{Y} \cdot \frac{X_i}{\partial X_i} \qquad (2)$$

where ∂Y is the change of output value while ∂X_i is the variance in input parameter.

In this study, the analysis was carried out only for PCB52 as an indicator for the whole model and PCBs. For PCB 52, temperature appeared to be the most important parameter that determined its fate in the catchment (Table 5). The influence of other parameters was more evident on only one or two compartments. Air residence time was the most influential parameter on air concentrations. Soil concentration was found to be mainly influence by temperature followed by degradation rate. In the river water, the most sensitive parameters were sediment deposition and re-suspension. Sediment deposition and re-suspension also have the biggest influence on the concentrations in fish. Degradation in sediment being the most important parameter for the sediment concentration.

Table 5. Sensitivity analysis for PCB 52 in the different compartments

Parameters	Assumed Cf (95%)	Air		Soil		Water		Fish		Sediment	
		-20%	+20%	-20%	+20%	-20%	+20%	-20%	+20%	-20%	+20%
K_{ow}	1.5	0.15	0.0	-1.0	0.7	37.0	-23.7	-3.8	1.7	-3.9	1.7
Water solubility	1.5	0.0	0.0	-1.4	1.2	-0.7	1.9	-1.9	0.7	-2.0	0.6
Vapour pressure	1.5	-0.5	0.5	25.4	-17.2	3.0	-0.9	1.7	-2.2	1.7	-2.2
Temperature	2.0	5.6	-1.7	-162.3	171.4	13.1	26.7	-19.7	-6.1	-20.4	-6.8
Degradation in air	4.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Degradation in soil	2.0	0.0	0.0	120.9	-81.5	4.4	-1.7	3.1	-3.0	3.1	-3.0
Degradation in water	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Degradation in sediment	2.0	0.0	0.0	0.0	0.0	30.4	-25.7	29.0	-26.9	29.1	-27.0
Rain rate	2.0	0.4	-0.2	-13.1	13.1	0.3	1.2	-0.9	0.0	-1.0	0.0
Aerosol dry deposition	2.0	0.0	0.0	-7.0	7.0	0.0	1.0	0.0	0.0	0.0	0.0
Water depth	1.5	0.0	0.0	0.0	0.0	-1.1	2.6	-2.4	1.3	-2.4	1.3
Air residence time	2.0	-68.9	68.8	-14.5	14.4	0.0	1.4	-1.1	0.0	-1.1	0.0
Water residence time	2.0	0.0	0.0	0.0	0.0	3.1	-0.8	1.9	-2.1	1.8	-2.1
OC fraction in sediment	1.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sediment deposition	1.5	0.0	0.0	0.0	0.0	119.6	-79.8	118.1	-80.9	-5.6	2.9
Sediment re-suspension	2.0	0.0	0.0	0.0	0.0	-95.5	95.5	-96.5	94.0	3.5	-4.5
Soil solids run off	3.0	0.0	0.0	1.8	-1.8	-2.0	3.6	-3.3	2.3	-3.3	2.2
Soil water run off	3.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Except for the sensitivity analysis, it is also important to communicate the uncertainty associated with the fate modelling. The analytical approach presented by MacLeod et al. (2002) has been applied to weigh the contributions of the most sensitive variables to uncertainty in the model outputs. The 95% confidence factors (Cfs) (the extent to which the values might diverge from the medians) for the input variables were estimated from reported values (Lamon et al., 2012b; MacLeod et al., 2002; Sweetman et al., 2002) (Table 5). The corresponding confidence factors in the outputs ($Cf_{outputs}$) of each compartment associated with the most sensitive variables were assessed (Supporting Information, Fig. SI2). The $Cf_{outputs}$ were calculated with the following equation (Eq. 3):

$$Log\ Cf_{output} = |S|\ log\ Cf_{input} \qquad (3)$$

where |S| is the partial derivative of the sensitivity equation (Eq. 2). Using this approach, the sensitivity was calculated with 0.1% variation for each individual input parameter (MacLeod et al., 2002). For PCB 52, air residence time was the most important parameter in terms of contribution to uncertainty in the modelling output in air compartment. In soil, temperature played the most important role in determining the uncertainty associated with the modelling results, whereas soil degradation was most important source of uncertainty for that in sediment. In water and fish, sediment re-suspension, sediment deposition and sediment degradation are the most influential parameters in determining the confidence factors in outputs. The graphic analysis of the contribution of the most sensitive parameters to uncertainty of outputs in different compartments is presented in Supporting Information Fig. SI2.

