

**Fate and Transport of Polychlorinated Biphenyls (PCBs) in the River Thames
Catchment – Insights from a Coupled Multimedia Fate and Hydrobiogeochemical
Transport Model**

Q. Lu^a, M.N. Futter^{b,*}, L. Nizzetto^{c,d}, G. Bussi^a, M. D. Jürgens^e, P.G.Whitehead^{a,*}

^a School of Geography and the Environment, University of Oxford, South Parks Road, Oxford, OX1 3QY, UK.

^b Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences, Uppsala, Sweden

^c Norwegian Institute for Water Research, NO-0349, Oslo, Norway

^d Research Centre for Toxic Compounds in the Environment, Masaryk University, 62500, Brno, Czech Republic

^e Centre of Ecology and Hydrology, Maclean Building, Benson Lane, Crowmarsh Gifford, Wallingford, Oxfordshire, OX10 8BB, UK

* Corresponding Authors: Martyn Futter (martyn.futter@slu.se); Paul Whitehead (paul.whitehead@ouce.ox.ac.uk)

Abstract:

The fate of persistent organic pollutants (POPs) in riverine environments is strongly influenced by hydrology (including flooding) and fluxes of sediments and organic carbon. Coupling multimedia fate models (MMFM) and hydrobiogeochemical transport models offers unique opportunities for understanding the environmental behaviour of POPs. While MMFMs are widely used for simulating the fate and transport of legacy and emerging pollutants, they use greatly simplified representations of climate, hydrology and biogeochemical processes. Using additional information about weather, river flows and water chemistry in hydrobiogeochemical transport models can lead to new insights about POPs behaviour in rivers. As most riverine POPs are associated with suspended sediments (SS) or dissolved organic carbon (DOC), coupled models simulating SS and DOC can provide additional information about POPs behaviour. Coupled simulations of river flow, DOC, SS and POPs dynamics offer the possibility of improved predictions of contaminant fate and fluxes by leveraging the additional information in routine water quality time series. Here, we present an application of a daily time step dynamic coupled multimedia fate and hydrobiogeochemical transport model (INCA-Contaminants) to simulate the behaviour of selected PCB congeners in the River Thames (UK). This is a follow-up to an earlier study where a Level III fugacity model was used to simulate PCB behaviour in the Thames. While coupled models are more complex to apply, we show that they can lead to significantly better representation of POPs dynamics. The present study shows the importance of accurate sediment and organic carbon simulations to successfully predict riverine PCB transport. Furthermore, it demonstrates the significant impact of short-term weather variation on PCB movement through the environment. Specifically, it shows the consequences of the severe flooding, which occurred in early 2014 on sediment PCB concentrations in the River Thames.

36 Key words: PCBs, River Thames, INCA, Sediment

37

1. Introduction:

Persistent Organic Pollutants (POPs) include a wide range of organic compounds characterized by their environmental persistence, toxicity, and potential for long-range transport (Lohmann et al., 2007; Urbaniak, 2007). Many POPs are of concern because they have carcinogenic properties and can be a significant public health threat (Ross, 2004). POPs can be produced either intentionally through human activity or unintentionally as by-products of human or natural activities. Production of so-called legacy POPs, including polychlorinated biphenyls (PCBs) has either stopped or is severely constrained. Despite significant efforts to limit their release, PCBs remain a problem in many parts of the world. In urban areas, PCB contamination can be associated with both point and diffuse sources. Point sources include industrial areas where there have been accidental PCB spills. Diffuse sources include runoff from contaminated sites and atmospheric deposition. PCBs have been widely used as dielectric, petroleum additives and coolant fluids in electrical equipment in the UK between 1955 and 1976. The emissions of PCBs to the environment peaked in early the 1970s and dropped rapidly after bans on production and restrictions in their use came into effect in 1977 (Sweetman et al., 2002). Prior to this, a voluntary ban on production of PCBs was implemented in the UK by the early 1970s (Schuster et al., 2010).

Current sources for PCBs to the aqueous environment in the UK include secondary emissions of PCBs in the catchment, contaminated soil, and direct atmospheric inputs or spills from old PCB-containing equipment. Atmospheric PCB concentrations have declined significantly throughout the UK in recent years (Schuster et al., 2010). This decline in concentrations should be reflected in a decline in atmospheric deposition. With the decline in atmospheric concentrations, emissions and mobilization from soil is likely to become proportionately more important (Nizzetto et al., 2010). Mass transport due to extreme weather-related events such as flooding may also be an important mechanism for the redistribution and mobilisation

of PCBs. Because of their hydrophobic nature, many POPs are strongly associated with organic carbon and can accumulate in soils, sediments and biota. These environmental reservoirs can be activated during flooding (Pulkrabová et al., 2008) or other disturbances (Eggleton and Thomas, 2004).

Unlike many other environmental parameters, POPs measurements are characterised by their relative infrequency, analytic complexity and expense. Typically, POPs samples are much less frequent than the routine water quality data monitored by the competent national authority and orders of magnitude less common than hydrological and weather observations. (Figure 1). The more frequent and less expensive routine water quality and hydrometeorological observations can provide additional information about POPs fate. The use of environmental proxies for POP transport is well established (Hung et al., 2010). Many hydrophobic compounds associate strongly with suspended sediment (Josefsson et al., 2011) and the relationship between dissolved organic carbon (DOC) and PCB transport is well established (Evans, 1988). DOC and suspended sediment data are routinely collected by many national monitoring agencies (Fölster et al., 2014) and regulatory authorities. Using the information in routine water quality and hydrometeorological time series can provide additional insights into POPs fate and transport (Figure 1). POPs cost per sample (Figure 1; vertical axis) is much higher than costs for water quality (WQ) or hydrometeorological measurements of precipitation, temperature or flow (PTQ). In part due to their high cost, POPs measurements are much less frequent than routine water quality measurements (WQ) which are often collected monthly at multiple sites in a river network. WQ samples, in turn, are less frequent than the routine weather and flow observations collected by national agencies. Typically, fugacity models focus solely on POPs data and employ highly simplified representations of the environment. Coupled multimedia fate and hydrobiogeochemical models like INCA-Contaminants make use of POPs, water quality and hydrometeorological

observations to deliver an integrated and intrinsically consistent representation of the system dynamics. Using complementary information can increase the available information while simultaneously reducing uncertainty in POPs fate and transport estimates.

The major aim of the study is: 1) to link hydrobiogeochemical cycles to PCB dynamics, specifically between landscapes and riverscapes; 2) to better understand the impact of short-term weather variations on PCB mobilisation and transport in the catchment; 3) to identify sensitive parameters in the modelling exercise.

2. Materials and Methods

2.1. The INCA-Contaminations Model

The Integrated Catchment model (INCA) was developed by Whitehead et al. (1998 to simulate the day to day series of flow pathways and to track nitrogen (N) dynamics in both the land and instream phase in the catchment. The model is process-based and is both vertically integrated, tracking the dynamic inputs from both diffuse sources and discrete points, and horizontally integrated, addressing spatial variations (e.g. land cover, underlying geology, hydrology, sediment production) through the catchment (Whitehead et al., 1998). Since the original N version, the model has been in continuous development and there is currently a suite of INCA models for carbon, sediment, chloride, metals, mercury and phosphorus (Crossman et al., 2013; Futter et al., 2007b; Jin et al., 2013; Lazar et al., 2010) which have been applied to approximately 100 catchments in Europe, North America, Asia and South America.

