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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) over the next 80 years had only a modest influence on PCB fate in the model. The most significant result was 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 (EA, 2007). However, 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) (NAEI, 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 the lipophilicity of PCBs, they are likely to bio-accumulate and bio-magnify in aquatic food chains (Elskus et al., 1994; Koenig et al., 2012). In the River Thames Catchment, the concentrations of PCBs in water are almost always found to be lower than the level of EU EQS, but the PCBs levels in Thames fishes suggested by recent studies (Jürgens, 2015; Jürgens et al., 2015) exceed the unrestricted consumption thresholds (5.9 μg/kg for ∑PCBs) which was proposed by the U.S. Environmental Protection Agency (U.S. EPA, 2000). The burden of PCBs in the sediments has the potential to be bioavailable for Thames fish (OSPAR, 2009b). Although limited sediment data is available for non-tidal section of Thames, a recent study suggested that the sediment concentrations of PCBs in the Thames estuary observed in 2011 significantly exceeded the Ecotoxicological Assessment Criteria derived by the Oslo and Paris Convention (OSPAR) (Nicolaus et al., 2015; Scrimshaw and Lester, 2001).

To predict the potential risks of PCBs, 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). Sweetman et al. (2002) applied a level IV fugacity model to assess the historical emissions and distribution of PCBs over the whole of the UK over the last 60 years, but only discussed their fate in river systems to a small extent. 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 to consider how climate change might exert positive or negative influences on their fate. Previous studies forecast 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. (2012), 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. The influence of climate change on PCBs at a 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 (EA, 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 (Jürgens, 2015; Jürgens et al., 2015). The selected congeners are among the 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 a of multi-media fate model 2) Corroborate the model predictions using field measurements or nearest literature reported values for three test PCB congeners (52, 118, 153), 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 (255 km are non-tidal, 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 which discharge into the River Thames and its tributaries (Williams et al., 2009). The bedrock of the 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 between 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 has been suggested that climate change could affect the river flows and could exacerbate water quality problems (nitrogen, phosphorus) of the Thames (Jin et al., 2012).

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 Fig. SI1 in the Supporting Information. 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-compartments (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 the 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). The level III fugacity model for the River Thames relies on two major sets of parameters: the physico-chemical properties of the selected chemicals (Table SI2) and environmental properties of the study area (Table SI3). 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 the Meteorological Office in England and Wales, the Environment Agency, or from similar environments taken from literature and adjusted for the study area as deemed appropriate.

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 2). Although hundreds of water samples in the River Thames have been examined by the Environment Agency, very few of them exceeded the detection limit of 0.001μg/L. To the best of our knowledge, no PCB congener-specific measurements in River Thames sediments have been carried out in recent years. The pollutant levels of PCBs in soil were collected from the UK Soil and Herbage Pollutant Survey (UKSHS) Report (EA, 2007) and a previous monitoring study (Vane et al., 2014). In the UKSHS Report, only average values for rural and urban areas of England were reported (EA, 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 carried out as part of the CEH (Centre of Ecology and Hydrology) Fish Archive Project (Jürgens, 2015; Jürgens et al., 2015; Rose et al., 2015). The observed data were for different fish species, including roach, perch, bream, bleak and eel. The PCB burden of eels is likely to be slightly higher than for other fish (Jürgens et al., 2015), but average values for all fish species were used to evaluate the model performance.

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, average values of gaseous PCBs emissions for the 2000s have been estimated using data from the National Atmospheric Emissions Inventory (NEAI) PCB emissions reports (NAEI, 2011). The major emissions of PCBs to River Thames water are from treated sewage wastewater effluents. The information related to PCBs values in the sewage works outflows in the 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 the Lake Thun catchment, Switzerland. The estimates of PCB emissions to Thames water were made by extrapolating the reported PCBs concentrations to all sewage works discharging to the 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 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 the medium emission scenario in the 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 the 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 the predictions by Jin. et al. (2010) (Table 1). 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 flows by the Environment Agency. The water residence time was estimated from the mean flow and from available values for the Thames estimated by Johnson et al. (2009) with a general relationship developed by Round et al. (1998) (Table 1). 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. The seasonal effects of climate change have been addressed by modelling PCB 52 (which is expected to be most affected) for 2080s summer climate conditions.

Temperature can be a dominant driver in determining the fate of chemicals in the environment (Lamon et al., 2012). 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 2). 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 are within or close to the 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 2). 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 data collected from previous studies were grouped into rural and urban domains (Table 2). The reported average values for urban soils of England in the UKSHS report were much lower than the data for the site in London. The survey area in London has a long history of urban and industrial activity, and may therefore be a contaminant hot spot (Vane et al., 2014). The model estimates of soil concentrations were compared to the average values of England generated from the UKSHS report. The predicted value for PCB 52 fell between the average measured values for soil in rural and urban areas (Table 2), whilst the values for PCBs 118 and 153 fell within the expected range although about half the measured average for rural areas.

The predicted sediment concentrations of the PCBs in the Thames were 9-13 μg/kg. Unfortunately, there appears to be no recent congener-specific monitoring data for PCBs in sediments of the Thames catchment. The most relevant data that exists is only for PCB as Aroclor-1248 in salt marsh sediment of Two Tree Island in the Thames estuary where 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 the 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 both very rural areas (>90%). The predicted sediment concentrations for the studied PCBs were about 6 times higher than the monitored data for sediments from the Mersey Estuary (Vane et al., 2007b), but were within the ranges of the reported values for sediment from the Clyde Estuary located in the conurbation of Glasgow (Vane et al., 2007a). There are no congener specific quality guidelines for PCBs in freshwater sediment, but Environmental Assessment Criteria (EAC) for ICES7 CBs in marine sediment have been set up within OSPAR (OSPAR, 2009b). The predicted sediment values for PCB 52 and PCB 118 significantly exceeded the EAC of 2.7 μg/kg for PCB 52 and of 0.6 μg/kg for PCB 118 (Nicolaus et al., 2015; OSPAR, 2009b), indicating a potential threat to the aquatic environment. But the concentration for PCB 153 was predicted to be lower than the EAC of 40 μg/kg for PCB153.

In the river system, the fugacity level III model indicated likely relative concentrations between water, fish and sediment. Here the fish compartment in the model represents the inclusion of all fish species. Average values of the observed concentrations for different fish species (roach, perch, bream, bleak and eel) were calculated for comparison with the modelled data (Table 2). 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 2). 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 ΣPCBs. 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.

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.

For PCB 52, 118 and 153 temperature appeared to be the most important parameter that determined its fate in the catchment (Table 3, Table SI4 and Table SI5). The influence of other parameters was only evident on one or two compartments. Air residence time was the most influential parameter for air concentrations. Soil concentration was found to be mainly influenced 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. For PCB 118 and PCB 153, the concentration variations obtained for each compartment were much less than for the lower chlorinated PCB 52. This would reflect the lower volatility/mobility and biodegradability of the heavier PCBs.

In addition to 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., 2012; MacLeod et al., 2002; Sweetman et al., 2002) (Table 3). The corresponding confidence factors in the outputs (Cf_{output}) of each compartment associated with the most sensitive variables were assessed (Supporting Information, Fig. SI2 - SI4). The Cf_{output} 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). The graphic analyses of the contribution of the most sensitive parameters to uncertainty of outputs in different compartments for the studied PCBs are presented in Supporting Information Fig. SI2 - SI4. For PCB 52, air residence time was the most important parameter in terms of contribution to uncertainty in the modelling output in the air compartment. In soil, temperature played the most important role in determining the uncertainty associated with the modelling results, whereas soil degradation was the most important source of uncertainty for 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. For the higher chlorinated PCBs 118 and 153, temperature played a more important role in determining the uncertainty in the modelled results in air, whereas air residence time was less important. The parameters that contributed most to the model outputs in water and fish were sediment deposition and resuspension. In soil, temperature and soil degradation were the most important parameters in determining the results for PCB 118 and PCB 153.

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 (EA, 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 204 kg for PCB 52, 401 kg for PCB 118, and 781 kg for PCB 153. These totals were distributed throughout the environmental compartments. In the case for PCB 52, the estimated 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 modelled distributions of PCB 118 and PCB 153 in the Thames Catchment in the 2000s are shown in Supporting Information in Fig. SI5 and Fig. SI6. The soil compartment was identified as the major sink/source for the transfer of PCBs in the Thames catchment (accounting for 83.2% of PCB 52, 92.8% of PCB 118, and 96.9% of PCB 153) (Table 4). 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 4). 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 the River Thames. The percentage of PCBs in fish would be only a tiny fraction of that within the catchment as a whole.