3.3. Discussion of the fate of PCBs and their dominant sinks in Thames Catchment

PCBs are no longer produced and are progressively being eliminated from use in the UK. In the Thames river catchment, there is no evidence of significant point sources or accidental spillage. Therefore, it is suspected that the closed and open usage of PCB-containing equipment in the Thames catchment serves as the main (diverse) source of the pollutants (Creaser C.S. et al., 2007). The total inputs of PCB 52, PCB 118 and PCB 153 to the whole system were estimated to be approximately 631.5 kg/yr, 103.7 kg/yr and 115.9 kg/yr respectively for the period between 2000 and 2008. The total mass of PCBs stored in the catchment system was then 204kg (Fig. 2) for PCB 52, 401kg for PCB 118, and 781kg for PCB 153. These totals were distributed throughout the environmental compartments. In the case for PCB 52, the amount in the environment was 0.59 kg in air, 170 kg in soil, 0.015 kg in water and 33.7 kg in sediment (Fig. 2). The corresponding capacities of each compartment for the chemical (*VZ*) were 4.3E+9 mol/Pa, 1.38E+12 mol/Pa, 8.1E+6 mol/Pa and 1.8E+9 mol/Pa. The soil compartment was identified as the major sink/source for the transfer of PCBs in the Thames catchment (accounting 83.2% for PCB 52, 92.8% for PCB 118, and 96.9% for PCB 153) (Table 6). The largest mass of PCBs being deposited in soil is due to its large volume (capacity), with this compartment covering about 99.8% of the catchment area.

The river bed-sediment was predicted to be the most important sink/source within the river. PCBs are hydrophobic, and PCBs that are released into the water would be expected to partition strongly to suspended sediment which would subsequently fall out of suspension to become bed-sediment. River bed-sediment is predicted to be responsible for 3-17% of total PCB in the catchment (Table 6). The model estimates the highest concentration and fugacity for the three PCB congeners to reside in the sediment compartment; where fugacity is a function of the escape tendency of chemicals and implies a higher tendency for PCB congeners to transfer from the sediment to other phases in the aquatic environment – indicating that the sediment could act as a significant secondary source of PCBs in River Thames. The percentage of PCBs in fish would be only a tiny fraction of that within the catchment as a whole.