The INCA-contaminants model used here is the newest member of the INCA family (Nizzetto et al., 2016) and was developed based on two extensively tested INCA models: the carbon model INCA-C (Futter et al., 2007a) and the sediment model INCA-Sed (Lazar et al.,

2010). INCA-C produces daily estimates of organic matter mass balance in multi-branched catchment, while the INCA-Sed simulates sediment production and delivery from land to the in-stream system and subsequent transport, deposition and remobilisation in the stream. All processes are forced by daily input time series of precipitation, hydrologically effective rainfall (precipitation net of evapotranspiration), soil moisture deficit and air temperature. In the INCA-contaminants model, a daily time step dynamic multimedia box model has been integrated in the INCA-C/INCA-Sed coupled structure (Nizzetto et al., 2016). All land phase equations are solved for a 1 km² cell and results are pro-rated to sub-catchment area. The processes in the INCA-contaminants model can be described in two main sections: 1) the land phase model simulating the multimedia distribution, transport, storage and transformation of contaminants in soils (Figure SI1); 2) the in-stream model describing the contaminations fate and transformation in the aquatic system (Figure. SI2). The major processes of contaminants delivery from the soil compartment to the in-stream system include: 1) surface runoff containing solid organic carbon (SOC) associated contaminants and dissolved contaminants (in the conditions of infiltration excess and saturation excess); and 2) diffuse runoff from the organic and mineral layers of the soil compartment. The contaminant fluxes were computed by multiplying the contaminant concentrations by the velocity components of the water and organic matter exchange in, between and out of the soil compartment, which were calculated using the equations adopted in the INCA-C and INCA-Sed models.

In INCA-contaminants, the soil is simulated as two vertically stacked boxes which can be conceptualized as a superficial organic layer and an underlying mineral layer (Figure. SI1). The SOC within each box is divided into easily accessible (SOC_{ea}) and potentially accessible (SOC_{pa}) fractions so as to simulate contaminant and SOC pools with different breakdown rates and different degrees of connectivity to soil water. Soil water (including DOC and a

truly dissolved phase) and soil air are included in each of the layers. The fraction of pore space is a model parameter and the relative volumes of air and water are determined dynamically based on soil moisture. The model also allows fixed or time varying contaminant inputs including wet and dry atmospheric deposition, litterfall associated pollutant inputs and accidental spills. All relevant model parameters can vary on a sub-catchment basis and according to soil and land use type. This degree of flexibility in the model allows the process rates, hydrological pathways and the mass of contaminants in soil to vary spatially across a catchment or region. Although the fugacity notation was not used in the mathematical formalism of INCA-contaminants, the diffusive exchange that controls the distribution of contaminants between different phases and soil layers was predicted using the thermodynamic equations derived from the fugacity models (Eq. SI1-SI15, Supporting Information). Contaminant concentrations in each phase of the soil layers were calculated based on the thermodynamic equilibrium partitioning coefficients including Henry's law constant (H), enthalpy of phase transfer between air and water, octanol-water equilibrium partitioning coefficients, enthalpy of phase transfer between water and octanol, and the scaling from octanol-water to SOC-water and DOC-water equilibrium partitioning coefficients.

The in-stream sub-model consists of a series of reaches (or stream segments). Each reach is comprised of a water column and underlying sediments. Within the water column, contaminants can be present in a truly dissolved phase (TPD), associated with DOC, and with an arbitrary number i of suspended solid classes ranked by their size (SUS $_i$). The underlying sediment consists of two vertically stacked layers. Only the upper layer undergoes material exchange with the overlying water column. The depth of the upper sediment layer is dynamically calculated depending on the deposition and erosion of sediment. The sediment exchange processes in the stream system could be dominant affecting the fate of

contaminants in the sediment layers. When deposition becomes the dominant dynamic processes, the contaminants associated with SUSi in the water column would accumulate into the upper sediment layer. In contrast, the contaminants in the lower bed sediment would re-integrate into the upper sediment layer and become available for dynamically enhanced exchange with the water column if erosion of sediment dominates the processes.

Within each sediment compartment, contaminants are present in TDP, DOC-associated and SOC-associated sub-phases (Figure. SI2). In addition to delivery from the surrounding catchment, inputs of contaminants to the in-stream phase include wet or dry atmospheric deposition, possible point sources, and diffusive air-water exchange (Eq. SI20). The influence of wind speed on the air-water exchange is included in the calculations (Eq. SI16-SI20). The reach mass balance of SUSi in the water column includes upstream inputs, entrainment associated with soil, flow erosion of channel bank, bed sediment erosion, downstream advection and settling of suspended sediment. The distribution of contaminants across different phases in the water column is calculated using a similar approach to that used for the computing of the partitioning within the soil compartment. More detailed information of the processes and equations of the INCA-Contaminants model is given in Nizzetto et al. (2016).

2.2 The River Thames Catchment

With a length of 346 km (255 km are non-tidal), the River Thames is the longest river in England and the second longest river in the UK. It officially rises at Thames Head near Cirencester, passes first through relatively rural areas and then through the most urbanised area in the UK including Greater London, which is mostly in the tidal area, and flows into the North Sea. Average flows range from about 1.5m³/s at Cricklade in the upper reaches, to around 29.8 m³/s near the middle of the non-tidal length at Days Weir and 65.8m³/s at its tidal limit at Teddington (see also Figure 2). The River Thames and its tributaries drain a catchment area of approximately 10,000 square kilometres (non-tidal part) in Southern

187 England, with both permeable and impermeable geologies (Crooks and Davies, 2001;
188 Whitehead et al., 1998) (Figure 2). The land cover of the catchment is characterised by
189 significant areas of arable agriculture and pasture throughout the catchment, while the urban
190 areas are mainly located lower in the catchment. Significant forest areas are found mainly in
191 the lower part of the catchment (Table 1).

192 Industrial activities and urbanisation in the catchment have created significant levels of
193 contamination in the Thames system. For example, PCBs remain at levels which may be of
194 environmental and health concern in Thames catchment soils (Vane et al., 2014), sediment
195 and resident fish (Jürgens et al., 2015; Lu et al., 2015).

196 A sampling campaign was conducted in 2013 to characterize sediment concentrations of a
197 range of PCB congeners at multiple depths and sites in the Thames River (Table 2). The
198 sediment samples were extracted in a soxhlet apparatus and cleaned up through a basic silica–
199 acid silica multilayer column followed by a gel permeation chromatography (GPC) column
200 (50/50 hexane/DCM) (Ma et al., 2015). The purified samples were then analysed on a
201 Thermo ‘Trace’ GC-MS. More detailed information about the sediment PCB measurements
202 in the Thames catchment is provided by Lu et al. (not yet published).

203 A level III fugacity model was previously used to estimate contaminant concentrations in fish
204 and sediment. The concentrations of PCBs in Thames fish and sediment were predicted to
205 significantly exceed the U.S. EPA unrestricted consumption advisory thresholds for Σ PCBs
206 (5.9 $\mu\text{g/kg}$) and the Environmental Assessment Criteria for ICES7 PCBs in marine sediment
207 (Lu et al., 2015). However, concentrations of PCBs in sediment were greatly overestimated
208 by the fugacity model when compared to recent measurements for Thames sediments which
209 were 0.16 $\mu\text{g/kg}$ for PCB 52, 0.20 $\mu\text{g/kg}$ for PCB 118, and 1.60 $\mu\text{g/kg}$ for PCB 153 on
210 average (Lu et al., not yet published). Catchment soils could be the most important source of
211 PCBs in the catchment while riverine sediments could be an important reservoir and

secondary source in the river system (Hope, 2008; Lu et al., 2015). With their greatly simplified representations of climate, hydrology and biogeochemical processes, level III fugacity models can only predict general conditions across a region and have limited ability to represent environmental variability. Unsteady state fugacity level IV models have also been developed and applied to explore the seasonal response and dynamic chemical concentrations in the environment (Dalla Valle et al., 2005; Sweetman et al., 2002). However, level IV fugacity models are only suitable to estimate the average contaminant mass and concentrations over a region large enough so that the wind dispersion would not be a dominant chemical removal processes in the catchment.