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 was 700 years and for degradation in soil was 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. Similar analyses have also been done for PCB 118 and PCB 153. The response times for PCB 118 were 0.34 d in air, 5413 d in soil, 0.002 d in water and 7.5 d in sediment, whereas those for PCB 153 were 0.33 d in air, 9175 d in soil, 0.002 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 and for that of air, water and mainly sediment to increase (Table 4). The sediment compartment is likely to act as the reservoir of PCBs in the 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 was predicted to drop 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 was predicted to drop from 33.7 kg to 3.76 kg in the 2020s and 3.07 kg in the 2080s, the proportion of that held in the catchment was predicted to increase from 16.5% to 23.3% in the 2020s and to 26% in the 2080s.

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 temperatures (Harner et al., 1995) (Table 5). As the concentration and percentage in air increases, the potential for the long range transportation of the PCBs is slightly enhanced by climate change (Dalla Valle et al., 2007). Compared to the predictions for annual average climate conditions in the 2080s (Table 5), the values for season variations have only been enhanced by another 5-10% for PCB 52 in summer (summer has the most significant variations in temperature, precipitation and river flow). The difference for other PCBs is expected to be less because, in the sensitivity analysis, PCB 52 was the most sensitive to changes in environmental parameters. A confounding factor not considered here was the possible effect 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.

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 of the PCBs concentrations in fish 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 ΣPCBs. This decline has also been detected for marine fish in recent years (1998-2007) (OSPAR, 2009a). However, besides the three studied PCBs, significant levels of many other PCB congeners have also been detected in Thames fish (Jürgens, 2015; Jürgens et al., 2015). 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 coefficients (K_{ow}) 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 the Thames catchment: tetra-PCB 52 (83.7%), penta-PCB 118 (92.8%) and hexa-PCB 153 (97%) (Table 4). 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 was predicted to decline 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 the soil compartment. With the influences of climate change, the evaporation of PCBs from soil to other compartments will be slightly enhanced due to the increased volatilisation of the PCB congeners because of increased temperatures. 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, a significant overall drop in PCBs concentrations in all compartments is expected. The rates of decrease were led by the decreasing trends of the assumed emission rates. With the decline in primary emissions, the soil compartment would become 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 forecast a drop in PCB concentrations in fish over the next decades. To inform decision making, additional measurements of the different congeners in sediment from different sites in the Thames would be recommended. With the influence of climate change, the evaporation of PCBs in soil was predicted to increase. Therefore, the mass and concentrations of PCBs in soil would drop faster than in the other compartments. The trend is the most noticeable for light (PCB 52) and less for heavier congeners (PCB 118, PCB 153).

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Appendix A. Supporting Information

References

Bogdal C., Scheringer M., Schmid P., Bläuenstein M., Kohler M., Hungerbühler K. Levels, fluxes and time trends of persistent organic pollutants in Lake Thun, Switzerland: Combining trace analysis and multimedia modeling. Science of The Total Environment 2010; 408: 3654-3663.

Breivik K., Sweetman A., Pacyna J.M., Jones K.C. Towards a global historical emission inventory for selected PCB congeners - a mass balance approach 2. Emissions. Science of the Total Environment 2002; 290: 199-224.

Crossman J., Whitehead P.G., Futter M.N., Jin L., Shahgedanova M., Castellazzi M., et al. The interactive responses of water quality and hydrology to changes in multiple stressors, and implications for the long-term effective management of phosphorus. Science of the Total Environment 2013; 454: 230-244.

Dalla Valle M., Codato E., Marcomini A. Climate change influence on POPs distribution and fate: A case study. Chemosphere 2007; 67: 1287-1295.

Dalla Valle M., Marcomini A., Jones K.C., Sweetman A.J. Reconstruction of historical trends of PCDD/Fs and PCBs in the Venice Lagoon, Italy. Environment International 2005; 31: 1047-1052.

EA. UKHSH Report No. 8: Environmental concentrations of polychlorinated biphenyls (PCBs) in UK soil and herbage, NO. 8. Bristol: Environment Agency, UK soil and herbage pollutant Survey, www.environment-agency.gov.uk, 2007.

Elskus A.A., Stegeman J.J., Gooch J.W., Black D.E., Pruell R.J. Polychlorinated biphenyl congener distributions in winter flounder as related to gender, spawning site, and congener metabolism. Environmental Science & Technology 1994; 28: 401-407.

European Union. Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy 2013/39/EU, 2013.

Gobas F.A.P.C., de Wolf W., Burkhard L.P., Verbruggen E., Plotzke K. Revisiting Bioaccumulation Criteria for POPs and PBT Assessments. Integrated Environmental Assessment and Management 2009; 5: 624-637.

Harner T., Mackay D., Jones K.C. Model of the long-term exchange of PCBs between soil and the atmosphere in the southern UK. Environmental Science & Technology 1995; 29: 1200-1209.

Hope B.K. A model for the presence of polychlorinated biphenyls (PCBs) in the Willamette River Basin (Oregon). Environmental Science & Technology 2008; 42: 5998-6006.

Jin L., Whitehead P.G., Futter M.N., Lu Z.L. Modelling the impacts of climate change on flow and nitrate in the River Thames: assessing potential adaptation strategies. Hydrology Research 2012; 43: 902-916.

Jin. L., Whitehead. P.G., Chovelon. G. Modelling flow and nitrogen dynamics in the River Thames: Implication of future climate induced water vulnerability in south-east England, 2010.

Johnson A.C. Natural Variations in Flow Are Critical in Determining Concentrations of Point Source Contaminants in Rivers: An Estrogen Example. Environmental Science & Technology 2010; 44: 7865-7870.

Johnson A.C., Acreman M.C., Dunbar M.J., Feist S.W., Giacomello A.M., Gozlan R.E., et al. The British river of the future: How climate change and human activity might affect two contrasting river ecosystems in England. Science of The Total Environment 2009; 407: 4787-4798.

Jürgens M.D. Biomonitoring of wild fish to assess chemical pollution in English rivers – an application of a fish tissue archive Lancaster Environment Centre. PHD. Lancaster University, UK, 2015.

Jürgens M.D., Chaemfa C., Hughes D., Johnson A.C., Jones K.C. PCB and organochlorine pesticide burden in eels in the lower Thames river (UK) Chemosphere 2015; 118: 103-111.

Kannan N., Tanabe S., Ono M., Tatsukawa R. Critical-evaluation of polychlorinated biphenyl toxicity in terrestrial and marine mammals - Increasing impact of non-ortho and mono-ortho coplanar polychlorinated-biphenyls from land to ocean. Archives of Environmental Contamination and Toxicology 1989; 18: 850-857.

Kilic S.G., Aral M.M. A fugacity based continuous and dynamic fate and transport model for river networks and its application to Altamaha River. Science of the Total Environment 2009; 407: 3855-3866.

Koenig S., Fernandez P., Sole M. Differences in cytochrome P450 enzyme activities between fish and crustacea: Relationship with the bioaccumulation patterns of polychlorobiphenyls (PCBs). Aquatic Toxicology 2012; 108: 11-17.

Lamon L., MacLeod M., Marcomini A., Hungerbuhler K. Modeling the influence of climate change on the mass balance of polychlorinated biphenyls in the Adriatic Sea. Chemosphere 2012; 87: 1045-1051.

Lohmann R., Breivik K., Dachs J., Muir D. Global fate of POPs: Current and future research directions. Environmental Pollution 2007; 150: 150-165.

Macdonald R.W., Harner T., Fyfe J. Recent climate change in the Arctic and its impact on contaminant pathways and interpretation of temporal trend data. Science of the Total Environment 2005; 342: 5-86.

Mackay D. Multimedia Environmental Models: the Fugacity Approach. Michigan: Lewis Publishers, 2001.

MacLeod M., Fraser A.J., Mackay D. Evaluating and expressing the propagation of uncertainty in chemical fate and bioaccumulation models. Environmental Toxicology and Chemistry 2002; 21: 700-709.

Macleod M., Riley W.J., McKone T.E. Assessing the influence of climate variability on atmospheric concentrations of polychlorinated biphenyls using a global-scale mass balance model (BETR-global). Environmental Science & Technology 2005; 39: 6749-6756.