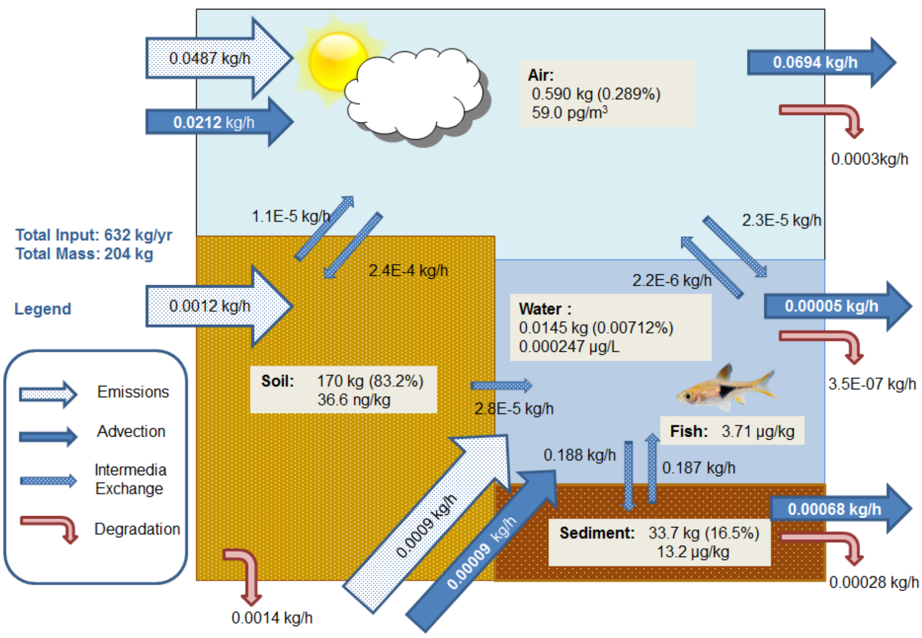

Fig. 2. The modelled distribution of PCB 52 in the river Thames catchment in the 2000s

The major contributors to the loss of PCBs from the catchment include advections (loss by air and water outflows) and degradation. The advective outflows accounted for about 74-97% of the total losses of the chemicals while degradation in different compartments accounted for the rest. To reveal the response of the catchment system to changing input, the corresponding characteristic time *VZ/D* was evaluated, where *D* is the transfer coefficient (Mackay, 2001; Sweetman et al., 2002). The output pathways for PCBs in the soil compartment include soil to air evaporation, soil runoff to water and degradation. For PCB 52, the corresponding time for evaporation to air was 1280 years, for runoff to water is 700 years and for degradation in soil is 14 years. Therefore, degradation is the most important loss process for the chemical in soil. Similar calculations have been done for the other compartments. Advective outflow dominates the loss of PCBs in air and with a response time of 8.5 h. Sediment deposition and re-suspension are the key transfer processes between water and sediment. The characteristic times are short in both directions (0.08 h for deposition and 7.5 d for re-suspension). Therefore, the exchange is rapid and the chemicals will approach equilibrium within a short time (Sweetman et al., 2002). The response times for PCB 52 in the catchment system were 0.35 d in air, 4,964 d in soil, 0.04 d in water and 7.5 d in sediment.

3.4. The Impacts of Climate change and Future Trend

The trend over the simulation periods was for a net loss of all the studied PCBs from the catchment (Fig. 3). The major factor influencing the changing flux of PCBs in the catchment was the dramatic drop in the primary emissions. As the primary emissions decline, the re-volatilisation of PCBs in the soil compartments becomes another source. There is a tendency for the residue percentage of PCBs in the soil compartment to decrease while for that of air, water and mainly sediment to increase (Table 6). The sediment compartment is likely to act as the reservoir of PCBs in Thames aquatic environment and could become a more important sink and secondary source in the future. For PCB 52, the total mass in Thames catchment soil dropped from 170 kg (83.3%) in 2000s to 12.2 kg (75.5%) in 2020s and to 8.5 kg (72.4%) in 2080s. Although the mass of PCB 52 in sediment dropped from 33.7 kg to 3.76 kg in 2020s and 3.07kg in 2080s, the proportion of that held in the catchment increased from 16.5% to 23.3% in 2020s and 26% in 2080s.

Table 6. The distribution of PCBs under various climate scenarios

	2000s (%)	2020s (%)		2080s (%)	
PCB 52		Scenario A	Scenario B	Scenario A	Scenario B
Air	0.289	1.16	1.17	1.52	1.83
Soil	83.2	75.5	75.7	72.4	67.9
Water	0.00712	0.0100	0.00937	0.0112	0.0122
Sediment	16.5	23.3	23.2	26.0	30.2
PCB 118	2000s (%)	2020s (%)		2080s (%)	
		Scenario A	Scenario B	Scenario A	Scenario B
Air	0.0136	0.137	0.133	0.176	0.219
Soil	92.8	90.6	91.0	89.9	88.1
Water	0.00218	0.00282	0.00269	0.00303	0.00355
Sediment	7.17	9.28	8.84	9.95	11.6
PCB 153	2000s (%)	2020s (%)		2080s (%)	
		Scenario A	Scenario B	Scenario A	Scenario B
Air	0.0101	0.0424	0.0424	0.0471	0.0579
Soil	96.9	96.8	96.8	96.7	96.3
Water	0.000918	0.000951	0.000932	0.000964	0.00110
Sediment	3.08	3.19	3.12	3.32	3.68