Associations between riverine PCB concentrations and land use have been reported by Black et al. (2000) and Hope (2008) and concentration changes in relation to river flows have also been suggested (Johnson, 2010; Meharg et al., 2003). In the river system, the fate of PCBs is coupled to the transport of suspended sediments (SS) and dissolved organic carbon (DOC). However, these issues are not typically addressed in fugacity modelling studies, so to better simulate the behaviour of PCBs in the River Thames catchment, the INCA-Contaminants model has been applied in the current study.

2.3. Model set up

To model the behaviour of selected PCB congeners in the River Thames Catchment, the current version of INCA-contaminants (version 1.0) was applied. Simulations were performed for the period of 1st Jan 2009 - 30th Sep 2014. The Thames system was divided into 8 reaches and sub-catchments from Cricklade to its tidal limit at Teddington (Figure 2, Table 1) based on Futter et al. (2014). Four types of land use were used in the INCA-contaminants model: arable, pasture, forest and urban (Table 1). The reach length, sub-catchment area and proportion of land cover in each sub-catchment were derived from previous studies (Futter et al., 2014; Jin et al., 2012) (Table 1). In addition to land use,

underlying geology could also be an important factor influencing the hydrologic response across the catchment (Futter et al., 2014). This is accounted for in the PERSiST (Precipitation, Evapotranspiration and Runoff Simulator for Solute Transport model) simulation which divided the catchment into chalk bedrock, non-chalk bedrock and Quaternary sand, slit and clay (Futter et al., 2014). Suspended grain size could be important in influencing the contaminant transport. In the INCA-contaminants model, five sediment size classes were used representing clay, silt, fine, medium and coarse sand.

The INCA-contaminants application presented here simulates the behaviour of six PCB congeners at eight points along the main stem of the Thames above the tidal limit. The selected congeners are six out of the seven PCBs representing a range of chlorination levels, that are most commonly monitored in the environment (ICES7 PCBs), including: the tri-chlorinated PCB 28, tetra-chlorinated PCB 52, penta-chlorinated PCB 101 and PCB 118 (dioxinlike), hexa-chlorinated PCB 153 and hepta-chlorinated PCB 180. The seventh member of ICES7 PCBs (hexa-chlorinated PCB 138) was not modelled, because the model output was limited to six congeners and PCB 138 was expected to behave similarly to PCB 153. For brevity of presentation, we focus on three PCB congeners (PCB 52, PCB 118 and PCB 153) and give only brief summary information about the others. Wet and dry atmospheric deposition were considered to be the major external inputs of PCBs to the catchment in the INCA-contaminants modelling. Primary sources of PCBs in the catchment were not included because PCBs are no longer used. The input data of the dry and wet deposition for were calculated based on estimates of deposition fluxes from Sweetman and Jones (2000). Initial concentrations of the three PCBs in the soil compartment were estimated according to recent measurements and predictions reported by the Environment Agency (2007), Vane et al. (2014) and Lu et al. (2015). The initial sediment concentrations for the PCBs were estimated with recent measurements at seven sites in the River Thames and its tributaries (samples

analysed in Lancaster University Environment Centre) (Lu et al., not yet published). The physical-chemical properties of the PCB congeners are important in determining the fate of these chemicals in the catchment. The octanol-water partition coefficient (K_{ow}) and half-lives of PCBs in each compartments were taken from the previous fugacity modelling study (Lu et al., 2015; Sinkkonen and Paasivirta, 2000; Sweetman et al., 2002). Other parameters of physical-chemical properties were mainly collected from Schenker et al. (2005).

The application of INCA-contaminants requires an input of daily time series of precipitation, air temperature, hydrologically effective rainfall (HER), soil moisture deficit (SMD) and wind speed as driving data (Crossman et al., 2013). The daily precipitation and temperature data were provided by the UK Met Office. In particular, time series of daily precipitation, minimum daily air temperature and maximum daily air temperature from 1st Jan 2009 to 30th Sep 2014 were obtained for all available meteorological stations within the Thames catchment, and a spatial average over the catchment was computed for all these variables. Mean daily air temperature was computed as the average of minimum and maximum daily values. The time series of wind speed data came from the Meteorological Station at CEH Wallingford. The other two data series (HER and SMD) were generated using the Precipitation, Evapotranspiration and Runoff Simulator for Solute Transport (PERSiST) model. PERSiST is conceptual watershed-scale rainfall-runoff model that is designed primarily to provide input data series to the INCA models (Futter et al., 2014). The water discharge simulated by PERSiST was calibrated against the observed daily flows at different sites of the River Thames by manually adjusting the model parameters within a recommended range. More information about the PERSiST application on the River Thames can be found in (Futter et al., 2014). Measured flows were obtained from the CEH National River Flow Archive. The INCA-Contaminants model was calibrated against a time series of observed water quality data (Table 2). Dissolved organic carbon (DOC) and suspended

sediments (SS) observations were obtained from the CEH Thames Initiative (<http://www.ceh.ac.uk/our-science/projects/river-thames-initiative>) routine sampling (1-2 times a week over the modelled period). Limited PCB measurement data is available for the Thames river system for recent years. To calibrate the modelling results, sediment samples from seven sites of the River Thames and its tributaries have been collected and analysed for PCBs and other organic pollutants in Lancaster University Environmental Centre Laboratory. The sediment samples had been divided into several layers depending on the structure of the samples and data from the uppermost and second layers were used in the modelling. More detailed information on the sediment analysis is provided elsewhere (Lu et al., not yet published)

2.3. Sensitivity analysis

In a complex model like INCA-contaminants, the outputs are controlled/influenced by combinations of hundreds of parameters. To identify the most influential parameters controlling modelled PCB concentrations, we performed a sensitivity analysis based on the methods outlined in Futter et al. (2014). As much as possible, we assessed the sensitivity of similar parameters to those analysed by Lu et al. (2015) (Table 4).

The sensitivity analysis was based on simulated annealing, a “hill climbing” method that attempts to improve model performance through a series of directed jumps. Parameters were sampled from a rectangular prior distribution. Thus, any parameter with a non-rectangular posterior distribution as determined from Kolmogorov-Smirnov statistics was deemed to be sensitive. Posterior parameter distributions were generated by using a Markov chain Monte-Carlo (MCMC) tool to run 50 chains of 100 model runs each. The best performing parameter set from each chain was retained for inclusion in the posterior parameter distribution. The goodness of fit of the predicted time series of river flow, DOC and suspended sediment with observed data was assessed using Nash Sutcliffe statistics (Futter et al., 2014; Nash and

Sutcliffe, 1970; Nizzetto et al., 2016). The model performance for the predictions of PCB concentrations in the river systems was evaluated using a limits-of-acceptability approach (Nizzetto et al., 2016). More information on sensitivity analysis using the MCMC tool is given in Futter et al. (2014) and Nizzetto et al. (2016).

3. Results and Discussion

3.1. Model performance

The PERSiST-INCA modelling for the daily runoff showed a good fit between predicted and measured data, with Nash-Sutcliffe statistics ranged from 0.58 to 0.68 in the eight Thames reaches simulated. The observed and simulated daily time series of river flow for Reach 6 are illustrated in Figure 3 as an example. The model was able to reproduce the pattern in instream DOC and suspended sediment concentrations for reaches where observed data were available (Reach 1, Reach 2, Reach 5 and Reach 6) (Figure 2). For the modelling period, the river flows were at low levels in the summer periods (June to September) and then higher throughout the winter (October to February). The flood at the beginning of 2014 was successfully simulated in the INCA modelling (Fig 2). The extreme flow peaks in early January 2014 could cause the extreme suspended sediment peaks in the river segments, as simulated in the modelling (Figure 3) (Lazar et al., 2010). However, no measurements of the suspended sediment concentrations were available for this period due to the flooding making fieldwork too dangerous.