Murphy J.M., Sexton D.M.H., Jenkins G.J., Boorman P.M., Booth B.B.B., Brown C.C., et al. UK Climate Projections' Science Report: Climate Change Projections. Met Office Hadley Centre, Exeter., 2009.

NAEI. UK Emissions of Air Pollutants 1970 to 2009, Defra AQ0711: DEFRA, http://naei.defra.gov.uk/reports/reports?report_id=796, 2011.

Nicolaus E.E.M., Law R.J., Wright S.R., Lyons B.P. Spatial and temporal analysis of the risks posed by polycyclic aromatic hydrocarbon, polychlorinated biphenyl and metal contaminants in sediments in UK estuaries and coastal waters. Marine Pollution Bulletin 2015.

Nowell L.H., Capel P.D., Dileanis P.D. Pesticides in Stream Sediment and Aquatic Biota: Distribution, Trends, and governing factors. United States: CRC Press LLC, 1999.

OSPAR. Assessment of trends and concentrations of selected hazardous substances in sediments and biota, http://www.ospar.org/v_publications/browse.asp?preset=1&menu=00080800000000_000000_000000&v0_0=sediment&v1_0=n_code%2Ctitle%2Clanguage%2CISBNNumber%2CYearOfPublication%2CSeriesName%2Cpublicationnumber&v2_0=&v0_1=&v1_1=SeriesName&v2_1=&v0_2=&v1_2=ISBNNumber&v2_2=&order=YearOfPublication+desc%2CPublicationNumber+desc&v1_3=&v2_3=, 2009a.

OSPAR. Backgound document on CEMP assessment criteria for QSR 2010, 2009b.

Paasivirta J., Sinkkonen S., Mikkelson P., Rantio T., Wania F. Estimation of vapor pressures, solubilities and Henry's law constants of selected persistent organic pollutants as functions of temperature. Chemosphere 1999; 39: 811-832.

Paul A.G., Hammen V.C., Hickler T., Karlson U.G., Jones K.C., Sweetman A.J. Potential implications of future climate and land-cover changes for the fate and distribution of persistent organic pollutants in Europe. Global Ecology and Biogeography 2012; 21: 64-74.

Rose M., Fernandes A., Mortimer D., Baskaran C. Contamination of fish in UK fresh water systems: Risk assessment for human consumption. Chemosphere 2015; 122: 183-189.

Round C.E., Young A.R., Fox K. A Regionally Applicable Model for Estimating Flow Velocity at Ungauged River Sites in the UK. Water and Environment Journal 1998; 12: 402-405.

Safe S., Bandiera S., Sawyer T., Robertson L., Safe L., Parkinson A., et al. Structure-function-relationships and mechanism of action. Environmental Health Perspectives 1985; 60: 47-56.

Schuster J.K., Gioia R., Sweetman A.J., Jones K.C. Temporal Trends and Controlling Factors for Polychlorinated Biphenyls in the UK Atmosphere (1991-2008). Environmental Science & Technology 2010; 44: 8068-8074.

Scrimshaw M.D., Lester J.N. Multivariate analysis of UK salt marsh sediment contaminant data with reference to the significance of PCB contamination. Environmental Science & Technology 2001; 35: 2676-2681.

Sweetman A.J., Cousins I.T., Seth R., Jones K.C., Mackay D. A dynamic level IV multimedia environmental model: Application to the fate of polychlorinated biphenyls in the United

Kingdom over a 60-year period. Environmental Toxicology and Chemistry 2002; 21: 930-940.

Teran T., Lamon L., Marcomini A. Climate change effects on POPs' environmental behaviour: a scientific perspective for future regulatory actions. Atmospheric Pollution Research 2012; 3: 466-476.

Thompson S., Mackay D., MacLeod M. A modeling strategy for planning the virtual elimination of persistent toxic chemicals from the Great Lakes: An illustration of four contaminants in Lake Ontario. Journal of Great Lakes Research 1999; 25: 814-827.

U.S. EPA. Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories: Volume II: Risk Assessment and Fish Consumption Limits. 2000.

Valle M.D., Codato E., Marcomini A. Climate change influence on POPs distribution and fate: A case study. Chemosphere 2007; 67: 1287-1295.

Van den Berg M., Birnbaum L.S., Denison M., De Vito M., Farland W., Feeley M., et al. The 2005 World Health Organization Reevaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-Like Compounds. Toxicol. Sci. 2006; 93: 223-241.

Vane C.H., Harrison I., Kim A.W. Assessment of polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in surface sediments of the Inner Clyde Estuary, UK. Marine Pollution Bulletin 2007a; 54: 1301-1306.

Vane C.H., Harrison I., Kim A.W. Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in sediments from the Mersey Estuary, U.K. Science of The Total Environment 2007b; 374: 112-126.

Vane C.H., Kim A.W., Beriro D.J., Cave M.R., Knights K., Moss-Hayes V., et al. Polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) in urban soils of Greater London, UK. Applied Geochemistry 2014; 51: 303-314.

Webster E., Mackay D., Wania F. Evaluating environmental persistence. Environmental Toxicology and Chemistry 1998; 17: 2148-2158.

Webster L., Roose P., Bersuder B., Kotterman M., Haarich M., Vorkamp K. Determination of polychlorinated biphenyls (PCBs) in sediment and biota. ICES Techniques in Marine Environmental Sciences 2013; No. 53.

Weisbrod A.V., Burkhard L.P., Arnot J., Mekenyan O., Howard P.H., Russom C., et al. Workgroup report: Review of fish bioaccurnulation databases used to identify persistent, bioaccumulative, toxic substances. Environmental Health Perspectives 2007; 115: 255-261.

Williams R.J., Keller V.D.J., Johnson A.C., Young A.R., Holmes M.G.R., Wells C., et al. A national risk assessment for intersex in fish arising from steroid estrogens. Environmental Toxicology and Chemistry 2009; 28: 220-230.

Wodarg D., Komp P., McLachlan M.S. A baseline study of polychlorinated biphenyl and hexachlorobenzene concentrations in the western Baltic Sea and Baltic Proper. Marine Chemistry 2004; 87: 23-36.

Table Captions List:

Table 1. Different scenarios examined in modelling the long-term fate of PCBs in the River Thames Catchment

Table 2. Comparison between estimated and measured concentrations of selected PCBs for the 2000s

Table 3. Sensitivity analysis for PCB 52 in the different compartments

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Fig. 1. Location map of the non-tidal River Thames Catchment showing the major tributaries and sub-catchments

Fig. 2. The modelled distribution of PCB 52 in the River Thames Catchment in the 2000s

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

- The fate of PCBs in Thames catchment was evaluated with a fugacity model
- We predict most PCBs mass in soil, but highest concentrations in fish and sediment
- As primary emissions decline, soil could act as a major secondary source of PCBs
- The PCB levels in fish are expected to drop below the US EPA’s threshold in 2020s
- Climate change over a 80yr period had only a modest effect on fate

Supporting Information to:

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

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1. Level III Fugacity Model

Figure SI1 shows the processes taken into account in the fugacity level III model. The intermedia transport and transformation rates are described with the constant D. The equations of the interphase transfer calculation are presented in Table SI1. More detailed information about the level III fugacity calculation is discussed in previous work carried out by Mackay (2001).

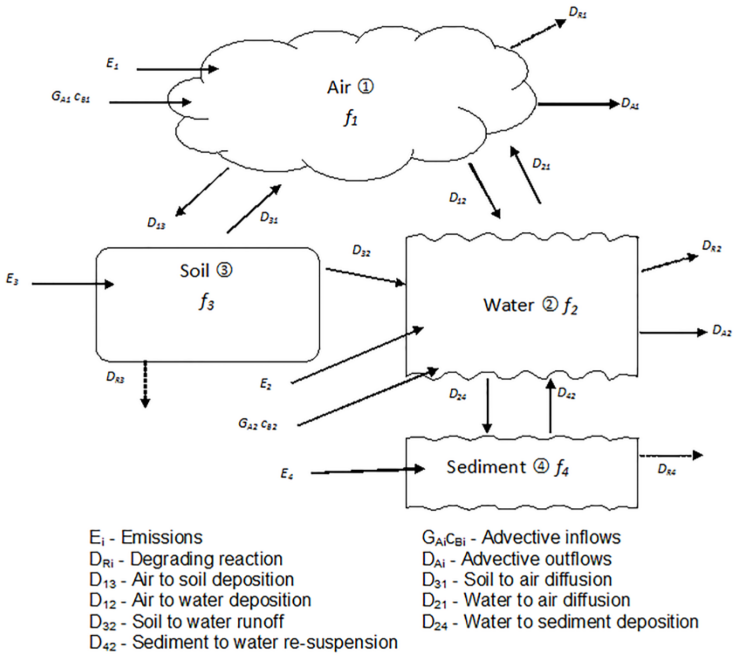


Fig.SI1. Level III fugacity model schematic diagram (adapted from Mackay, 2001).