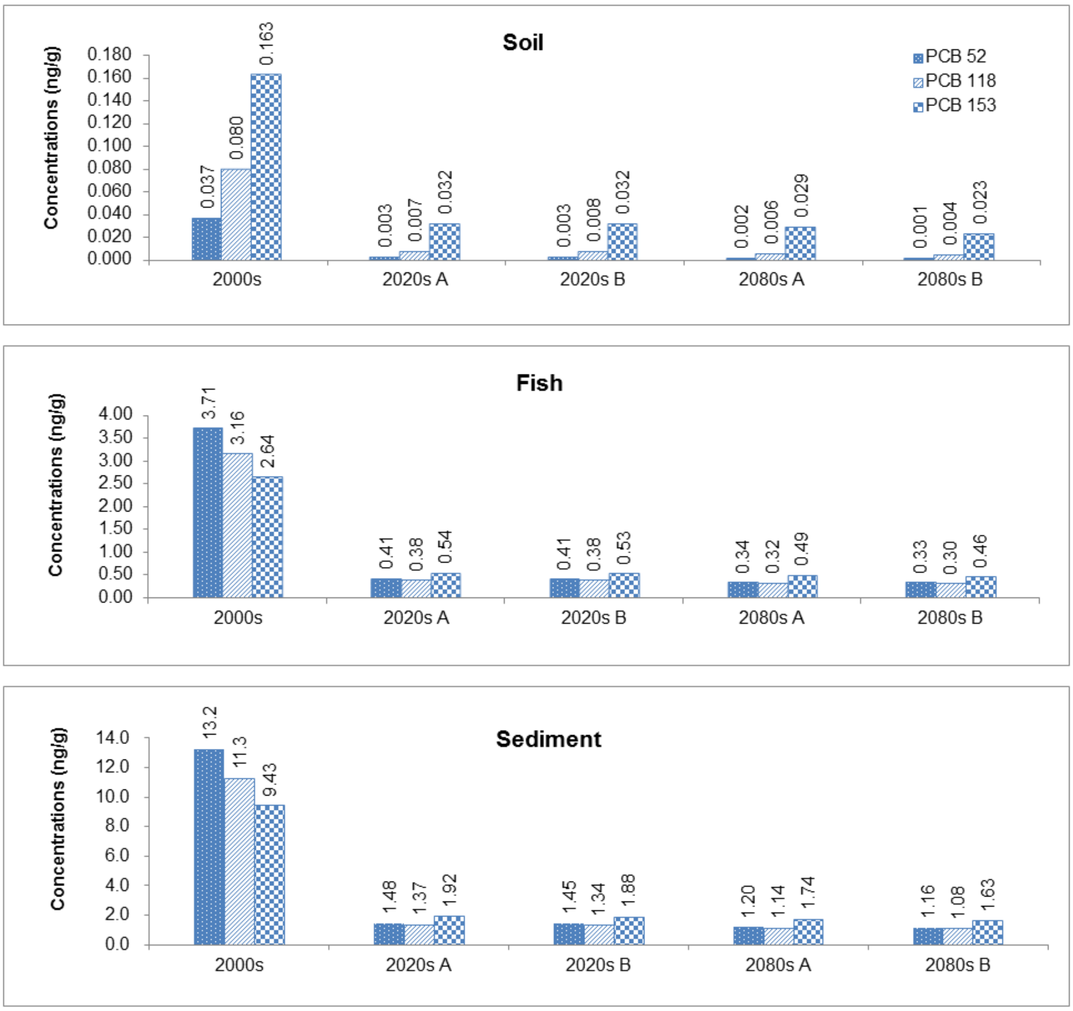

Fig. 3. The predicted concentrations of selected PCBs in soil, fish and sediment of river Thames catchment under different climate scenarios

The overall influence of climate change on PCBs fate does not appear to be dramatic (Fig. 3). The largest influence was on concentrations in soil, probably due to the faster evaporation and degradation rates with the influence of increased temperature (Harner et al., 1995) (Table 7). As the percentage residing and concentrations in air increases, the potential for the long range transportation of the PCBs is slightly enhanced by climate change issues (Dalla Valle et al., 2007). A confounding factor not considered here was the possible effects of higher temperature on the emission rates. With rising temperature, both the primary and secondary emissions of PCBs will be enhanced through the increased volatility. Moreover, the potential secondary effects of climate change on the catchment, such as wind speed change and land use change, were also not considered.

