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

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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 insights 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 (The Integrated Catchment (INCA) Contaminants model) 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 much 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 important 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.

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

38

39 **Acronyms**

40 POPs – Persistent Organic Pollutants

41 PCBs – Polychlorinated Biphenyl

42 DOC – Dissolved Organic Carbon

43 WQ – Water Quality

44 PTQ – Precipitation, Temperature, Flow

45 INCA – the Integrated Catchment model

46 INCA-C – the Integrated Catchment Carbon model

47 INCA-Sed – the Integrated Catchment Sediment model

48 SOC – Solid Organic Carbon

49 SOC_{ea} – Solid Organic Carbon easily accessible fraction

50 SOC_{pa} – Solid Organic Carbon potentially accessible fraction

51 H – Henry's law constant

52 TPD – Truly Dissolved Phase

53 SUS_i – arbitrary number i of Suspended Solid classes ranked by their Size

54 PERSiST – Precipitation, Evapotranspiration and Runoff Simulator for Solute Transport model

55 K_{ow} – The octanol – water partition coefficient

56 HER – Hydrologically effective Rainfall

57 SMD – Soil Moisture Deficit

58 CEH – Centre for Ecology and Hydrology

59 SS – Suspended Sediments

60 GPC – Gel Permeation Chromatography

61 GC-MS – Gas Chromatography - Mass Spectrometry

62 MCMC – Markov Chain - Monte Carlo tool

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 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 great 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 the early 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, contaminated soil, and direct atmospheric inputs or spills from old PCB-containing equipment. Atmospheric PCB concentrations have strongly declined throughout the UK in recent years (Schuster et al., 2010). This decline in concentration should cause 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 high cost. 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). It is well accepted that the more frequent and less expensive routine water quality and hydrometeorological observations can be used as environmental proxies to provide additional information about POPs fate and transport (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 these routine water quality and hydrometeorological time series can provide additional insights into POPs fate and transport (Figure 1). The cost per sample for POPs analysis (Figure 1; vertical axis) is much higher than costs for water quality (WQ) or hydrometeorological measurements of precipitation, temperature or flow (PTQ). The big difference in sample costs is one reason that POPs measurements are much less frequent than routine water quality measurements (WQ) which are often collected monthly at multiple sites across 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 (the Integrated Catchment model for Contaminants) make use of POPs samples, water quality measurements

113 and hydrometeorological observations to deliver an integrated and intrinsically consistent
114 representation of the system dynamics. Using such complementary environmental data can
115 increase the available information while simultaneously reducing uncertainty in POPs fate
116 and transport estimates.

117 Here, the River Thames catchment (Southern England) has been used as the study area. The
118 legacy of industrial activities and urbanisation has resulted in high levels of contamination in
119 the catchment. For example, PCBs remain at levels which may be of environmental and
120 health concern in the catchment soils (Vane et al., 2014), sediment and resident fish (Jürgens
121 et al., 2015; Lu et al., 2015). A level III fugacity model was previously used to estimate
122 contaminant concentrations in fish and sediment, which predicted the concentrations of PCBs
123 in Thames fish to exceed the U.S. EPA unrestricted consumption advisory thresholds for
124 Σ PCBs (5.9 $\mu\text{g/kg}$) and the sediment concentrations to exceed the Environmental Assessment
125 Criteria for ICES7 PCBs in marine sediment (Lu et al., 2015). However, concentrations of
126 PCBs in sediment were greatly overestimated by the fugacity model when compared to recent
127 measurements for Thames sediments which were 0.17 $\mu\text{g/kg}$ for PCB 52, 0.20 $\mu\text{g/kg}$ for PCB
128 118, and 1.70 $\mu\text{g/kg}$ for PCB 153 on average (Lu et al, in preparation - see supporting
129 information). Catchment soils could be the most important current source of PCBs in the
130 catchment while riverine sediments could be an important reservoir and secondary source in
131 the river system (Hope, 2008; Lu et al., 2015). With their greatly simplified representations of
132 climate, hydrology and biogeochemical processes, level III fugacity models can only predict
133 general conditions across a region and have limited ability to represent environmental
134 variability. Unsteady state fugacity level IV models have also been developed and applied to
135 explore the seasonal response and dynamic chemical concentrations in the environment
136 (Dalla Valle et al., 2005; Sweetman et al., 2002). However, level IV fugacity models are only
137 suitable to estimate the average contaminant mass and concentrations over a region large

138 enough so that the wind dispersion would not be a dominant chemical removal processes in
139 the catchment.

140 In the River Thames catchment, there were few recent measurements available for PCBs.
141 However, routine measurements for suspended sediments and dissolved organic carbon
142 throughout the river network and daily river flow measurements at multiple sites were
143 available. To better simulate the behaviour of PCBs in the River Thames catchment, the
144 newly developed INCA-Contaminants model has been applied. The major aim of the study
145 was: 1) to link hydrobiogeochemical cycles to PCB dynamics, specifically between
146 landscapes and riverscapes; 2) to better understand the impact of short-term weather
147 variations on PCB mobilisation and transport in the catchment; 3) to identify sensitive
148 parameters in the modelling exercise.

150 **2. Materials and Methods**

151 **2.1 The River Thames Catchment**

152 With a length of 346 km (255 km are non-tidal), the River Thames is the longest river in
153 England and the second longest river in the UK. It officially rises at Thames Head near
154 Cirencester, passes first through relatively rural areas and then through the most urbanised
155 area in the UK including Greater London, which is in the tidal area, and flows into the North
156 Sea. Average flows range from about 1.5m³/s at Cricklade in the upper reaches, to around
157 29.8 m³/s near the middle of the non-tidal length at Days Weir and 65.8m³/s at its tidal limit
158 at Teddington (see Figure 2). The River Thames and its tributaries drain a catchment area of
159 approximately 10,000 square kilometres (non-tidal part) in Southern England, with both
160 permeable and impermeable geologies (Crooks and Davies, 2001; Whitehead et al., 1998)
161 (Figure 2). The land cover of the catchment is characterised by arable agriculture and pasture

162 throughout the catchment, while the urban areas are mainly located lower in the catchment.