Table SI1. Level III fugacity model calculation – Interphase Transfer D Value Equations (adapted from Mackay, 2001).

Compartments	Processes	D Values	
Air (1) -Water (2)	Diffusion	$D_V = 1/(1/k_{VA}A_{12}Z_A + 1/k_{VW}A_{12}Z_W)$	$D_{12} = D_V + D_{RW2} + D_{QD2} + D_{QW2}$ $D_{21} = D_V$
	Rain dissolution	$D_{RW2} = A_{12}\ U_Q\ Z_W$	
	Wet deposition	$D_{QW2} = A_{12}\ U_R\ Q\ v_Q\ Z_Q$	
	Dry deposition	$D_{QD2} = A_{12}\ U_Q\ v_Q\ Z_Q$	
Air(1) - Soil(3)	Diffusion	$D_{RW3} = A_{13}\ U_R\ v_Q Z_W$	$D_{13} = D_E + D_{RW3} + D_{QW3} + D_{QD3}$ $D_{31} = D_E$
	Rain dissolution	$D_E =1/(1/k_{EA}A_{13}Z + Y_3/(A_{13}(B_{MA}Z_A + B_{MW}Z_W)))$	
	Wet deposition	$D_{QW3} = A_{13}\ U_R\ Q\ v_Q\ Z_Q$	
	Dry deposition	$D_{QD3} = A_{13}\ U_Q\ v_Q\ Z_Q$	
Soil(3) - Water(2)	Soil runoff	$D_{SW} = A_{13}\ U_{EW}\ Z_E$	$D_{32} = D_{SW} + D_{WW}$ $D_{23} = 0$
	Water runoff	$D_{WW} = A_{13}\ U_{WW}\ Z_W$	
Sediment(4) -Water(2)	Diffusion	$DY = 1/(1/k_{SW}A_{24}Z_W + Y_4/B_{W4}A_{24}Z_W)$	$D_{24} = D_Y + D_{DS}$ $D_{42} = D_Y + D_{RS}$
	Deposition	$D_{DS} = U_{DP}\ A_{23}\ Z_P$	
	Desuspension	$D_{RS} = U_{RS}\ A_{23}\ Z_S$	
Reaction either bulk phase i or sum of all phases		$D_{Ri} = k_{Ri}\ V_i\ Z_i$	$D_{Ri} = \Sigma(k_{Rij}\ V_{ij}\ Z_{ij})$
Advection bulk phase		$D_{Ai} = G_i\ Z_i$ or $U_i\ A_I\ Z_i$	

* k_{VA} - air side MTC over water; k_{VW} - water side MTC; U_R – rain rate; Q - scavenging ratio; V_Q - Vol. fraction aerosols ;
U_Q - dry deposition velocity; k_{EA} - air side MTC over soil; Y_3 - diffusion path length in soil; B_{MA} - molecular diffusivity in air;
B_{MW} - molecular diffusivity in water; U_{EW} - solids runoff rate from soil; U_{WW} - water runoff rate from soil;
k_{SW} - Water side MTC over sediment; Y_4 - diffusion path length in sediment; U_{DP} - sediment deposition rate;
U_{RS} - sediment resuspension rate;

2. Input Parameters

In Table SI2 and Table SI3 input physico-chemical properties of the study PCBs and input environmental parameters of the River Thames catchment for the fugacity level III model simulations are presented.

Table SI2. 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)

Table SI3. Environmental Properties of the River Thames Catchment

Parameter	Value	Data Sources
Temperature (ºC)	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 et al. (2009)
Rain rate (m/h)	1.03E-04	Sweetman et al. (2002)
Average precipitation (mm)	1.88	Meteorological Office
Average wind speed (m/s)	3.28	Meteorological Office
Atmosphere height (m)	1000	Mackay (2001)
Density of air (kg/m^3)	1.86	Mackay (2001)
Density of water (kg/m^3)	1000	—
Depth of soil (m)	0.3	—
Depth of sediment (m)	0.1	—
Volume fraction of aerosol in air	1.30E-11	Sweetman et al. (2002)
Density of aerosol (kg/m^3)	2.50E+03	Mackay (2001)
Volume fraction of suspended particles in water	5.00E-06	Sweetman et al. (2002)
Density of suspended particles(kg/m^3)	2.50E+03	Mackay (2001)
Volume fraction of fish	1.00E-06	Sweetman et al. (2002)
Density of fish (kg/m^3)	1.08E+03	Mackay (2001)
Volume fraction of air in soil	0.2	Sweetman et al. (2002)
Volume fraction of water in soil	0.3	Sweetman et al. (2002)
Volume fraction of solids in soil	0.5	Sweetman et al. (2002)
Volume fraction of water in sediment	0.63	Sweetman et al. (2002)
Volume fraction of solids in sediment	0.37	Sweetman et al. (2002)
Organic carbon in suspended particles (g/g)	0.2	—
Residence time in sediment (h)	5.00E+04	Mackay (2001)
Air side air-water MTC* (m/h)	3	Sweetman et al. (2002)
Water side air-water MTC (m/h)	0.03	Sweetman et al. (2002)
Aerosol dry deposition velocity (m/h)	10.8	Swackhamer et al. (1988); Sweetman et al. (2002)
Soil air phase diffusion MTC (m/h)	0.02	—
Soil water phase diffusion MTC (m/h)	1.00E-05	—
Soil air boundary layer MTC (m/h)	1	Sweetman et al. (2002)
Sediment-water MTC (m/h)	0.01	Lamon et al. (2012)
Sediment deposition velocity (m/h)	5.84E-04	Gevao et al. (1997); Sweetman et al. (2002)
Sediment re-suspension velocity (m/h)	1.11E-04	Gevao et al. (1997); Sweetman et al. (2002)
Soil water runoff rate (m/h)	3.00E-05	Gevao et al. (1997); Sweetman et al. (2002)
Soil solids runoff rate (m/h)	2.30E-08	Sweetman et al. (2002)
Scavenging ratio	2.00E+05	Sweetman et al. (2002)

*MTC – Mass transfer coefficient

3. Change in Parameters with Temperature

The temperature dependency of physicochemical parameters for PCBs congeners, including vapour pressure (P_s), Henry's law constant (H), partition coefficients (K_{ow}), and water solubility (S_s, S_l), has been calculated by using the following equations (SI1- SI5):

$\log P_S = A_{PS} - B_{PS}/T$ (SI1)

$\log S_S = A_{SS} - B_{SS}/T$ (SI2)

$\log S_L = A_{SL} - B_{SL}/T$ (SI3)

$\log H = A_H - B_H/T$ (SI4)

$\log K_{ow} = A_Z - B_Z \log S_L$ (SI5)

where T is the temperature in [K] and Ai and Bi are empirical dimensionless factors (Dalla Valle et al., 2007; Paasivirta et al., 1999). The values for Ai and Bi are described in detail by Paasivirta et al. (1999).

The variations of degradation rates as a function of temperature were calculated according to the Arrhenius equation (Eq. SI6):

$k = Ae^{\frac{-Ea}{RT}}$ (SI6)

Here, A is a constant and Ea represents the activation energy. The activation energy value for degradation in air is 7, 10 and 12 kj/mol for PCB 52, PCB118 and PCB 152 respectively (listed in Table 1); the value for water, soil and sediment is assumed to be 30 kJ/mol (Kong et al., 2013).

4. Bioconcentration Factor (BCF) and Biota-Sediment Accumulation Factor (BSAF)

Bioconcentration describes the accmulation of water contaminants in aquatic organisms (fish in this case). The bioconcentraiton factor (BCF) is defined as (EA, 2011; Gobas et al., 2009):

$BCF = \frac{C_f}{C_w}$ (SI7),

where C_f, C_w are the chemical concentrations in fish and water.