Table 7. Comparison between the predicted concentrations of selected PCBs under scenario B compared to scenario A in the 2080s.

2080s B/2080s A	PCB 52	PCB 118	PCB 153
Air	1.00	1.01	1.01
Water	0.908	0.951	0.938
Fish	0.967	0.949	0.937
Soil	0.779	0.796	0.819
Sediment	0.965	0.949	0.937

The contamination of PCBs in fish is a concern as fish are relevant to human and ecosystem health. The modelling results indicate a significant drop in fish concentrations of the PCBs over the next decades (Fig. 3). The sum concentration of the studied PCBs in fish tissue is expected to drop from 9.51 ng/g in 2000-2010 to 1.32 ng/g in the 2020s which would now place it below the U.S. EPA unrestricted consumption thresholds (5.9 ng/g) for $\sum PCBs$. However, besides the three studied PCBs, significant levels of many other PCB congeners have also been detected in Thames fish (CEH fish tissue Archive). The influence of climate change on the fish concentrations of the studied PCBs was limited, with only 3-6% decrease in scenario B compared to scenario A.

3.5. Influence of differing congener properties on their fate

The predicted fate of the PCBs in the Thames catchment varied between the congeners. The studied PCBs belong to three different congener groups. Hexa-PCB 153 and penta-PCB 118 have higher Octanol-Water Partition Coefficient (Kow) than tetra-PCB 52, therefore, are more likely to accumulate in the organic-rich soil. This was reflected in the percentage residing in the soil compartment of Thames catchment: tetra-PCB 52 (83.7%), penta-PCB 118 (92.8%) and hexa-PCB 153 (97%) (Table 6). As the primary emissions decline, soil becomes an important secondary source for PCBs in the catchment. The re-volatilisation for PCB 52 in the soil exceeds the others due to its higher vapour pressure. The concentration of

PCB 153 declined slower than that of other congeners, which would be related to its slower degradation rate. The heavier PCBs could stay longer than the lower congeners in soil compartment. With the influences of climate change, the evaporation of PCBs from soil to other compartments has been slightly enhanced. This may be caused by the increased volatilisation of the PCB congeners due to the temperature increase induced by climate change. The trend is more noticeable for PCB 52 and PCB 118 as they are more volatile and are more sensitive to the temperature increase than PCB 153.

4. Conclusion

The fugacity level III model offers a helpful approach to predict the distribution and long term fate of PCBs in the river Thames catchment. The modelled results suggest that the majority of the PCBs in the catchment will reside in the soil, whilst the highest concentrations of PCBs were predicted to lie in the sediment compartment. However, little recent observed sediment data is available for comparison. Over the next 80 years, we expect little transfer of PCBs between different compartments, especially for the heavier PCB congeners. But, there is a significant overall drop in PCBs concentrations in all compartments. The rates of decrease were led by the decreasing trends of the assumed emission rates. With the decline in primary emissions, the soil compartment became a significant ongoing secondary source of PCBs for the catchment environment. For the water environment the sediment serves as the major reservoir and would become a more important sink for PCBs in the system over time. In line with the other compartments, the modelling also forecasted a drop in PCBs concentrations in fish over the next decades. To inform decision making, additional data collection efforts regarding to the congener specific measurement of PCBs in sediment from different sites of Thames would be recommended. With the influence of climate change, the evaporation of PCBs in soil were considered to increase. Therefore, the mass and concentrations of PCBs in soil dropped faster than the other compartments. The trend is the most noticeable for light (PCB 52) and less for heavier congeners (PCB 153).

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