163 Forests are found mainly in the lower part of the catchment (Table 1).

165 2.2 The INCA-Contaminations Model

166 The Integrated Catchment model (INCA) was developed by Whitehead et al. (1998) to
167 simulate the day to day series of flow pathways and to track nitrogen (N) dynamics in both
168 the land and instream phase in the catchment. The model is process-based and is both
169 vertically integrated, tracking the dynamic inputs from both diffuse sources and discrete
170 points, and horizontally integrated, addressing spatial variations (e.g. land cover, underlying
171 geology, hydrology, sediment production) through the catchment. Since the original version,
172 which modelled nitrogen concentrations, the model has been in continuous development and
173 there is currently a suite of INCA models for carbon, sediment, chloride, metals,
174 mercury,phosphorus and pathogens (Crossman et al., 2013; Futter et al., 2007; Jin et al., 2013;
175 Lazar et al., 2010; Whitehead et al., 2016) which have been applied to approximately 100
176 catchments in Europe, North America, Asia and South America.

177 The INCA-contaminants model used here is the newest member of the INCA family
178 (Nizzetto et al., 2016) and was developed based on two extensively tested INCA models: the
179 carbon model INCA-C (Futter et al., 2007) and the sediment model INCA-Sed (Lazar et al.,
180 2010). INCA-C produces daily estimates of organic matter mass balance in multi-branched
181 catchment, while the INCA-Sed simulates sediment production and delivery from land to the
182 in-stream system and subsequent transport, deposition and remobilisation in the stream. All
183 processes are forced by daily input time series of precipitation, hydrologically effective
184 rainfall (the part of total precipitation that contributes to runoff), soil moisture deficit and air
185 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 SI 1); 2) the in-stream model describing the contaminations fate and transformation in the aquatic system (Figure. SI 2). 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 (derived from 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 represented as two vertically stacked boxes, which can be conceptualised as a superficial organic layer and an underlying mineral layer (Figure. SI 1). The SOC within each box is divided into easily accessible (SOC_{ea}) and potentially accessible (SOC_{pa}) fractions 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

211 pathways and the mass of contaminants in soil to vary spatially across a catchment or region.

212 Although the fugacity notation was not used in the mathematical formalism of INCA-
213 contaminants, the diffusive exchange that controls the distribution of contaminants between
214 different phases and soil layers was predicted using the thermodynamic equations derived
215 from the fugacity models (Eq. SI 1-SI 15, Supporting Information). Contaminant
216 concentrations in each phase of the soil layers were calculated based on the thermodynamic
217 equilibrium partitioning coefficients including Henry's law constant (H), enthalpy of phase
218 transfer between air and water, octanol-water equilibrium partitioning coefficients, enthalpy
219 of phase transfer between water and octanol, and the scaling from octanol-water to SOC-
220 water and DOC-water equilibrium partitioning coefficients.

221 The in-stream sub-model consists of a series of reaches (or stream segments). Each reach is
222 comprised of a water column and underlying sediments. Within the water column,
223 contaminants can be present in a truly dissolved phase (TPD), associated with DOC, and with
224 an arbitrary number i of suspended solid classes ranked by their size (SUS i). The underlying
225 sediment consists of two vertically stacked layers. Only the upper layer undergoes material
226 exchange with the overlying water column. The depth of the upper sediment layer is
227 dynamically calculated depending on the deposition and erosion of sediment. The sediment
228 exchange processes in the stream system could be dominant affecting the fate of
229 contaminants in the sediment layers. When deposition becomes the dominant dynamic
230 processes, the contaminants associated with SUS i in the water column would accumulate into
231 the upper sediment layer. In contrast, the contaminants in the lower bed sediment would re-
232 integrate into the upper sediment layer and become available for dynamically enhanced
233 exchange with the water column if erosion of sediment dominates the processes.

234 Within each sediment compartment, contaminants are present in TDP, DOC-associated and
235 SOC-associated sub-phases (Figure. SI 2). 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. SI 20). The influence of wind speed on the air-water exchange is included in the calculations (Eq. SI 16-SI 20). The reach mass balance of SUSi in the water column includes upstream inputs, entrainment associated with soil, flow erosion of the 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).

2.3. 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). 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. 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. The input data of the dry and wet deposition were calculated based on estimates of deposition fluxes from Sweetman and Jones (2000). Primary sources of PCBs in the catchment were not included because PCBs are no longer used. 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 at the Lancaster University Environment Centre) (Lu et al., in preparations, see supporting information). 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 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 simulation which divided the catchment into chalk bedrock, non-chalk bedrock and Quaternary sand, slit and clay (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 (<http://nrfa.ceh.ac.uk>). The INCA-Contaminants model was calibrated against a time series of observed water quality data. The number of available data points for each of the sub-catchments is summarized in 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), which covered four of the eight sub-catchments (Reach 1, Reach 2, Reach 5 and Reach 6) (Table 2). Limited PCB measurement data was available for the Thames river system for recent years. A sampling campaign was conducted in 2013 to characterize sediment concentrations of a range

of PCB congeners at multiple depths and sites in the Thames River (see supporting information). The samples were analysed in the Lancaster University Environmental Centre Laboratory. The sediment samples were extracted in a soxhlet apparatus and cleaned up through a basic silica–acid silica multilayer column followed by a gel permeation chromatography (GPC) column (50/50 hexane/DCM) (Ma et al., 2015). The purified samples were then analysed on a Thermo ‘Trace’ GC-MS. The method and results will be published in detail in a companion paper. To evaluate the model performance, the modelled values for PCBs in the sediment were compared to the measured sediment concentrations.

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 ranging 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 (Figure 3). 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 particular 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 concentrations, 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 were available for three Thames reaches (Reach 3, Reach 5 and Reach 6) (Table 2). There is a large variance within the observed values due to the spatial and geological differences in sampling locations. Model predictions within the minimum and maximum range of the observed data were considered as acceptable, valued as '0' in Table 5. Values outside of the range were described as the ratio of a over b (a/b), where '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. The 'a/b' values above 0 indicated the predictions for PCB contaminations to be over the maximum values of the observed data. The model generated very good predictions for Reach 6 (Figure SI 3, Figure SI 4, Figure 4), with all the values set to 0. There were a few outliers in Reach 3 and Reach 5, but they were close to the boundary of the acceptable range. Only in one case (PCB 52 in lower sediment of Reach 5), the predicted values were a factor of 6-8 higher than the average measured values (Table 5). The model performed better for heavier PCB congeners (Table 5). Given the complexity of the INCA-contaminants modelling, in integrating so many different factors, the simulation for PCB contaminations in the Thames system was deemed acceptable.