To assess the model performance for the predictions of PCBs in the Thames system, the simulated upper and lower sediment SOC associated contaminants values obtained using the best set of hydrological and biogeochemical parameters from the sensitivity analysis were compared to the observed values. Measured PCBs values in upper and lower sediment layers

336 were available for three Thames reaches (Reach 3, Reach 5 and Reach 6) (Table 2). There is
337 a big variance within the observed values due to the spatial and geological differences in
338 sampling locations. Model predictions within the minimum and maximum range of the
339 observed data were considered as acceptable, valued as '0' in Table 5. Values outside of the
340 range were described as the ratio of a over b (a/b), where 'b' is the range between the
341 minimum and maximum observed values and 'a' is the distance of the outlier to the closest
342 boundary of the range. The ' a/b ' values above 0 indicated the predictions for PCB
343 contaminations to be over the maximum values of the observed data. The model generated
344 very good predictions for Reach 6 (Figure SI3, Figure SI4, Figure 4), with all the values set to
345 0. There were a few outliers in Reach 3 and Reach 5, but they were close to the boundary of
346 the acceptable range. Only in one case (PCB 52 in lower sediment of Reach 5), the predicted
347 values were a factor of 6-8 higher than the average measured values (Table 5). The model
348 performed better for heavier PCB congeners (Table 5). Given the complexity of the INCA-
349 contaminants modelling, in integrating so many different factors, the simulation for PCB
350 contaminations in the Thames system was deemed as acceptable.

351 The sensitivity analysis showed that model predictions were influenced by PCB physico-
352 chemical properties, simulated atmospheric inputs and parameters related to land-phase
353 sediment mobilisation. (Table 6). Simulations were sensitive to octanol:water partition
354 coefficients and estimated in-soil degradation rates. PCB 153 was the only congener sensitive
355 to simulated atmospheric deposition rates. The sensitivity to groundwater time constants is
356 linked to the effect of that parameter on in-stream suspended sediment dynamics.

357 3.2. The dynamics of PCB concentrations in the River Thames system

358 In the INCA modelling, the predicted bulk water concentrations of the PCBs showed
359 pronounced seasonality. The modelling results for concentrations of PCB 52 (Figure SI3),
360 PCB 118 (Figure SI4), and PCB 153 (Figure 4) in different phases for Reach 6 are presented

as examples. The highest concentrations are simulated during summer low flow periods. Low concentrations are simulated during winter high flow periods, indicating that the water concentrations of PCBs are affected by the dilution of river flow. Through the year, the PCB concentrations in Thames water were estimated to be below 1000 ng/m³ for the majority of the time. This level coincides with detection limits of the Environment Agency monitoring programme. In some extreme low flow conditions, the contaminations in water could be 2-6 fold above the detection limit (Figure 4). The simulated increase in PCB concentrations during summer low flow periods is consistent with observations made in a northern English river (Meharg et al., 2003). They observed a 2-order of magnitude rise in total PCB concentrations during summer. While this increase is much higher than that obtained in our simulations, it does lend credence to the simulated temporal dynamics of riverine PCB concentrations. The model also predicted similar seasonal pattern for upper and lower sediment truly dissolved contaminants, with high levels in summer and low levels in winter. However, the pattern is not as significant as that of the water bulk concentrations. No significant differences were detected in the simulation of concentration dynamics between the studied PCB congeners.

The model predicted the concentrations of the studied PCB congeners in the upper sediment layer of the River Thames (SOC associated) to range from around 10 to 100 µg/kg of OC between early 2009 and late 2013. Afterwards in the winter 2013/2014, sharp increases in the PCB concentrations in the upper sediment were predicted. The rapid increases were most remarkable for the lower sub-catchments (Reach 6, Reach 7, and Reach 8) and heavier PCB congeners. The upper sediment SOC associated concentration for PCB 52 in Reach 6 was modelled to increase 24- fold, while those for PCB 118 and PCB 153 increased 26- fold and 32-fold respectively in winter 2013/2014 (Figures 4, SI3 and SI4). However, this could not be verified with measured data due to lack of observed data concerning the PCBs behaviour in

the period of the sharp increase. Both modelled data and observed flow indicated that extreme flooding has happened in the River Thames Catchment during the winter 2013/2014. Both large increases (Pulkrabová et al., 2008) and decreases (Barber and Writer, 1998) in sediment PCB concentrations have been reported after flooding. The model predictions presented here suggest that large increases in upper sediment PCB concentrations occurred after the severe floods of 2014. This hypothesis of increased concentrations of PCBs in sediment is consistent with what is known about low pre-flood concentrations of bulk sediment PCBs measured in 2013 Lu et al. (not yet published), which are well below the concentrations reported elsewhere in catchment soils (Vane et al., 2014). The extremely high flows during winter 2013/2014 could have mobilized a large amount of contaminated soil within the catchment and deposited it in the river sediment. The high flows during winter 2013/2014 were quite unusual for the Thames (Huntingford et al., 2014). Previous studies found much higher PCB concentrations in urban soils than that in rural soils in England (Environment Agency, 2007; Lu et al., 2015). The lower sub-catchments of Reach 6, 7 and 8 are characterised by urban land use. Moreover, with higher flows in the lower catchments, more contaminated soil would be washed off to the river, thus could lead to remarkable increases in the PCB concentrations. The model also represented a slow change of the PCB concentrations (SOC associated) in the lower sediment layer of the River Thames during the simulation period (Figures 4, SI3 and SI4). It could be a reflection of the long residence time of the pore water in lower bed sediments.

In the Environment Agency river water monitoring records, there have been few reported detections of PCBs in recent years (Lu et al., 2015). However, this could be due to the relatively high detection limits of their methods. There is an inverse relationship between detection limit and analytical cost, with higher costs associated with lower detection limits. Unfortunately, in a time of fiscal austerity, agencies with the responsibility for water quality

monitoring are under increasing pressure to rationalize or cut monitoring. Given the importance of long time series for the sustainable management of water quality in the Thames (Howden et al., 2010), the UK (Battarbee et al., 2014) and elsewhere (Fölster et al., 2014), there is a pressing need to derive the maximum information possible from existing monitoring programs and to ensure their continuity. Given these pressures, it is unlikely that monitoring agencies will be able to devote significant new resources to low level analysis of environmental contaminants .

Models such as INCA-Contaminants can play an important role in maximizing the value of agency monitoring data. The fate and transport of PCBs and other POPs is connected to the cycling of DOC and suspended sediments in rivers and their catchments. Coupling these cycles in modelling frameworks can lead to new insights about the environmental behaviour of POPs and pose new hypotheses about their eventual fate. Using routine agency monitoring data to augment the information obtained during POPs sampling campaigns can reduce the predictive uncertainties about contaminant fate and transport and help to ensure the longevity of monitoring programs by demonstrating their multi-functional nature.

Despite a ban on their production and significant clean-up efforts, PCBs and other legacy POPs remain a problem in the Thames catchment and elsewhere. As atmospheric deposition continues to decline, mobilisation from contaminated soils will become an ever more important vector for POPs transport to the river. This problem is likely to become worse if climate change leads to increased flooding, and may contribute to ongoing contamination of the Thames ecosystem and delay achievement of Water Framework Directive good ecological status. The sensitivity of POPs releases from soils on SOC ageing (as elucidated in recent studies (Nizzetto et al. (2016); (Zheng et al., 2015) is also a factor which deserves further attention.