Similar to the case of bioconcentration, biota-sediment accumulation is the bio-accumulation of sediment contaminants in organisms. The biota-sediment accumulation factors (BSAFs) of the PCB congeners were calculated using the following equation (Eq.SI8) (Nowell et al., 1999; Weisbrod et al., 2007):

$BSAF = \frac{C_f/f_t}{C_s/f_{soc}}$ (SI8), where C_f, C_s are the chemical concentrations in fish and sediment, f_t stands for the fraction of lipid in fish, and f_{soc} is the organic carbon content in sediment.

5. Sensitivity and Uncertainty Analysis

Table SI4 and Table SI5 show the sensitivity results for PCB 118 and PCB 153 in each environmental compartment with a simple ±20% variation of an individual input parameter. The uncertainty analysis for PCB 52, PCB118 and PCB 153 in the compartments of air, soil, water, fish and sediment in the River Thames catchment were presented in Fig. SI2 - SI4. The horizontal axis represents the logarithmic value of confidence factors in input parameters while the vertical axis represents the logarithmic value of corresponding uncertainty in modelling outputs attributed to that input. Three diagonal lines in each diagram are for reference purposes with sensitivity set to 1,0.5 and 0.1.

Table SI4. Sensitivity analysis for PCB 118 in the different compartments

Parameters	Air		Soil		Water		Fish		Sediment	
	-20%	+20%	-20%	+20%	-20%	+20%	-20%	+20%	-20%	+20%
K_{ow}	0.00	0.00	0.00	0.00	-0.04	-0.03	0.00	0.00	0.00	0.00
Water solubility	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Vapour pressure	0.04	0.03	-0.10	-0.10	-0.01	0.00	-0.01	0.00	-0.01	0.00
Temperature	-0.33	-0.34	0.54	0.60	0.04	0.04	0.04	0.04	0.04	0.04
Degradation in air	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Degradation in soil	0.00	0.00	-1.23	-0.82	-0.10	-0.05	-0.10	-0.05	-0.10	-0.05
Degradation in water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Degradation in sediment	0.00	0.00	0.00	0.00	-0.39	-0.34	-0.39	-0.34	-0.39	-0.34
Rain rate	-0.03	-0.03	0.04	0.04	0.00	0.00	0.00	0.00	0.00	0.00
Aerosol dry deposition	-0.02	-0.02	0.04	0.04	0.00	0.00	0.00	0.00	0.00	0.00
Water depth	0.00	0.00	0.00	0.00	-0.03	-0.03	-0.03	-0.03	-0.03	-0.03
Air residence time	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Water residence time	0.00	0.00	0.00	0.00	-0.02	-0.04	-0.02	-0.04	-0.02	-0.04
OC fraction in sediment	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sediment deposition	0.00	0.00	0.00	0.00	-1.20	-0.81	-1.20	-0.81	0.04	0.02
Sediment re-suspension	0.00	0.00	0.00	0.00	0.97	0.96	0.97	0.96	-0.03	-0.03
Soil solids run off	0.00	0.00	-0.01	-0.01	0.06	0.06	0.00	0.00	0.06	0.06
Soil water run off	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table SI5. Sensitivity analysis for PCB 153 in the different compartments

Parameters	Air		Soil		Water		Fish		Sediment	
	-20%	+20%	-20%	+20%	-20%	+20%	-20%	+20%	-20%	+20%
K_{ow}	0.00	0.00	0.00	0.00	-0.02	-0.01	0.00	0.00	0.00	0.00
Water solubility	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Vapour pressure	0.05	0.04	-0.14	-0.12	-0.04	-0.03	-0.04	-0.03	-0.04	-0.03
Temperature	-0.39	-0.39	1.20	1.16	0.28	0.28	0.28	0.28	0.28	0.28
Degradation in air	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Degradation in soil	0.00	0.00	-1.20	-0.81	-0.28	-0.19	-0.28	-0.19	-0.28	-0.19
Degradation in water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Degradation in sediment	0.00	0.00	0.00	0.00	-0.18	-0.17	-0.18	-0.17	-0.18	-0.17
Rain rate	-0.04	-0.04	0.12	0.11	0.03	0.03	0.03	0.03	0.03	0.03
Aerosol dry deposition	-0.04	-0.04	0.11	0.11	0.03	0.03	0.03	0.03	0.03	0.03
Water depth	0.00	0.00	0.00	0.00	-0.04	-0.04	-0.04	-0.04	-0.04	-0.04
Air residence time	0.08	0.08	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00
Water residence time	0.00	0.00	0.00	0.00	0.04	0.03	0.04	0.03	0.04	0.03
OC fraction in sediment	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sediment deposition	0.00	0.00	0.00	0.00	-1.19	-0.81	-1.19	-0.81	0.05	0.03
Sediment re-suspension	0.00	0.00	0.00	0.00	0.97	0.95	0.97	0.95	-0.04	-0.04
Soil solids run off	0.00	0.00	-0.03	-0.03	0.22	0.22	0.22	0.22	0.22	0.22
Soil water run off	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

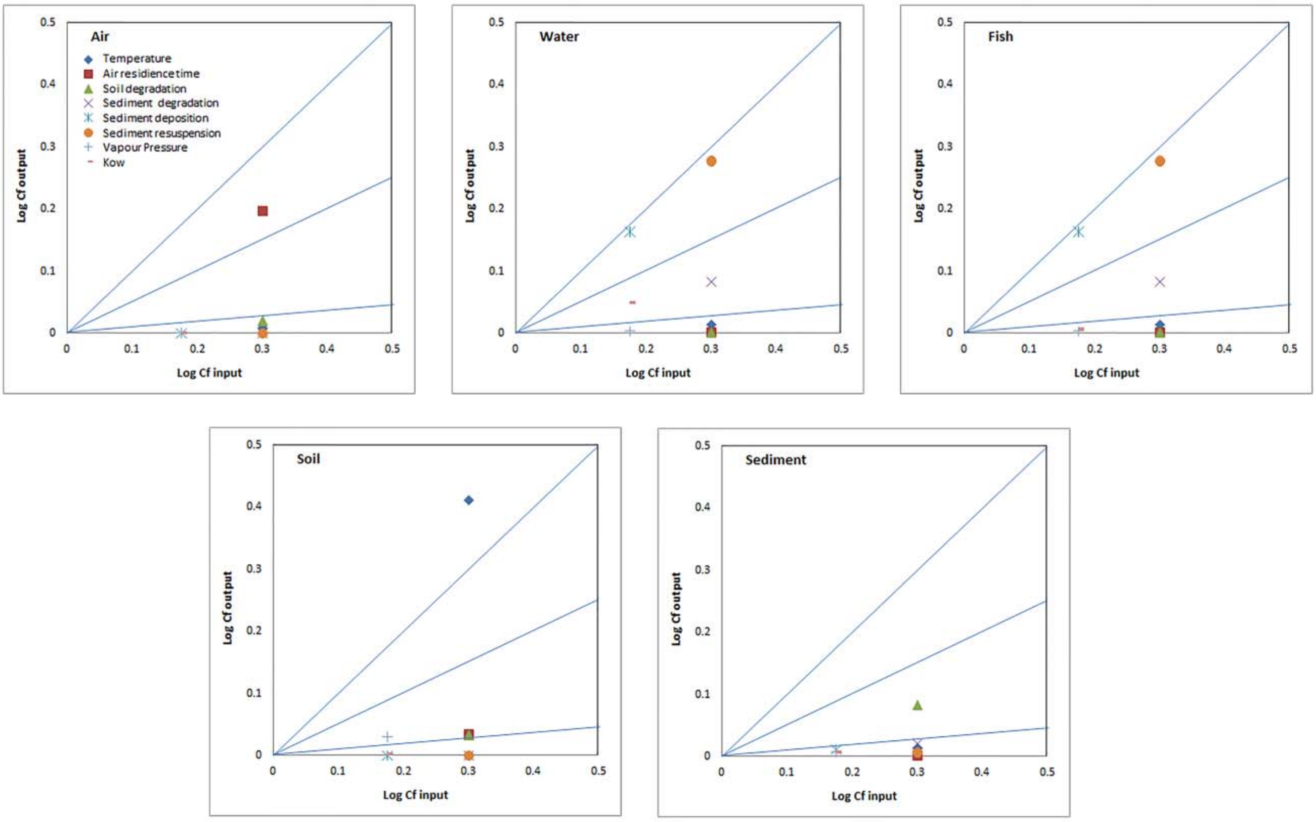


Fig. SI2. Graphic analysis of the contribution of the most sensitive parameters to modelling outputs in the compartments of air, soil, water, fish and sediment for PCB 52.