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

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

In the INCA modelling, the predicted bulk water concentrations of the PCBs showed pronounced seasonality. The modelling results for concentrations of PCB 52 (Figure SI 3), PCB 118 (Figure SI 4), 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. For the majority of the time, the PCB concentrations in Thames water were estimated to be below the Environment Agency monitoring programme detection limit of 1000 ng/m³ (<http://www.geostore.com/environment-agency/>). In some extreme low flow conditions, the contaminations in water could be 2- to 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), where a 2-order of magnitude rise in total PCB concentrations was observed 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 clear as that of the water bulk concentrations. There was little difference between the studied PCB congeners in the simulation of concentration dynamics.

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, SI 3 and SI 4). 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 (see supporting information), 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, SI 3 and SI 4). 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 the analytical method used by the Environment Agency. 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 is also a factor, which deserves further attention.

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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 both to suspended sediment and dissolved organic carbon (DOC) dynamics and to hydrologic variation. By using the more frequent and less expensive DOC and suspended sediment (SS) data available from routine monitoring of the River Thames Catchment as well as long term river flow records 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 large, rapid increases in sediment PCB concentrations following the extreme flooding in the winter 2013/2014. Targeting limited resources to monitoring during and after high-flow events would be very beneficial to corroborate the findings and improve our understating of processes, but this may not always be possible, because monitoring during high-flow events can be difficult, impractical or dangerous.

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

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 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

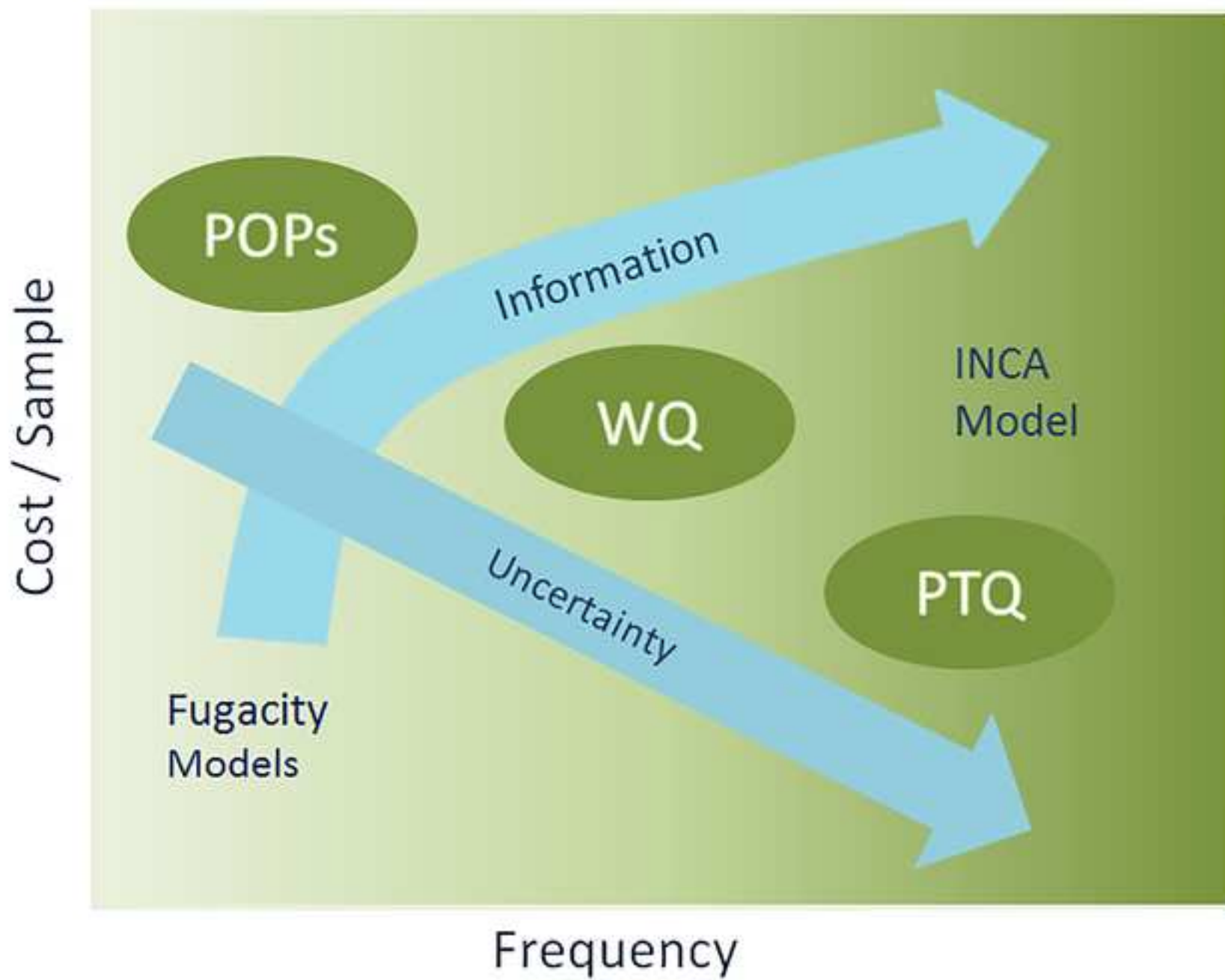
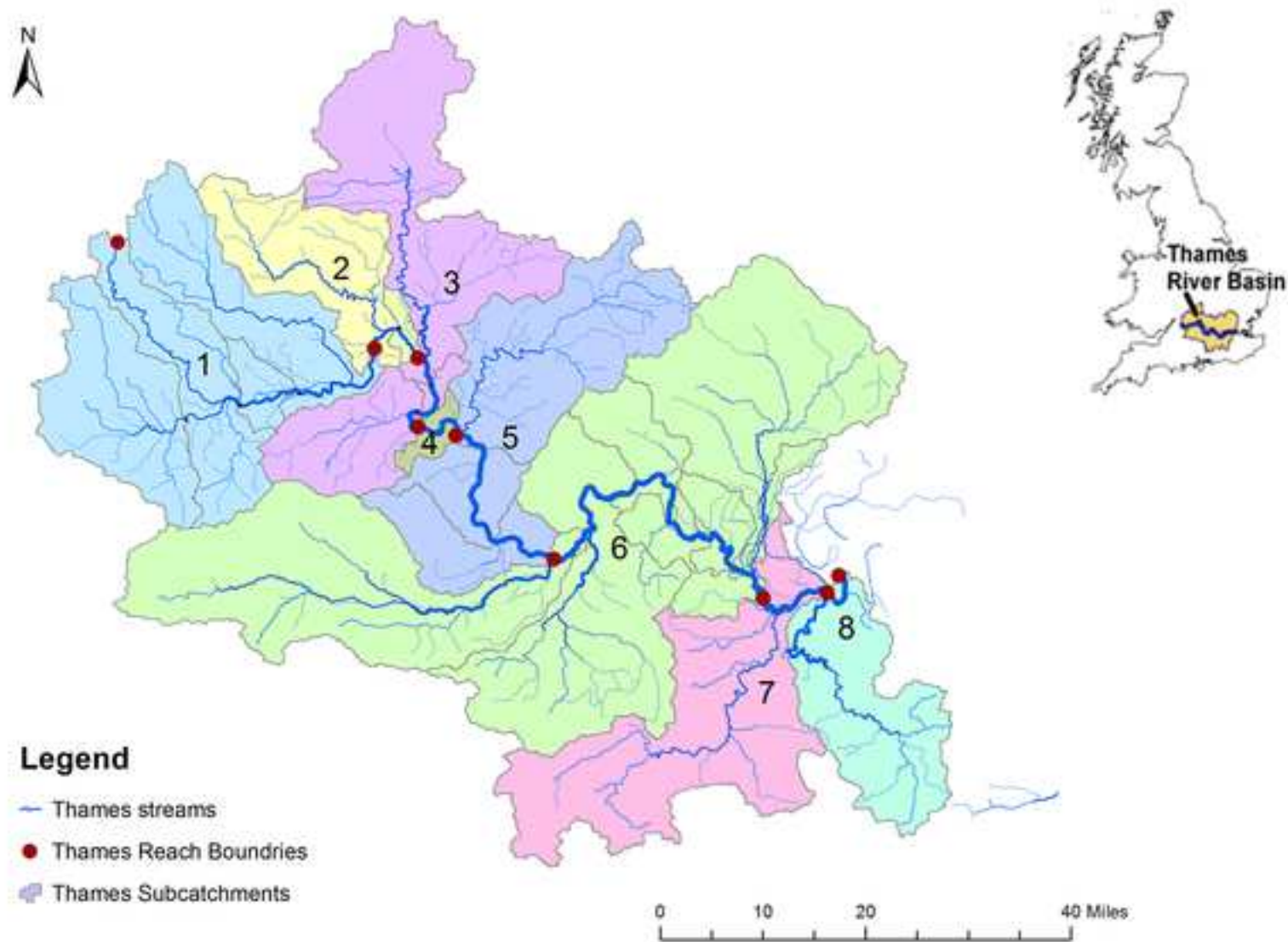