4. Conclusion

Modelling POPs such as PCBs in natural river systems has always been difficult due to the inherent complexity of contaminant fate pathways, modelling approaches which are more appropriate at a global than a local scale as well as infrequent and expensive monitoring of PCB concentrations in the system. It is well established that the fate of PCBs and other hydrophobic POPs in river systems is closely related to suspended sediment and dissolved organic carbon (DOC) dynamics. By using the more frequent and less expensive DOC and suspended sediment (SS) data available from routine monitoring of the River Thames Catchment as inputs to a novel modelling framework, it has been possible to obtain additional insights into contaminants fate and thus provide more useful information for decision making. The INCA-Contaminants model presented here successfully simulated river flows, suspended sediment and DOC concentrations at multiple points in the river system. Furthermore, unlike an earlier fugacity level III model application (Lu et al., 2015), the INCA-Contaminants model reproduced observed sediment PCB concentrations for a range of congeners at multiple locations in the River Thames. The model predictions of pronounced seasonal cyclical patterns in water concentrations of PCBs were consistent with observations from another contaminated river (Meharg et al., 2003). Most interestingly, model simulations suggested significant, rapid increases in sediment PCB concentrations following the extreme flooding in the winter 2013/2014. This finding should be corroborated with more frequent monitoring of sediment PCB concentrations during and after flooding, but monitoring during high-flow events may not always be safe or practical.

Acknowledgements

The river flow data and the wind speed data were provided by the CEH Wallingford. The authors would also like to thank Mike Bowes for the DOC and suspended sediment data. The lead author is grateful to Karl Davis and Wolfson College (Oxford) for providing the Steward Award to support the academic visit to Swedish University of Agricultural Science (SLU). MNF was supported by the Swedish Research Council, FORMAS.

References

- Barber L.B., Writer J.H. Impact of the 1993 flood on the distribution of organic contaminants in bed sediments of the upper Mississippi River. *Environmental science & technology* 1998; 32: 2077-2083.
- Battarbee R.W., Shilland E.M., Kernan M., Monteith D.T., Curtis C.J. Recovery of acidified surface waters from acidification in the United Kingdom after twenty years of chemical and biological monitoring (1988–2008). *Ecological Indicators* 2014; 37: 267-273.
- Black R.W., Hagglund A.L., Voss F.D. Predicting the probability of detecting organochlorine pesticides and polychlorinated biphenyls in stream systems on the basis of land use in the Pacific Northwest, USA. *Environmental Toxicology and Chemistry* 2000; 19: 1044-1054.
- Crooks S., Davies H. Assessment of land use change in the Thames catchment and its effect on the flood regime of the river. *Physics and Chemistry of the Earth, Part B: Hydrology, Oceans and Atmosphere* 2001; 26: 583-591.
- Crossman J., Whitehead P.G., Fitter 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., 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.
- Eggleton J., Thomas K.V. A review of factors affecting the release and bioavailability of contaminants during sediment disturbance events. *Environment international* 2004; 30: 973-980.
- Environment Agency. 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.

- Evans H.E. The binding of three PCB congeners to dissolved organic carbon in freshwaters. *Chemosphere* 1988; 17: 2325-2338.
- Fölster J., Johnson R.K., Futter M.N., Wilander A. The Swedish monitoring of surface waters: 50 years of adaptive monitoring. *Ambio* 2014; 43: 3-18.
- Futter M., Butterfield D., Cosby B., Dillon P., Wade A., Whitehead P. Modeling the mechanisms that control in - stream dissolved organic carbon dynamics in upland and forested catchments. *Water Resources Research* 2007a; 43.
- Futter M., Erlandsson M., Butterfield D., Whitehead P., Oni S., Wade A. PERSiST: a flexible rainfall-runoff modelling toolkit for use with the INCA family of models. *Hydrology and Earth System Sciences* 2014; 18: 855-873.
- Futter M.N., Butterfield D., Cosby B.J., Dillon P.J., Wade A.J., Whitehead P.G. Modeling the mechanisms that control in-stream dissolved organic carbon dynamics in upland and forested catchments. *Water Resources Research* 2007b; 43.
- 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.
- Howden N., Burt T., Worrall F., Whelan M., Bierozza M. Nitrate concentrations and fluxes in the River Thames over 140 years (1868–2008): are increases irreversible? *Hydrological Processes* 2010; 24: 2657-2662.
- Hung C.-C., Gong G.-C., Ko F.-C., Chen H.-Y., Hsu M.-L., Wu J.-M., et al. Relationships between persistent organic pollutants and carbonaceous materials in aquatic sediments of Taiwan. *Marine pollution bulletin* 2010; 60: 1010-1017.
- Huntingford C., Marsh T., Scaife A.A., Kendon E.J., Hannaford J., Kay A.L., et al. Potential influences on the United Kingdom's floods of winter 2013/14. *Nature Climate Change* 2014; 4: 769-777.
- Jin L., Whitehead P.G., Baulch H.M., Dillon P.J., Butterfield D.A., Oni S.K., et al. Modelling phosphorus in Lake Simcoe and its subcatchments: scenario analysis to assess alternative management strategies. *Inland Waters* 2013; 3: 207-220.
- 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.
- 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.
- Josefsson S., Karlsson O.M., Malmaeus J.M., Cornelissen G., Wiberg K. Structure-related distribution of PCDD/Fs, PCBs and HCB in a river–sea system. *Chemosphere* 2011; 83: 85-94.
- 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.
- Lazar A.N., Butterfield D., Futter M.N., Rankinen K., Thouvenot-Korppoo M., Jarritt N., et al. An assessment of the fine sediment dynamics in an upland river system: INCA-Sed modifications and implications for fisheries. *Science of the total environment* 2010; 408: 2555-2566.

- Lohmann R., Breivik K., Dachs J., Muir D. Global fate of POPs: Current and future research directions. *Environmental Pollution* 2007; 150: 150-165.
- Lu Q., Johnson A.C., Jürgens M.D., Sweetman A., Jin L., Whitehead P. The distribution of Polychlorinated Biphenyls (PCBs) in the River Thames Catchment under the scenarios of climate change. *Science of The Total Environment* 2015; 533: 187-195.
- Lu Q., Jürgens M.D., Johnson A.C., Graf C., Sweetman A., Crosse J., et al. The Current Occurrence of Organic Chemicals in Thames Fish and Sediment. not yet published.
- Ma Y., Halsall C.J., Crosse J.D., Graf C., Cai M., He J., et al. Persistent organic pollutants in ocean sediments from the North Pacific to the Arctic Ocean. *Journal of Geophysical Research: Oceans* 2015; 120: 2723-2735.
- Meharg A.A., Wright J., Leeks G.J., Wass P.D., Owens P.N., Walling D.E., et al. PCB congener dynamics in a heavily industrialized river catchment. *Science of the total environment* 2003; 314: 439-450.
- Nash J., Sutcliffe J.V. River flow forecasting through conceptual models part I—A discussion of principles. *Journal of hydrology* 1970; 10: 282-290.
- Nizzetto L., Butterfield D., Futter M.N., Lin Y., Allan I., Larssen T. Assessment of contaminant fate in catchments using a novel integrated hydrobiogeochemical-multimedia fate model. *Science of the Total Environment*, accepted 2016.
- Nizzetto L., Macleod M., Borga K., Cabrerizo A., Dachs J., Di Guardo A., et al. Past, Present, and Future Controls on Levels of Persistent Organic Pollutants in the Global Environment. *Environmental Science & Technology* 2010; 44: 6526-6531.
- Pulkrabová J., Suchanová M., Tomaniová M., Kocourek V., Hajšlová J. Organic pollutants in areas impacted by flooding in 2002: A 4-year survey. *Bulletin of environmental contamination and toxicology* 2008; 81: 299-304.
- Ross G. The public health implications of polychlorinated biphenyls (PCBs) in the environment. *Ecotoxicology and environmental safety* 2004; 59: 275-291.
- Schenker U., MacLeod M., Scheringer M., Hungerbühler K. Improving data quality for environmental fate models: A least-squares adjustment procedure for harmonizing physicochemical properties of organic compounds. *Environmental science & technology* 2005; 39: 8434-8441.
- 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.
- Sinkkonen S., Paasivirta J. Degradation half-life times of PCDDs, PCDFs and PCBs for environmental fate modeling. *Chemosphere* 2000; 40: 943-949.
- 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.
- Sweetman A.J., Jones K.C. Declining PCB concentrations in the UK atmosphere: Evidence and possible causes. *Environmental Science & Technology* 2000; 34: 863-869.
- Urbaniak M. Polychlorinated biphenyls: sources, distribution and transformation in the environment—a literature review. *Acta Toxicologica* 2007; 15: 83-93.