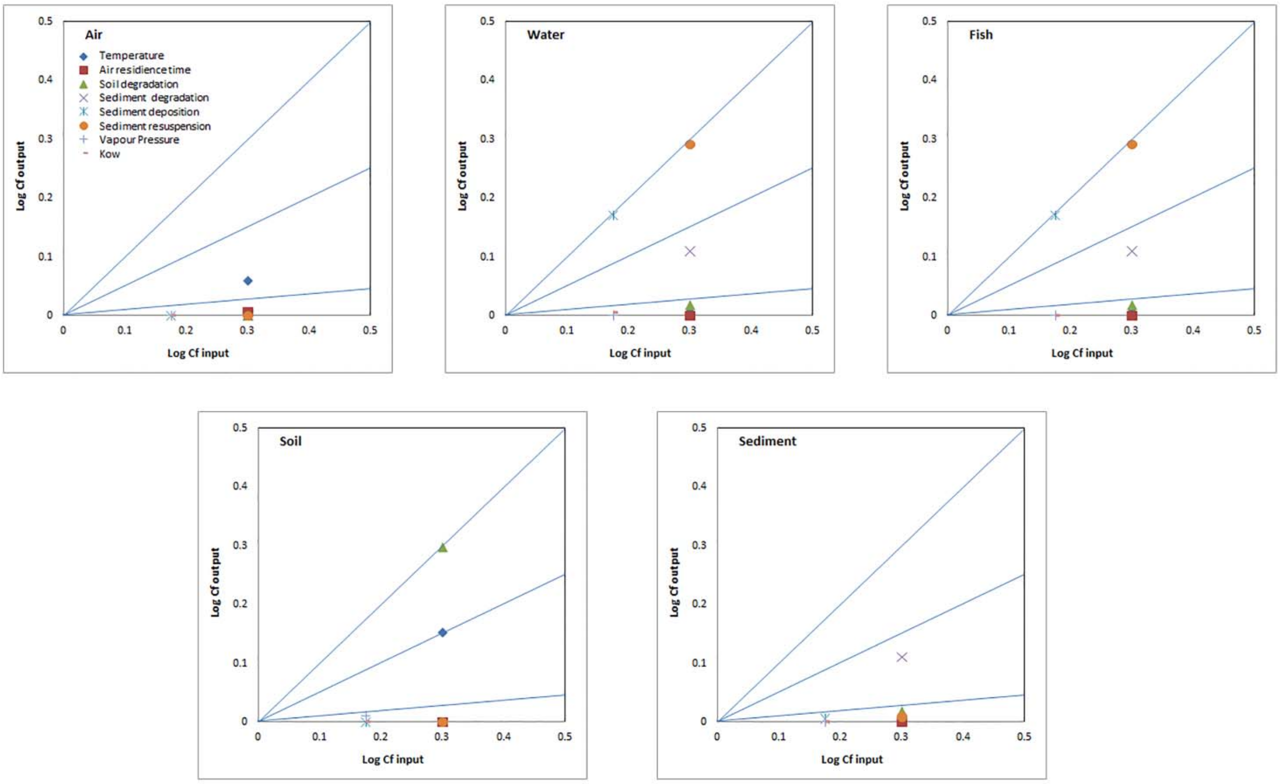


Fig. SI3. Graphic analysis of the contribution of the most sensitive parameters to modelling outputs in the compartments of air, soil, water, fish and sediment for PCB 118.

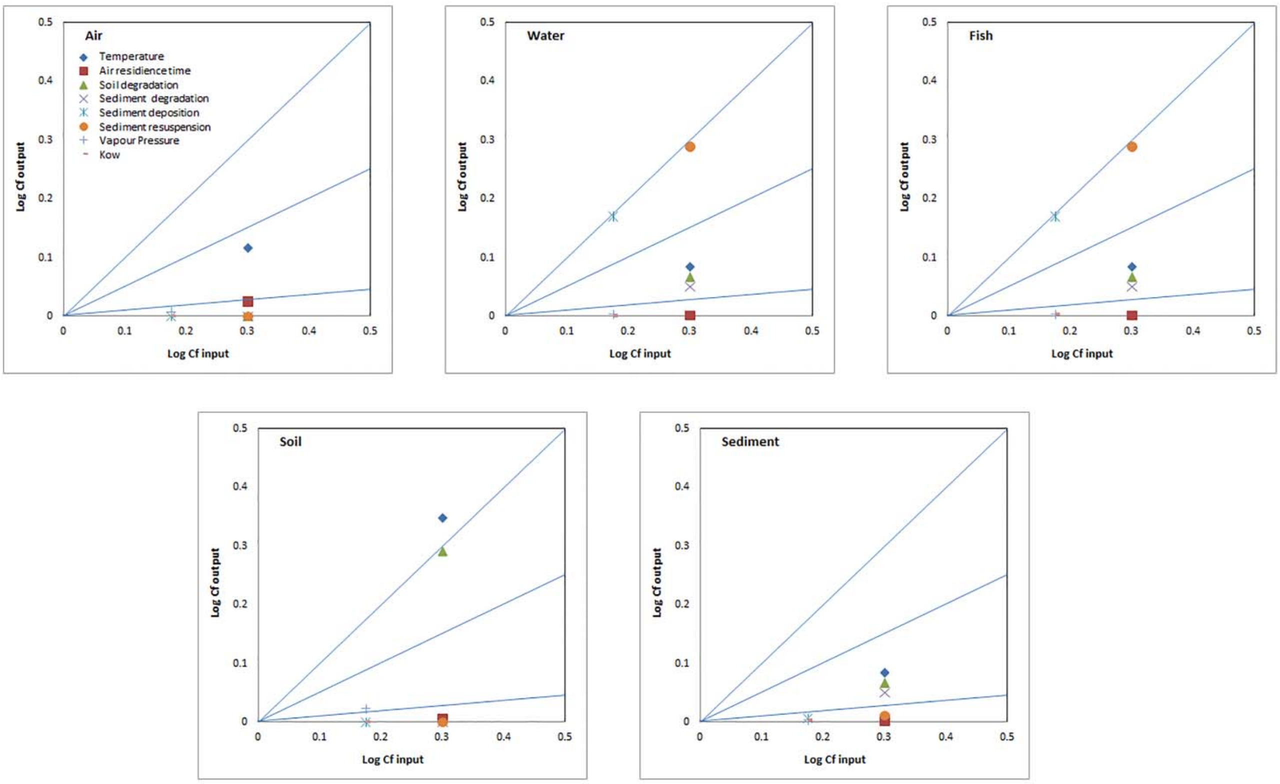


Fig. SI4. Graphic analysis of the contribution of the most sensitive parameters to modelling outputs in the compartments of air, soil, water, fish and sediment for PCB 153.

6. The Fate of PCBs in the Catchment

Fig. SI5 and Fig. SI6 illustrate the fate of PCB 118 and PCB 153 in the River Thames catchment in the 2000s.

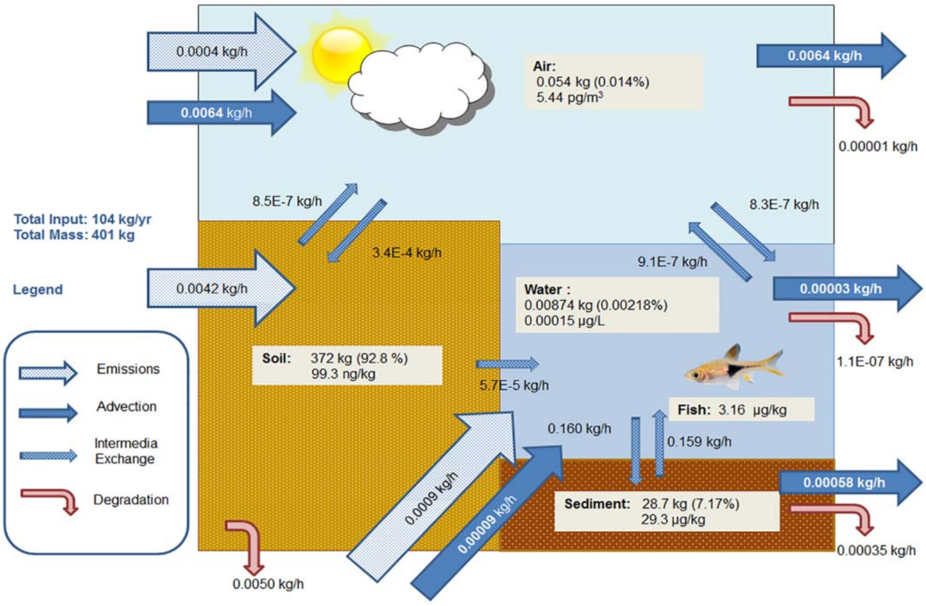


Fig. SI5. The modelled distribution of PCB 118 in the River Thames catchment in the 2000s