Figure 2



1. Cricklade to Pinkhill
2. Pinkhill to Osney
3. Osney to Culham

4. Culham to Days Weir
5. Days Weir to Caversham
6. Caversham to Shepperton

7. Shepperton to Molesey
8. Molesey to Teddington

Figure 3

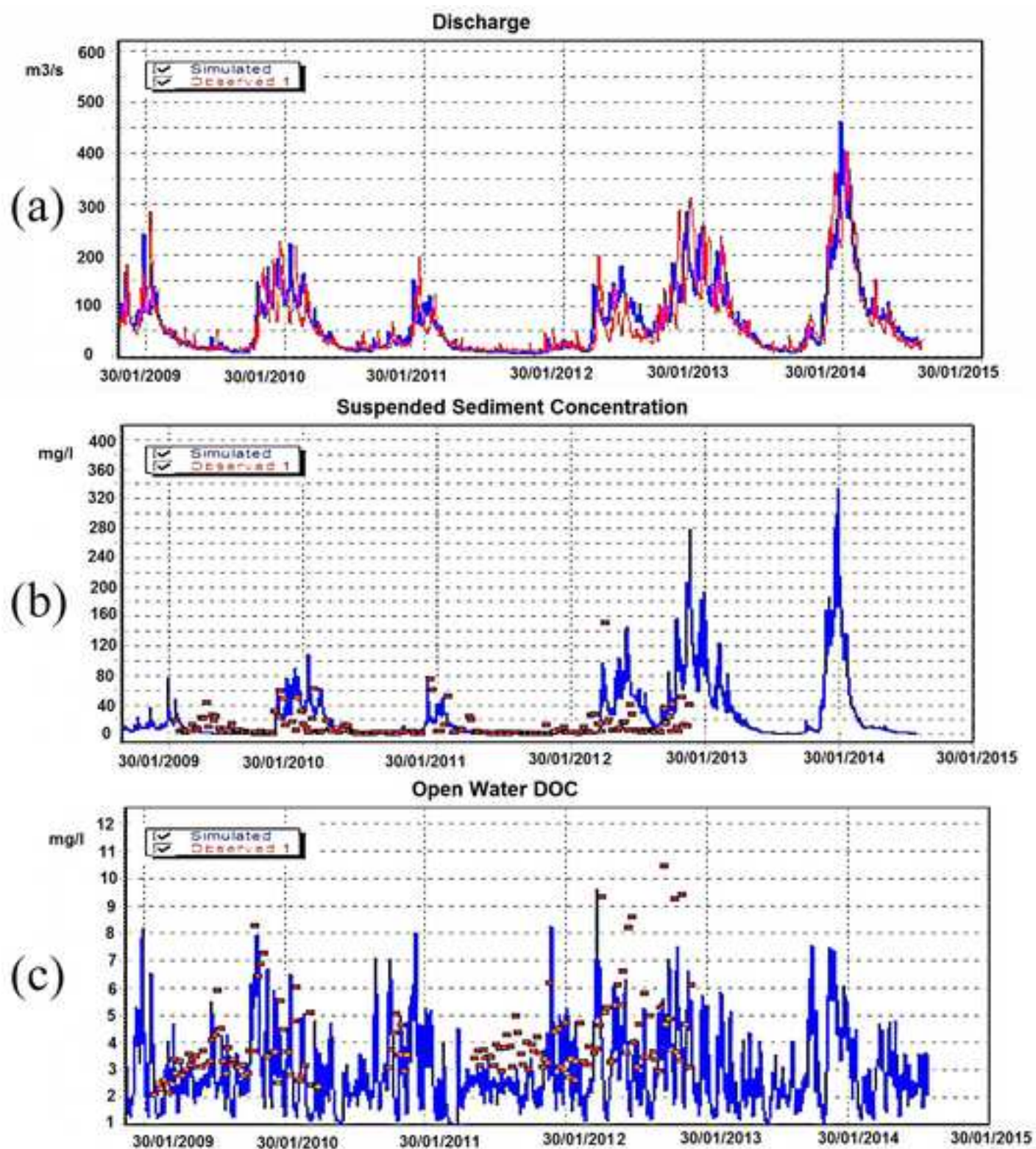
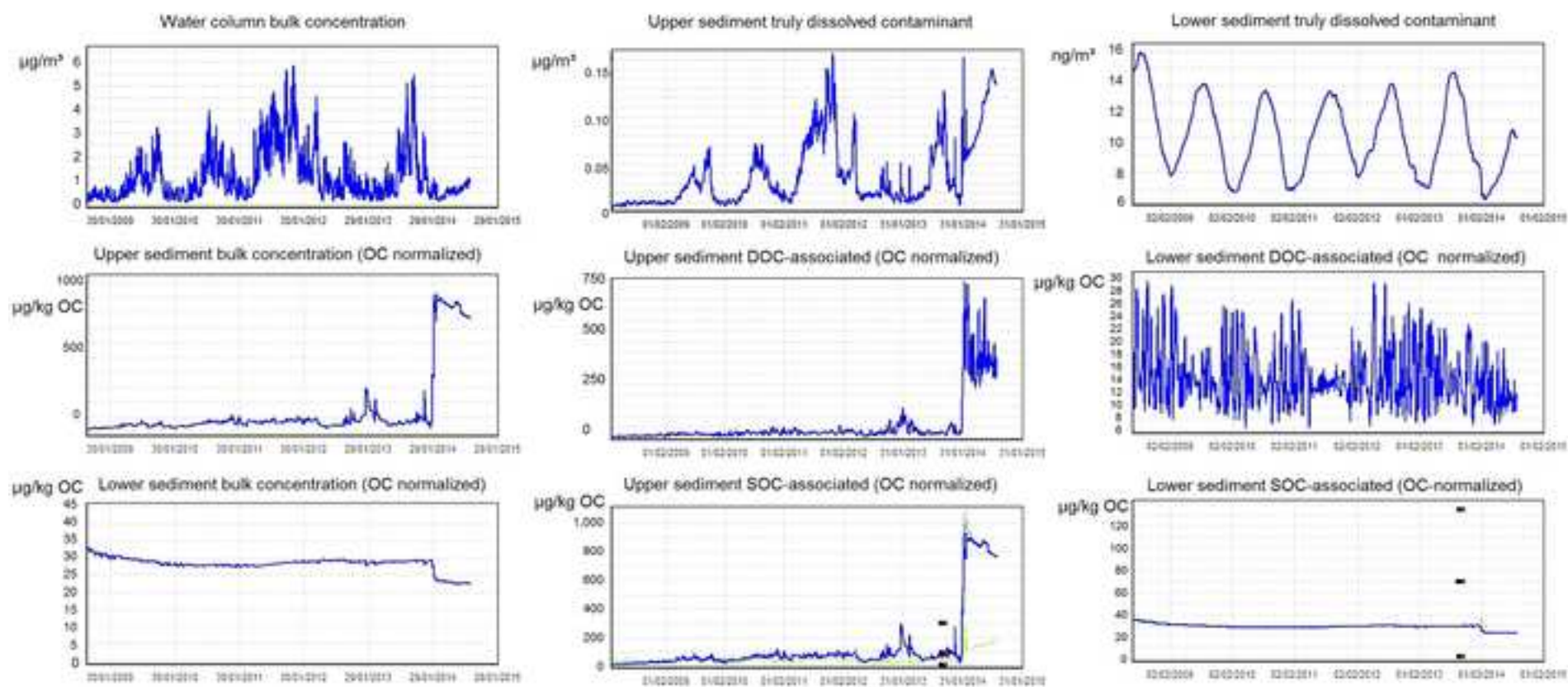


Figure 4



Supporting Information to:

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

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1. The INCA-Contaminants Model

Figure SI1 shows the structure of the soil compartment in the INCA-contaminants. The major soil phases partitioning processes and advection processes taken into account in the modelling includes (Nizzetto et al., 2016):