- 580 Vane C.H., Kim A.W., Beriro D.J., Cave M.R., Knights K., Moss-Hayes V., et al. Polycyclic
581 aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) in urban soils of
582 Greater London, UK. *Applied Geochemistry* 2014; 51: 303-314.
- 583 Whitehead P.G., Wilson E.J., Butterfield D. A semi-distributed Integrated Nitrogen model for
584 multiple source assessment in Catchments (INCA): Part I - Model structure and
585 process equations. *Science of the Total Environment* 1998; 210-211: 547-558.
- 586 Zheng Q., Nizzetto L., Liu X., Borga K., Starrfelt J., Li J., et al. Elevated Mobility of
587 Persistent Organic Pollutants in the Soil of a Tropical Rainforest. *Environmental*
588 *Science & Technology* 2015; 49: 4302-4309.

Table Captions List:

- Table 1. Sub-catchment information of the Thames system (according to LCM2000 land coverage map (CEH), see also Figure. 2 for a map of the sub-catchments)
- Table 2. Numbers of observed values available for sub-catchments of the River Thames
- Table 3. Data sources for the INCA-contaminants modelling
- Table 4. Model parameter values (min-max)
- Table 5. The model performance for predictions of upper and lower sediment SOC associated PCB concentrations based on initial manual calibration
- Table 6. Summary of sensitive parameters from the Monte Carlo analysis

600

List of Figure Captions

Figure 1. Conceptual figure showing the relationship between (i) different data sources useful for understanding POPs fate in the environment and (ii) multi-media fate and hydrobiogeochemical modelling frameworks. –POPs samples are typically expensive and infrequent. The additional information in water quality (WQ) and hydrometeorological (PTQ: precipitation, temperature and flow) time series can augment and contextualize the information in POPs measurements, thereby reducing the uncertainties in POPs fate and transport estimates. Fugacity models require less information inputs and mainly focus on POPs data, but employ highly simplified representation of environmental parameters and have high uncertainties; INCA models make use of POPs data as well as the more frequent and less expensive WQ and flow PTQ data, thus it is possible to obtain additional insights and reduce uncertainty.

Figure 2. Map of the River Thames Catchment showing the points where flow, water chemistry and sediment PCB concentrations were simulated.

Figure 3. (a) Observed and simulated flow for reach 6 (Caversham - Shepperton); (b) Observed and simulated suspended sediment data for reach 6; (c) Observed and simulated DOC data for reach 2 (Pinkhill - Osney).

Figure 4. The simulated dynamics concentrations of PCB 153 in water column, upper sediment and lower sediment layers for Reach 6.

Table Captions List:

Table 1. Subcatchment information of the Thames system (according to LCM2000 land coverage map (CEH), see also Figure. 2 for a map of the subcatchments)

Table 2. Numbers of observed values available for subcatchments of the River Thames

Table 3. Data sources for the INCA-contaminants modelling

Table 4. Model parameter values (min-max)

Table 5. The model performance for predictions of upper and lower sediment SOC associated PCB concentrations based on initial manual calibration

Table 6. Summary of sensitive parameters from the Monte Carlo analysis

Table 1. Subcatchment information of the Thames system (according to LCM2000 land coverage map (CEH), see also Figure. 2 for a map of the sub-catchments)

No.	Reach Name	Length (km)	Area (km ²)	Land use %			
				Arable	Pasture	Forest	Urban
1	Cricklade to Pinkhill	54.1	1609	74.4	16.5	2.8	6.3
2	Pinkhill to Osney	12.4	526	60.3	16.3	5.0	18.5
3	Osney to Culham	19.0	1288	72.5	15.3	2.2	10.0
4	Culham to Days Weir	9.30	58	78.9	0.0	2.8	18.3
5	Days Weir to Caversham	35.2	1154	72.9	10.3	8.2	8.6
6	Caversham to Shepperton	70.4	3632	44.0	12.2	15.1	28.7
7	Shepperton to Molesey	9.54	1102	38.9	13.1	25.3	22.7
8	Molesey to Teddington	7.74	589	30.6	15.4	17.7	36.3

Table 2. Numbers of observed values available for sub-catchments of the River Thames

No.	Reach Name	Flow	SS	DOC	PCBs (upper sediment + lower sediment)					
					28	52	101	118	153	180
1	Cricklade Castle to Pinkhill	2098	147	173						
2	Pinkhill to Osney	2098	172	146						
3	Osney to Culham	2098			4+5	4+5	4+5	4+5	4+5	4+5
4	Culham to Days Weir	2098								
5	Days Weir to Caversham	2098	174	147	2+2	2+2	2+2	2+2	2+2	2+2
6	Caversham to Shepperton	2098	173	147	6+6	6+6	6+6	6+6	6+6	6+6
7	Shepperton to Molesey	2098								
8	Molesey to Teddington	2098								

Table 3. Data sources for the INCA-contaminants modelling

Parameters	Description	Sources
<i>Hydrological inputs:</i>		
Precipitation and air temperature	Daily time series	Met Office
SMD and HER	Daily time series	PERSiST model derived
Wind Speed	Daily time series	Meteorological Station at CEH Wallingford
<i>Hydrological properties:</i>		
Base flow index	Measurements for flow rating derived from each flow gauge and extrapolated to other tributaries	Environment Agency and Thames Water
Land use data	Ecological land classification and land use classifications GIS layer	LCM2000 land coverage map (CEH);
Reach and subcatchments boundaries	Used the same 8 subcatchments that were defined by Futter, Erlandsson et al. (2014) in the PERSiST application	Delineated based on the location of flow measuring stations (Futter, Erlandsson et al. 2014)
Residence time	Measurements for groundwater residence time for each sub-catchment	Calculated from hydrological response curves (Crossman, Whitehead et al. 2013)
<i>Physical-chemical properties and contaminants (PCBs) Inputs:</i>		
Half-lives and K _{ow}	The octanol-water partition coefficient and the degradation of PCBs in different media	Taken from Lu, Johnson et al. (2015)
ΔU_{AW} (kJ/mol) ΔU_{OW} (kJ/mol)	Enthalpy of phase transfer between air and water, Enthalpy of phase transfer between water and octanol	Taken from Schenker, MacLeod et al. (2005)
Advection inputs to the whole catchment	Atmospheric dry and wet depositions	Calculated using the deposition fluxes estimated by Sweetman and Jones (2000) for the UK atmosphere
<i>Observed data:</i>		
Flow data	Daily time series	CEH National River Flow Archive.
Suspended sediment and DOC	Routine sampling (4-7 times per month)	Water Quality data from CEH Thames Initiative
Upper and lower sediment layer SOC-associated contaminant (OC normalised)		Sediment samples were collected from 7 sites in the River Thames and its tributaries and analysed for PCBs at Lancaster University Environmental Centre

Table 4. Model parameter values (min-max)