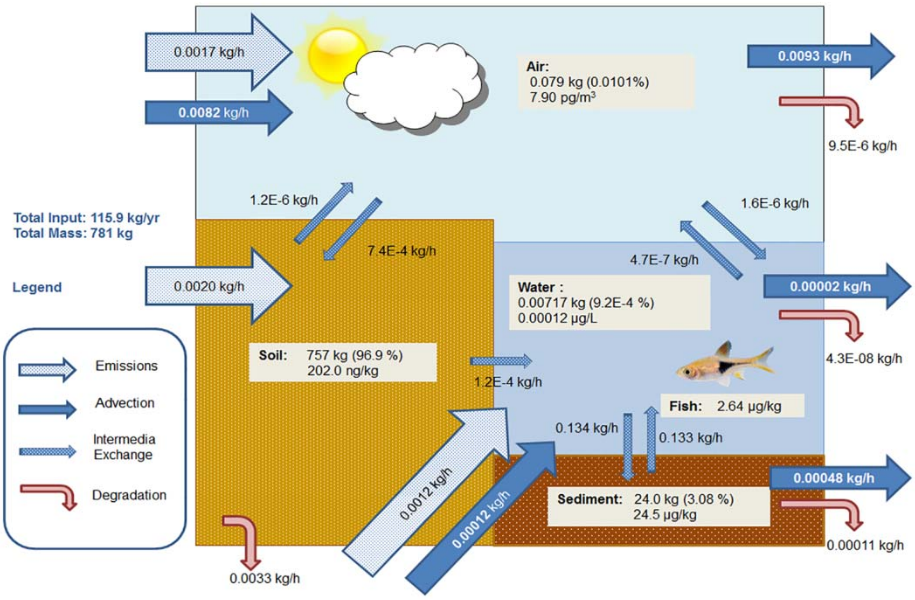


Fig. SI6. The modelled distribution of PCB 153 in the River Thames catchment in the 2000s

7. References

Bamford H.A., Poster D.L., Baker J.E. Henry's law constants of polychlorinated biphenyl congeners and their variation with temperature. Journal of Chemical and Engineering Data 2000; 45: 1069-1074.

Crossman J., Whitehead P.G., Futter M.N., Jin L., Shahgedanova M., Castellazzi M., et al. The interactive responses of water quality and hydrology to changes in multiple stressors, and implications for the long-term effective management of phosphorus. Science of the Total Environment 2013; 454: 230-244.

Dalla Valle M., Codato E., Marcomini A. Climate change influence on POPs distribution and fate: A case study. Chemosphere 2007; 67: 1287-1295.

EA. Estimation of fish bioconcentration factor (BCF) from depuration data. Bristol: Environment Agency, https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/291527/scho0811buce-e-e.pdf, 2011.

Gevao B., Hamilton-Taylor T., Murdoch C., Jones K.C., Kelly M., Tabner B.J. Depositional time trends and remobilization of PCBs in lake sediments. Environmental Science & Technology 1997; 31: 3274-3280.

Gobas F.A.P.C., de Wolf W., Burkhard L.P., Verbruggen E., Plotzke K. Revisiting Bioaccumulation Criteria for POPs and PBT Assessments. Integrated Environmental Assessment and Management 2009; 5: 624-637.

Hiederer R., Kochy M. Global soil organic carbon estimates and the Harmonized World Soil Database, ISSN 1831-9424, EUR Scientific and Technical Research series, 2012.

Johnson A.C., Acreman M.C., Dunbar M.J., Feist S.W., Giacomello A.M., Gozlan R.E., et al. The British river of the future: How climate change and human activity might affect two contrasting river ecosystems in England. Science of The Total Environment 2009; 407: 4787-4798.

Kong D., MacLeod M., Li Z., Cousins I.T. Effects of input uncertainty and variability on the modelled environmental fate of organic pollutants under global climate change scenarios. Chemosphere 2013; 93: 2086-2093.

Lamon L., MacLeod M., Marcomini A., Hungerbuhler K. Modeling the influence of climate change on the mass balance of polychlorinated biphenyls in the Adriatic Sea. Chemosphere 2012; 87: 1045-1051.

Mackay D. Multimedia Environmental Models: the Fugacity Approach. Michigan: Lewis Publishers, 2001.

Mackay D., W-Y. S., K-C. M. Illustrated Handbook of Physical-chemical Properties and Environmental Fate for Organic Chemicals. Vol 1-Monoaromatic Hydrocarbons, Chlorobenzenes and PCBs. Lewis, Boca Raton, FL, USA, 1992.

Nowell L.H., Capel P.D., Dileanis P.D. Pesticides in Stream Sediment and Aquatic Biota: Distribution, Trends, and governing factors. United States: CRC Press LLC, 1999.

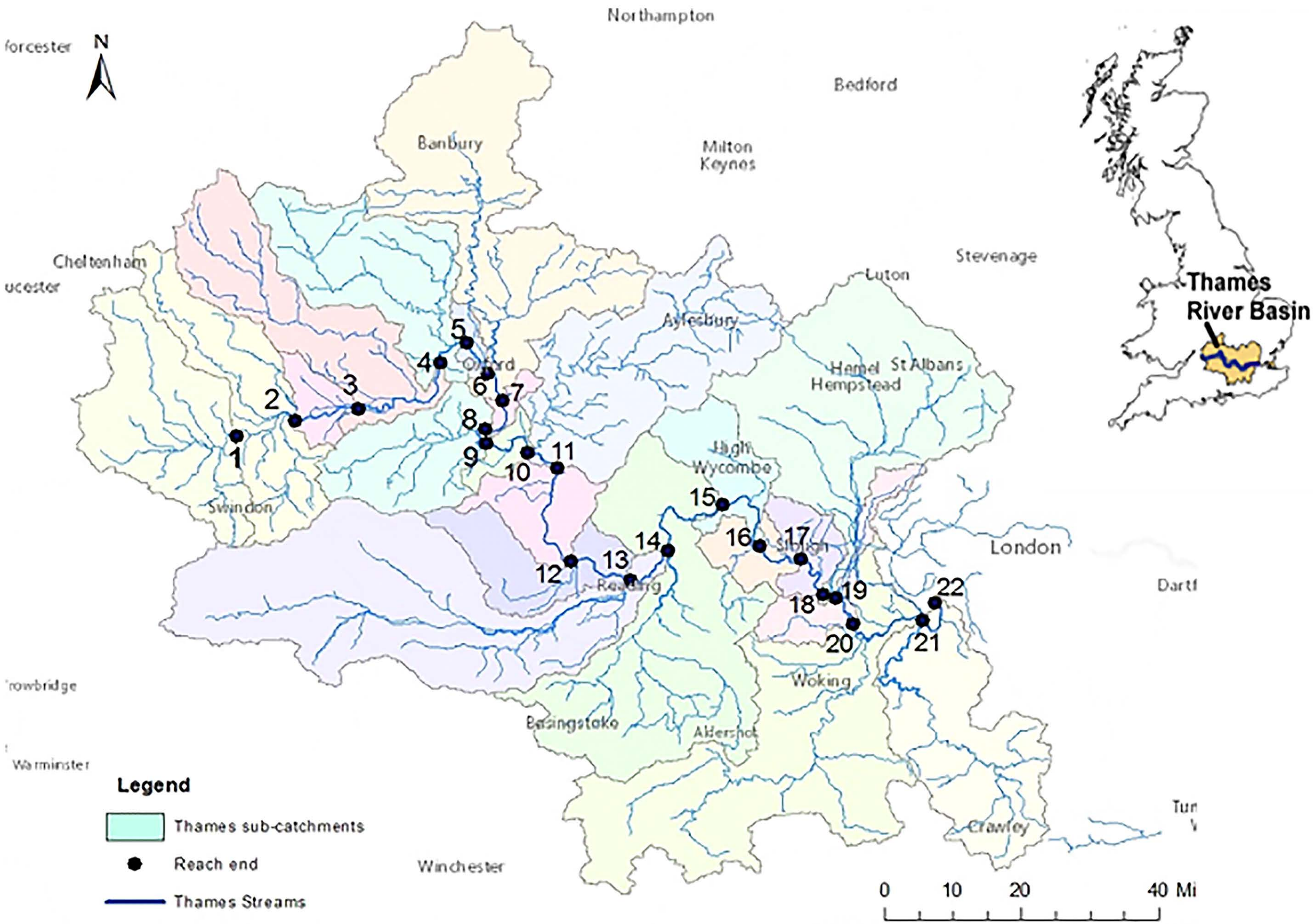
Paasivirta J., Sinkkonen S., Mikkelson P., Rantio T., Wania F. Estimation of vapor pressures, solubilities and Henry's law constants of selected persistent organic pollutants as functions of temperature. Chemosphere 1999; 39: 811-832.