- Wet and dry atmospheric depositions;
- Inputs from application of fertilizers or accidental spills;
- Partitioning among subphases of the soil compartment (e.g. solid organic carbon (SOC), dissolved organic carbon (DOC), soil water and soil air)
- Diffusion across different layers in the soil water and soil air;
- Diffusive air and upper soil exchange of contaminants;
- Bioturbation;
- Vertical advection from upper to lower soil layer (driven by water flow);
- Losses due to surface and diffuse runoff;
- Degradation of contaminants and formation of degradation products;

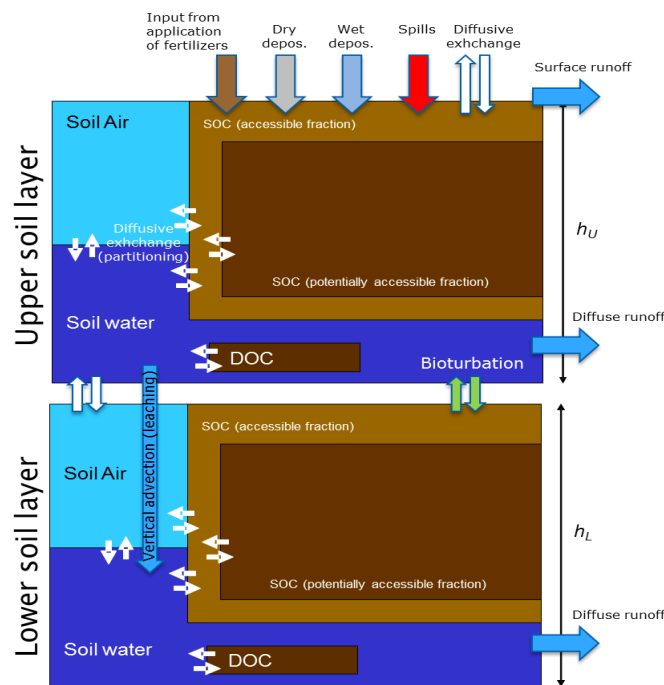


Figure. SI 1 Structure of the soil compartment, adapted from Nizzetto et al. (2016)