	Parameters	Min	Max	Unit
Landscape:	Thermal conductivity of soil	0.1	5	-
	Direct runoff residence time	0.8	1.2	days
	Organic layer residence time	2.4	3.6	days
	Mineral layer residence time	8	12	days
Instream:	Time to equilibrate	0.005	0.7	1/days
Subcatchment:	Groundwater residence time	20	30	days
	Scalingfactor (a4)	0.7	10	kg/m ²
	Non-linear coefficient (a6)	0.7	0.9	-
Reach:	Scaling factor (a7)	8E-05	1	-
	Scaling factor (a8)	2E-07	1E-04	s ² /kg
	Scaling factor (a9)	3.0E-10	1.0E-7	kg/m ² /m ³
	Non-linear coefficient (a10)	0.01	1.2	-
Contaminations:				
PCB 52	Henry's law constant	13.6	54.4	Pa m ³ /mol
	Koc	4.5E+05	1.8E+06	-
	Degradation half-life (water column)	598	2392	days
	Degradation half-life (sediment)	1750	7000	days
	Atmospheric dry particle deposition	2.0E+05	2.0E+07	ng/day/km ²
PCB 118	Atmospheric wet deposition	2.0E+05	2.0E+07	ng/day/km ²
	Henry's law constant	5.4	21.6	Pa m ³ /mol
	Koc	2.2E+06	8.9E+06	-
	Degradation half-life (water column)	1250	5000	days
	Degradation half-life (sediment)	1825	7300	days
PCB 153	Atmospheric dry particle deposition	2.0E+05	2.0E+07	ng/day/km ²
	Atmospheric wet deposition	2.0E+05	2.0E+07	ng/day/km ²
	Henry's law constant	9.2	36.8	Pa m ³ /mol
	Koc	3.6E+06	1.4E+07	-
	Degradation half-life (water column)	2395	9584	days
	Degradation half-life (sediment)	3292	13166	days
	Atmospheric dry particle deposition	2.0E+05	2.0E+07	ng/day/km ²
	Atmospheric wet deposition	2.0E+05	2.0E+07	ng/day/km ²

Table 5. The model performance for predictions of upper and lower sediment SOC associated PCB concentrations based on initial manual calibration

	Reach 3		Reach 5		Reach 6	
	Upper sediment	Lower sediment	Upper sediment	Lower sediment	Upper sediment	Lower sediment
PCB 28	0	0	2/1	0	0	0
PCB 52	3/4	0	3/1	100/1	0	0
PCB 101	0	0	0	0	0	0
PCB 118	1/6	0	1/2	5/1	0	0
PCB 153	0	0	0	0	0	0
PCB 180	0	0	0	0	0	0

* 0 – predicts within the range of the min and max observed values; a/b: the ratio of a over b, ‘b’ is the range between the minimum and maximum observed values and ‘a’ is the distance of the outlier to the closest boundary of the range.

Table 6. Summary of sensitive parameters from the Monte Carlo analysis

Name	Land Cover	Reach	Contaminant	P
Octanol Water Partition Coefficient			PCB 101	0.04
Atmospheric Dry Deposition	Arable		PCB 153	0.05
Atmospheric Dry Deposition	Grassland		PCB 153	0.03
Atmospheric Dry Deposition	Urban		PCB 153	0.10
Sediment Transport Capacity Scaling Factor		2		0.01
Sediment Transport Capacity Scaling Factor		3		0.03
Sediment Transport Nonlinear Coefficient		3		0.09
Sediment Transport Capacity Scaling Factor		4		0.05
Sediment Transport Capacity Scaling Factor		5		0.06
Sediment Transport Nonlinear Coefficient		5		0.02
Groundwater Time Constant		5		0.09
Organic Layer Easily Accessible Degradation Half Life		6	PCB 153	0.10
Organic Layer Potentially Accessible Half Life		8	PCB 52	0.06

Figure 1
[Click here to download high resolution image](#)

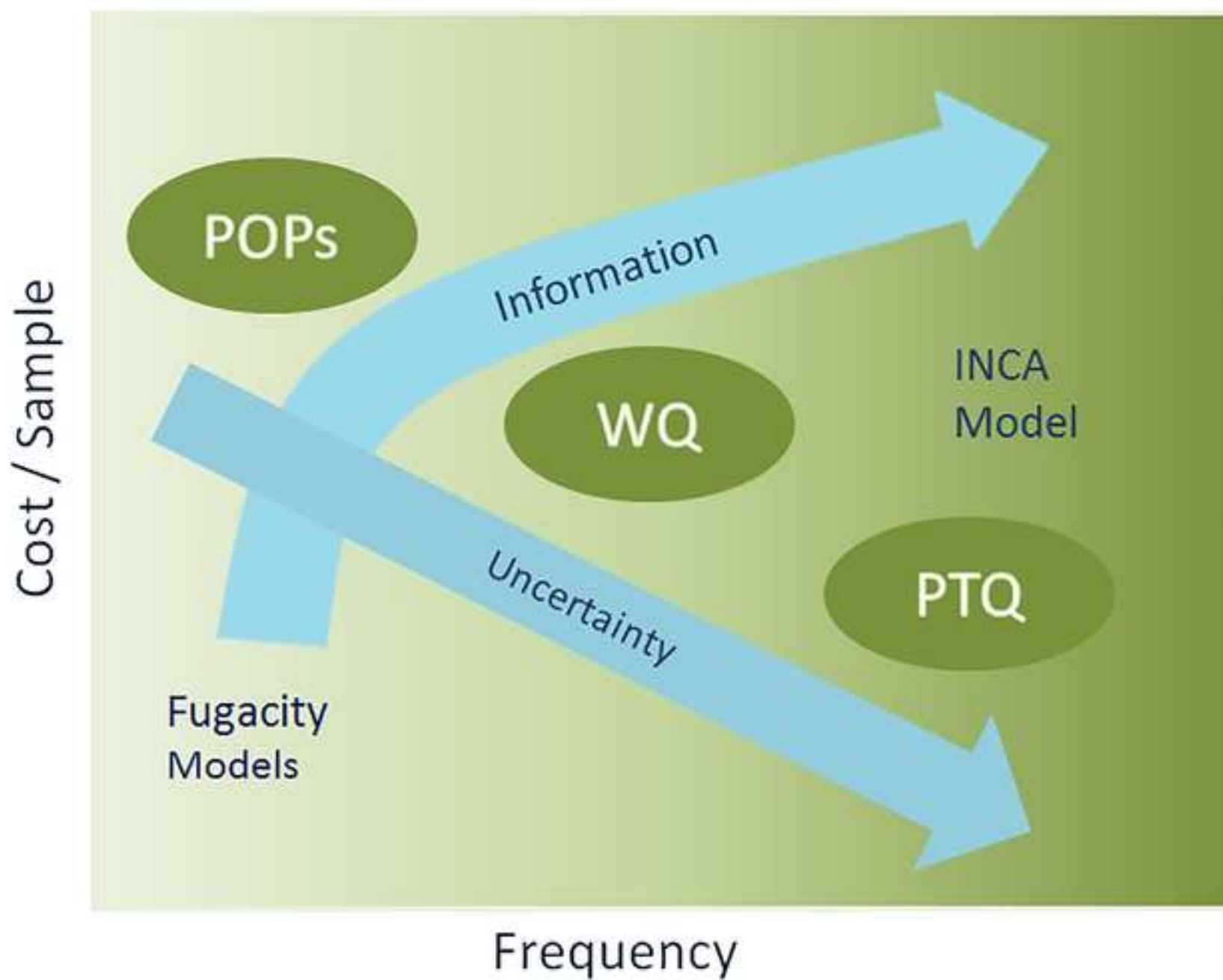


Figure 2
[Click here to download high resolution image](#)