Sinkkonen S., Paasivirta J. Degradation half-life times of PCDDs, PCDFs and PCBs for environmental fate modeling. Chemosphere 2000; 40: 943-949.

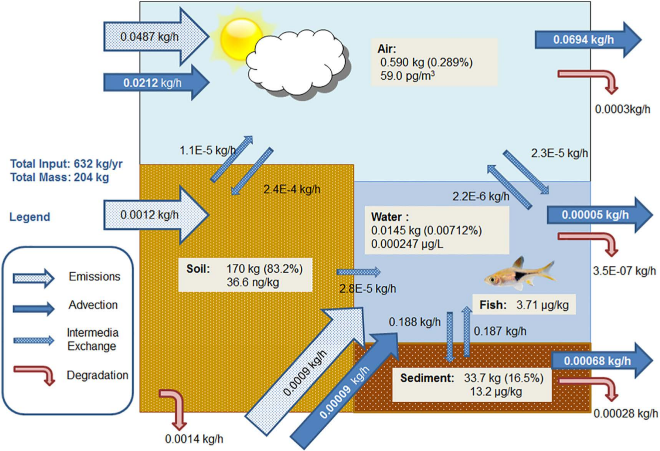
Swackhamer D.L., McVeety B.D., Hites R.A. Deposition and evaporation of polychlorobiphenyl congeners to and from Siskiwit Lake, Isle-Royale, Lake-Superior. Environmental Science & Technology 1988; 22: 664-672.

Sweetman A.J., Cousins I.T., Seth R., Jones K.C., Mackay D. A dynamic level IV multimedia environmental model: Application to the fate of polychlorinated biphenyls in the United Kingdom over a 60-year period. Environmental Toxicology and Chemistry 2002; 21: 930-940.

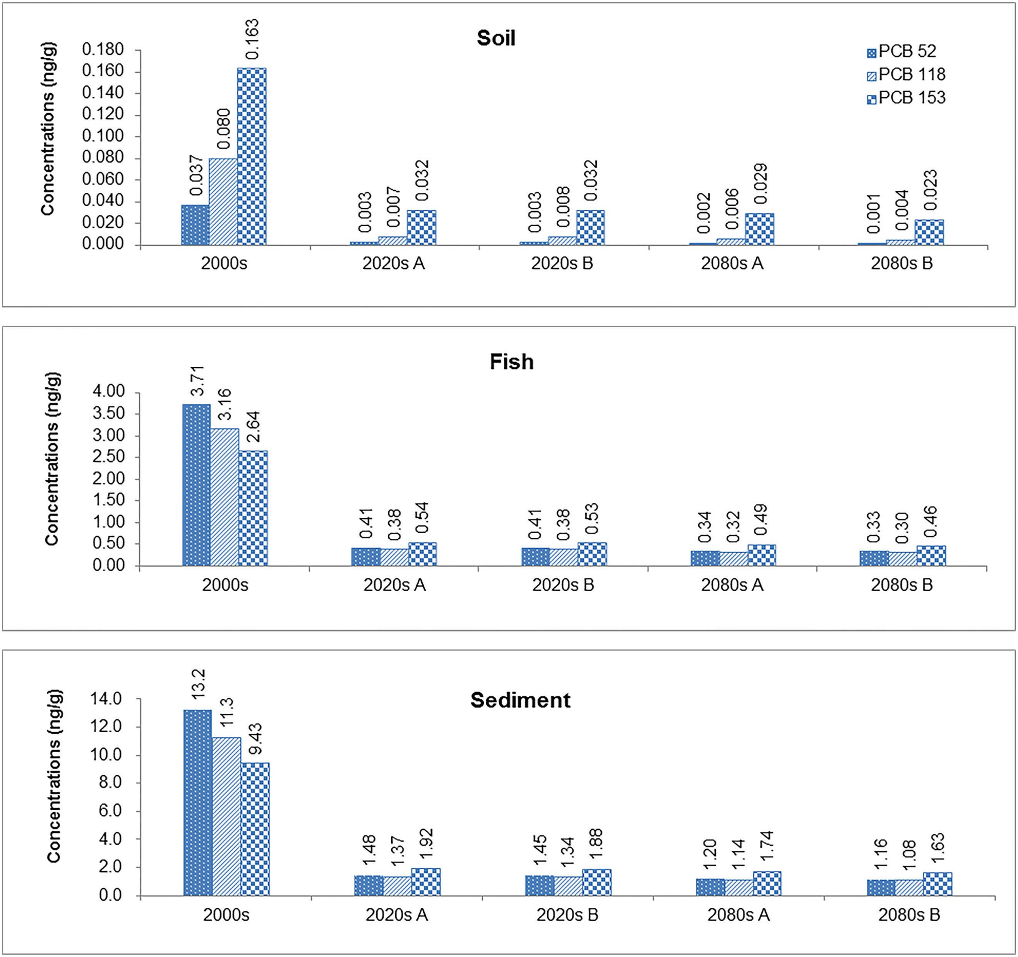
Weisbrod A.V., Burkhard L.P., Arnot J., Mekenyan O., Howard P.H., Russom C., et al. Workgroup report: Review of fish bioaccurnulation databases used to identify persistent, bioaccumulative, toxic substances. Environmental Health Perspectives 2007; 115: 255-261.



1 Cricklade Castle	7 Sandford	13 Caversham	18 Bell
2 Buscot	8 Abingdon	14 Shiplake	19 Egham
3 Rushey	9 Culham	15 Marlow	20 Shepperton
4 Pinkhill	10 Day's Weir	16 Bray	21 Mosley
5 King's Weir	11 Benson	17 Romney	22 Teddington
6 Osney	12 Whitchurch		



0.0487 kg/h
0.0212 kg/h
Air:
0.590 kg (0.289%)
59.0 pg/m³
0.0694 kg/h
0.0003kg/h
1.1E-5 kg/h
2.4E-4 kg/h
2.3E-5 kg/h
2.2E-6 kg/h
Total Input: 632 kg/yr
Total Mass: 204 kg
Legend
0.0012 kg/h
Water :
0.0145 kg (0.00712%)
0.000247 µg/L
0.00005 kg/h
3.5E-07 kg/h
Emissions
Advection
Intermedia Exchange
Degradation
Soil: 170 kg (83.2%)
36.6 ng/kg
2.8E-5 kg/h
Fish: 3.71 µg/kg
0.188 kg/h
0.187 kg/h
0.0009 kg/h
0.00009 kg/h
0.00068 kg/h
Sediment: 33.7 kg (16.5%)
13.2 µg/kg
0.00028 kg/h
0.0014 kg/h


Soil
Concentrations (ng/g)
0.180
0.160
0.140
0.120
0.100
0.080
0.060
0.040
0.020
0.000
PCB 52
PCB 118
PCB 153
0.037
0.080
0.163
0.003
0.007
0.032
0.003
0.008
0.032
0.002
0.006
0.029
0.001
0.004
0.023
2000s
2020s A
2020s B
2080s A
2080s B
Fish
Concentrations (ng/g)
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
3.71
3.16
2.64
0.41
0.38
0.54
0.41
0.38
0.53
0.34
0.32
0.49
0.33
0.30
0.46
2000s
2020s A
2020s B
2080s A
2080s B
Sediment
Concentrations (ng/g)
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
13.2
11.3
9.43
1.48
1.37
1.92
1.45
1.34
1.88
1.20
1.14
1.74
1.16
1.08
1.63
2000s
2020s A
2020s B
2080s A
2080s B