The equations of the equilibrium partitioning among soil compartments are presented as follows (Eq. SI1-SI15):

The mass of easily accessible SOC in the upper soil

$$m_{S,Uea} = m_{S,U} \times f \quad kg \quad SI \ 1$$

The mass of potentially accessible SOC in upper soil

$$m_{S,Upa} = m_{S,U} \times (1-f) \quad kg \quad SI \ 2SI \ 3$$

Air-water partitioning coefficient

$$LogH_T = LogH_{25^0} - \frac{(10^3 \cdot \Delta U_{AW} + R \cdot 298.15)}{\ln(10) \cdot R} \cdot \left(\frac{1}{T} - \frac{1}{298.15} \right)$$

$$K_{AW} = \frac{H_T}{R \cdot T} \quad \text{SI 4}$$

Water-SOC partitioning coefficient

$$\text{Log}K_{OWT} = \text{Log}K_{OAW25^0} - \frac{(10^3 \cdot \Delta U_{AO})}{\ln(10) \cdot R} \cdot \left(\frac{1}{T} - \frac{1}{298.15} \right) \quad \text{SI 5}$$

$$K_{W-SOC} = K_{OC} = K_{OWT} \cdot r_{OC} \cdot \frac{1}{\rho_{OC}} \quad m^3 \text{ kg}^{-1} \quad \text{SI 6}$$

Water-DOC partitioning coefficient

$$K_{W-DOC} = \frac{10^{(0.93 \cdot \text{Log}K_{OWT} - 0.45)}}{\rho_{DOC}} \quad m^3 \text{ kg}^{-1} \quad \text{SI 7}$$

Contaminant equilibrium concentration in the fluid and accessible SOC fraction

$$C_{SOC_{ea},eq} = C_{w,eq} \cdot K_{W-SOC} \quad ng \text{ kg}^{-1} \quad \text{SI 8}$$

$$C_{DOC,eq} = C_{w,eq} \cdot K_{W-DOC} \quad ng \text{ kg}^{-1} \quad \text{SI 9}$$

$$C_{G,eq} = C_{w,eq} \cdot K_{AW} \quad ng \text{ m}^{-3} \quad \text{SI 10}$$

$$mCON_{TOT_{ea}} = C_{SOC_{ea},eq} \cdot m_{S,U_{ea}} + C_{DOC,eq} \cdot m_{D,U} + C_{W,eq} \cdot V_{W,U} + C_{G,eq} \cdot V_{G,U} \quad ng \quad \text{SI 11}$$

$$C_{W,eq} = \frac{mCON_{TOT_{ea}}}{K_{W-SOC} \cdot m_{S,U_{ea}} + K_{W-DOC} \cdot m_{D,U} + K_{AW} \cdot V_{G,U} + V_{W,U}} \quad ng \text{ m}^{-3} \quad \text{SI 12}$$

Multicompartment mass exchange of contaminants in soil

$$F_{W-SOC_{ea},U} = (C_{SOC_{ea},U(t-1)} - C_{SOC_{ea},eq,U}) \cdot k_{eq,S} \cdot m_{S,U_{ea}(t-1)} \quad ng \text{ d}^{-1} \quad \text{SI 13}$$

$$F_{W-DOC,U} = (C_{DOC,U(t-1)} - C_{DOC,eq,U}) \cdot k_{eq,S} \cdot m_{DOC,U(t-1)} \quad ng \text{ d}^{-1} \quad \text{SI 14}$$

$$F_{W-G,U} = (C_{G,U(t-1)} - C_{G,eq,U}) \cdot k_{eq,S} \cdot V_{G,U(t-1)} \quad ng \text{ d}^{-1} \quad \text{SI 15}$$

Where: $m_{S,U}$ - mass of SOC in upper soil; $m_{S,U_{ea}}$ - mass of SOC easily accessible in upper soil; $m_{S,U_{pa}}$ - mass of SOC potentially accessible in upper soil; f - fraction of readily accessible organic carbon; H_T - henry's law constant; ΔU_{AW} - enthalpy of phase transfer between air and water; R - ideal gas constant (8.314 J/K/mol); K_{AW} - temperature corrected air-water equilibrium partitioning coefficient; K_{OW} - octanol water equilibrium partitioning coefficient; ΔU_{OA} - enthalpy of phase transfer between octanol and air; K_{OA} - octanol air equilibrium partitioning coefficient; K_{W-SOC} - temperature corrected SOC-water equilibrium partitioning coefficient; K_{OC} - water organic carbon partitioning coefficient; r_{OC} - empirical coefficient; ρ_{OC} - the density of organic carbon; K_{W-DOC} - temperature corrected DOC-water equilibrium partition coefficient; $C_{SOC_{ea},eq}$ - equilibrium concentration of contaminant in the easily accessible fraction of SOC; $C_{DOC,eq}$ - equilibrium concentration of contaminant associated to DOC; $C_{G,eq}$ - equilibrium concentration of contaminant in the soil gas; $C_{W,eq}$ - equilibrium concentration of contaminant in the water; $mCON_{TOT_{ea}}$ - the total of a given contaminant in the bulk soil; $V_{G,U}$ and $V_{W,U}$ - the volume of air and water in the upper soil; $F_{W-SOC_{ea}}$, $F_{W-DOC,U}$ and $F_{W-G,U}$ - the diffusive fluxes of contaminants between water and SOC_{ea}, water and DOC and water and gases in the upper soil layer; $C_{SOC_{ea}(t-1)}$, $C_{DOC(t-1)}$ and $C_{G(t-1)}$ - predicted concentration of contaminant in the easily accessible fraction of SOC, in the soil DOC and in the soil gas phase at the t-1 time step; $k_{eq,S}$ - a mass transfer rate expressing the rate at which partitioning equilibrium is reached.