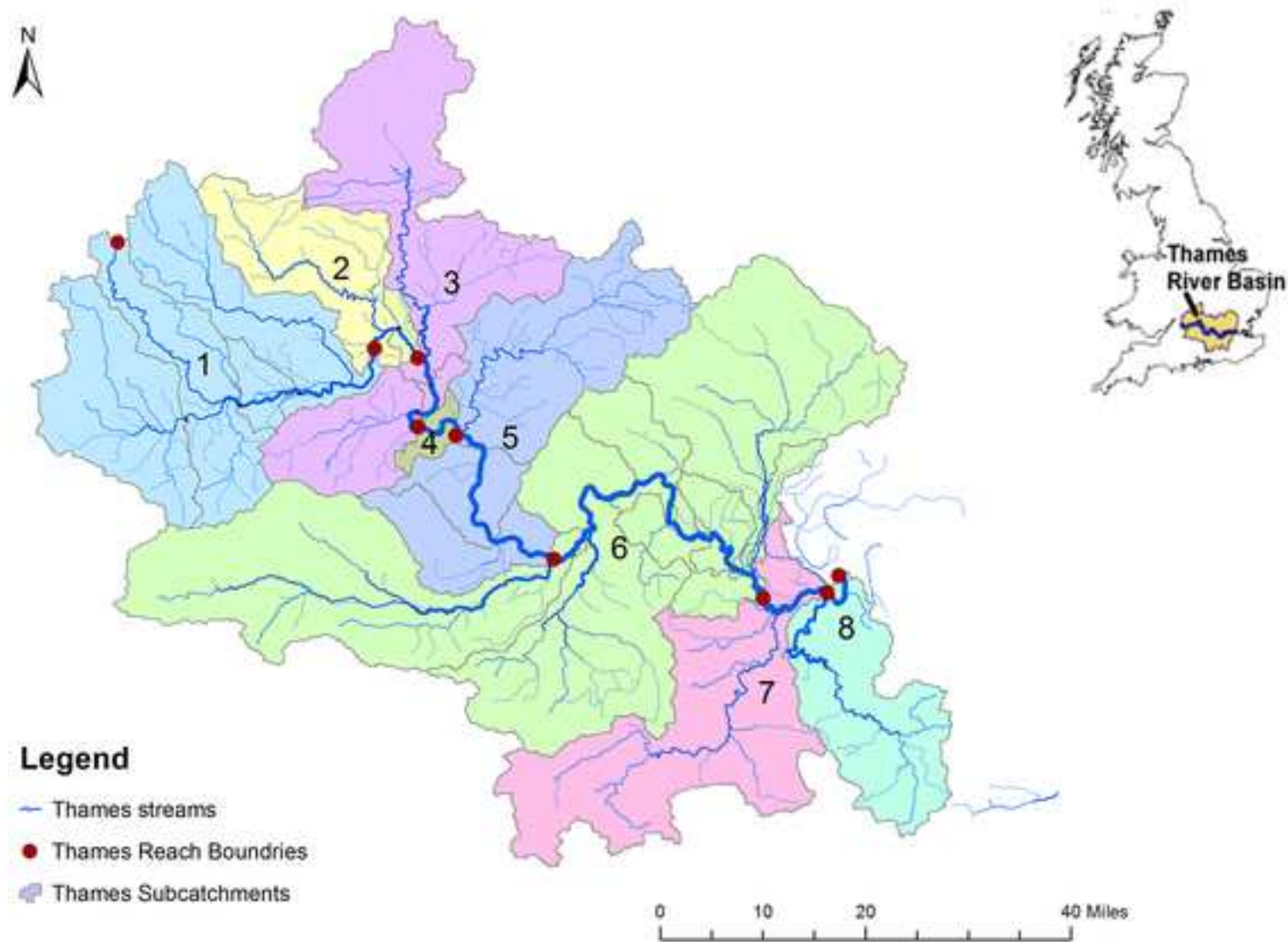


Figure 3
[Click here to download high resolution image](#)

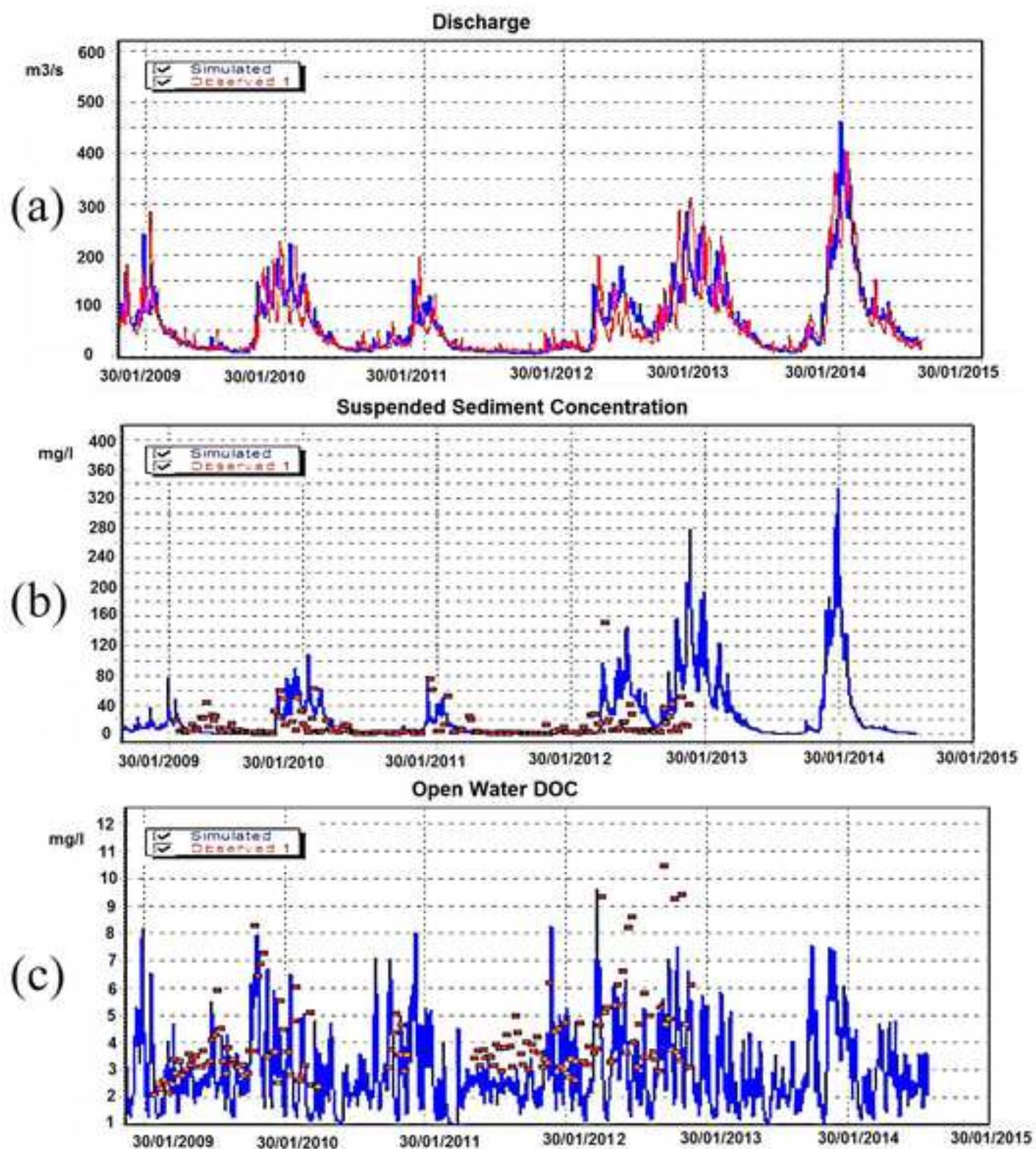


Figure 4
[Click here to download high resolution image](#)