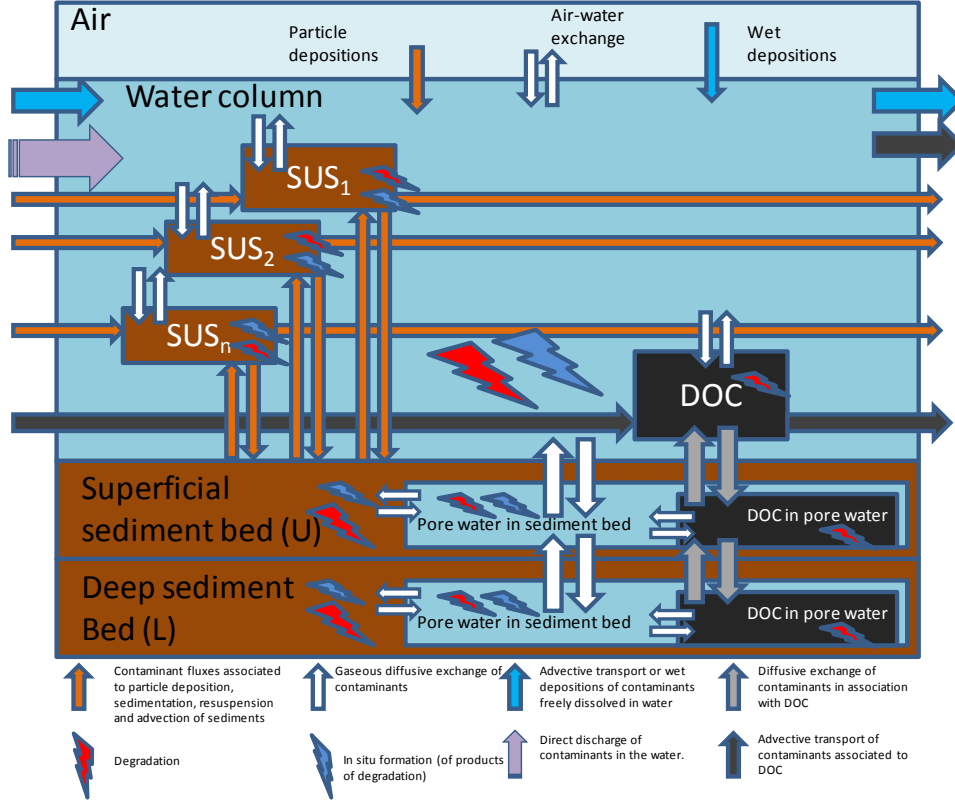


Figure. SI 2 Structure of the in-stream compartment, adapted from Nizzetto et al. (2016)

The structure of the in-stream compartment is illustrated in Figure. SI 2. The main processes in the in-stream phase include:

- Wet and dry atmospheric deposition;
- Advection from upstream and from the catchment;
- Air-water diffusive exchange of gaseous substances;
- Diffusion exchange between water and bed sediment;
- Partitioning among suspended sediment (SS), DOC and truly dissolved phase in water;
- Degradation of contaminants and formation of degradation products;
- Settling and resuspension fluxes associated with sediment dynamics;
- Bio-turbation;
- Diffusive exchange between superficial and deep bed sediments;
- Downstream advection;

The calculation of the air-water exchange flux was given by the following equations (Eq. SI 16-SI 20):

$$\frac{1}{v_{aw}} = \frac{1}{v_w} + \frac{1}{K_{AW} \cdot v_a} \quad d \cdot m^{-1} \quad \text{SI 16}$$

$$v_{H2O} = (0.2 \cdot u_{10} + 0.3) \cdot 864 \quad m \cdot d^{-1} \quad \text{SI 17}$$

$$v_a = v_{H2O} \left(\frac{D_a}{D_{H2O}} \right)^{0.67} \quad m \cdot d^{-1} \quad \text{SI 18}$$

$$D_{H2O} = 10^{-3} \cdot \frac{\left(T_w^{1.75} \left[\left(\frac{1}{28,97} \right) + \left(\frac{1}{18} \right) \right]^{\frac{1}{2}} \right)}{1 \cdot [20.1^{1/3} + 18^{1/3}]^2} \cdot 10^{-4} \quad m^2 s^{-1} \quad SI \ 19$$

$$F_{a-w} = v_{aw} \left(C_{w,st} - \frac{C_A}{K_{aw}} \right) \cdot L \cdot wdt \quad ng \ d^{-1} \quad SI \ 20$$

Where: v_{aw} - **overall air-water transfer velocity**; v_a, v_w – Airside and Waterside transfer velocity in the two-film model describing air-water exchange of gaseous compounds; v_{H2O} - diffusion velocity of water vapour in air; u_{10} - wind speed at 10 m from the water surface; D_a – the molecular diffusivity of the compound in air; D_{H2O} - the molecular diffusivity of water vapor in air; T_w - the absolute temperature of water; F_{a-w} - the air-water exchange; C_w - the TDP concentration in the stream water; C_A - the air concentration; K_{aw} - temperature dependent air-water equilibrium partitioning coefficient; L and wdt - length and width of the river segment.

More detailed information about the model calculation is given by Nizzetto et al. (2016).

2. Measured Sediment Concentrations

To characterize the current occurrence of PCBs in the sediment of the River Thames, a sediment sampling campaign was conducted between September and December 2013 (before the flooding period). Several sediment cores (30-40 cm long) were collected from seven sites in the River Thames and its tributaries:

- the river Thames at two sites in Wallingford: at Wallingford Bridge near the left bank (TH, Wallingford) and near the right bank about 800 m further downstream, just downstream of a small tributary at Winterbrook (TH, Winterbrook),
- a small sewage impacted Thames tributary: Littlemore Brook both upstream (LM, US of STW) and downstream of Oxford sewage works (LM, DS of STW),
- the river Ock just upstream of Abingdon (OCK, Abingdon)
- the river Kennet in Newbury (KE, Newbury)
- The Cut, a river draining mainly urban areas, downstream of Bracknell (CUT, Bracknell)

One to two sediment cores from each site were used for determining the sediment concentrations of PCBs. The sediment cores have been sliced into 5-8 layers. The divisions were made where the appearance (e.g. colour, grain size etc.) changed. Only the two upper sediment layers (surface and the second layer) have been analysed for PCB concentrations. The sediment samples were analysed in the Lancaster University Environmental Centre Laboratory (UK) and the analytical methods were based on previously established and approved procedures (Ma et al., 2015). The sediment samples were extracted in a soxhlet apparatus and cleaned up through a basic silica-acid silica multilayer column followed by a gel permeation chromatography (GPC) column. To minimise any inherent experimental bias, samples with a mixture of sites and sediment layers have been selected to extract for each batch. All samples were spiked with recovery standards containing ^{13}C -labelled PCBs: 28, 52, 101, 138, 153, 180 before the extraction. After cleanup, all extracts were transferred to GC vials containing 25 μ l keeper (dodecane, containing a known amount of internal standards: PCB 30, ^{13}C -PCB141, ^{13}C -PCB208), and were blown down under nitrogen to so

that the sample would end up in the 25 µl dodecane. All the purified samples were then analysed on a Thermo ‘Trace’ GC-MS (Thermo-Fisher Scientific).

Additionally the moisture content and the organic carbon content of the sediment samples were determined by the Centralised Chemistry Group at CEH, Lancaster, UK. The sediment concentrations of PCBs are illustrated in Table SI 1.

Table SI 1. PCB concentrations in sediments

Sampling site	Samples	PCB 52	PCB 118	PCB 153
		µg/kg dry weight		
TH, Wallingford	Sample 1 Surface	0.005	0.002	0.006
	Sample 1 Second	0.002	0.003	0.015
	Sample 2 Surface	0.189	0.414	16.312
	Sample 2 Second	0.029	0.100	5.852
TH, Winterbrook	Sample 1 surface	0.016	0.015	0.050
	Sample 1 Second	0.011	0.012	0.037
	Sample 2 surface	0.060	0.055	0.112
	Sample 2 Second	0.045	0.064	1.063
LM US of STW	Sample 1 Surface	0.111	0.235	1.126
	Sample 1 second	0.877	0.406	1.281
	Sample 2 Surface	0.044	0.049	0.155
	Sample 2 second	0.148	0.334	0.986
LM DS of STW	Surface	0.440	0.615	3.725
	Second	0.423	0.625	3.765
OCK, Abingdon	Sample 1 Second	<LOQ	0.007	0.017
	Sample 2 surface	0.011	0.006	0.017
	Sample 2 Second	0.050	0.013	0.022
KE, Newbury	Sample 1 surface	0.201	0.253	1.504
	Sample 1 Second	<LOQ	0.004	0.011
	Sample 2 Surface	0.033	0.023	0.060
	Sample 2 Second	0.020	0.025	0.095
CUT, Bracknell	Sample 1 surface	0.405	0.524	1.511
	Sample 1 Second	0.364	0.449	1.327
	Sample 2 surface	0.345	0.518	1.128
	Sample 2 Second	0.357	0.583	2.337

3. Predicted PCB Dynamics in the Thames System

The simulated dynamics of PCB 52 and PCB 118 in the in-stream system for Reach 6 are illustrated in Figure SI 3 and Figure SI 4.

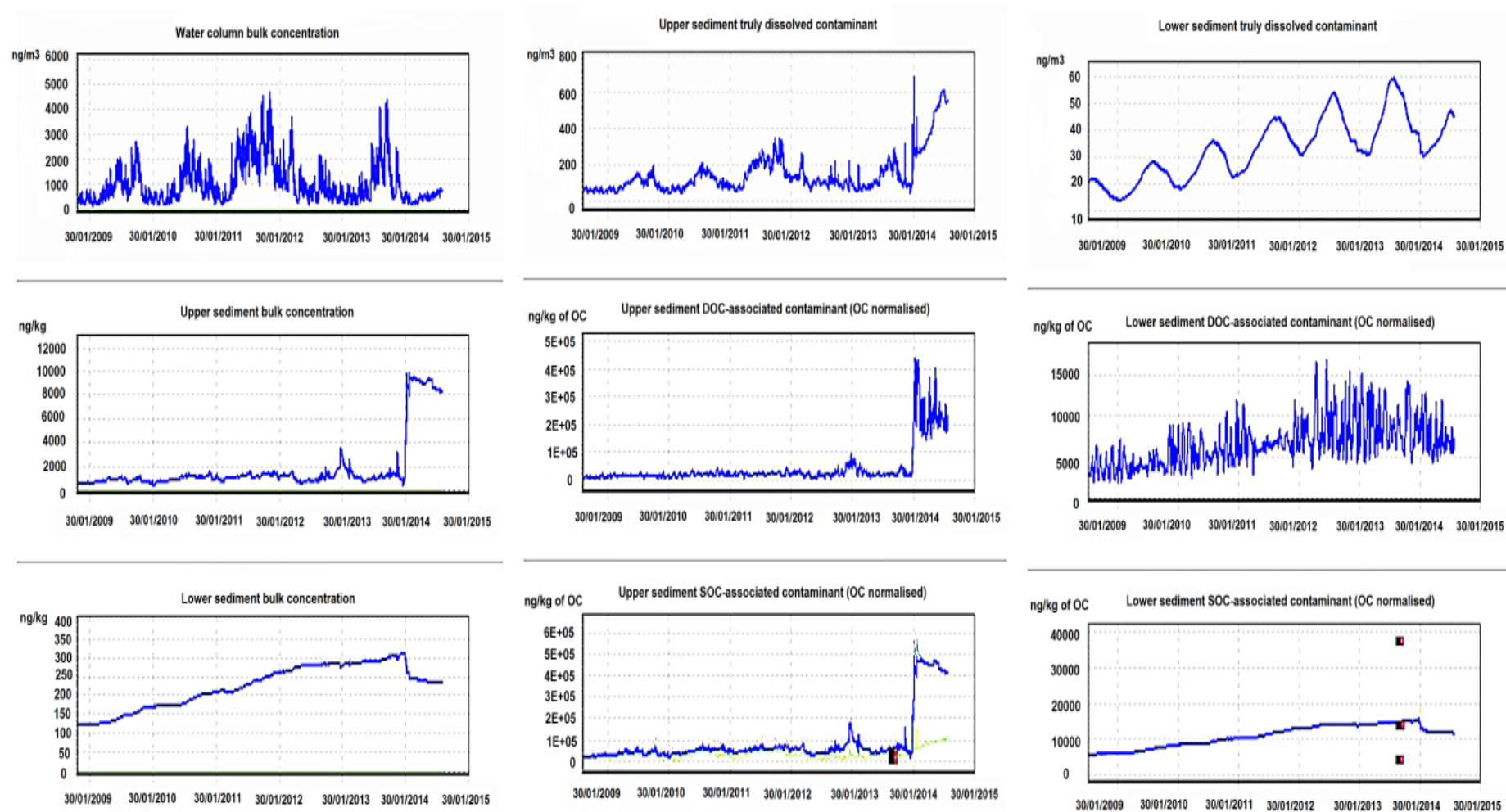


Figure SI 3. The simulated dynamics of PCB 52 in water column, upper sediment and lower sediment layers for Reach 6

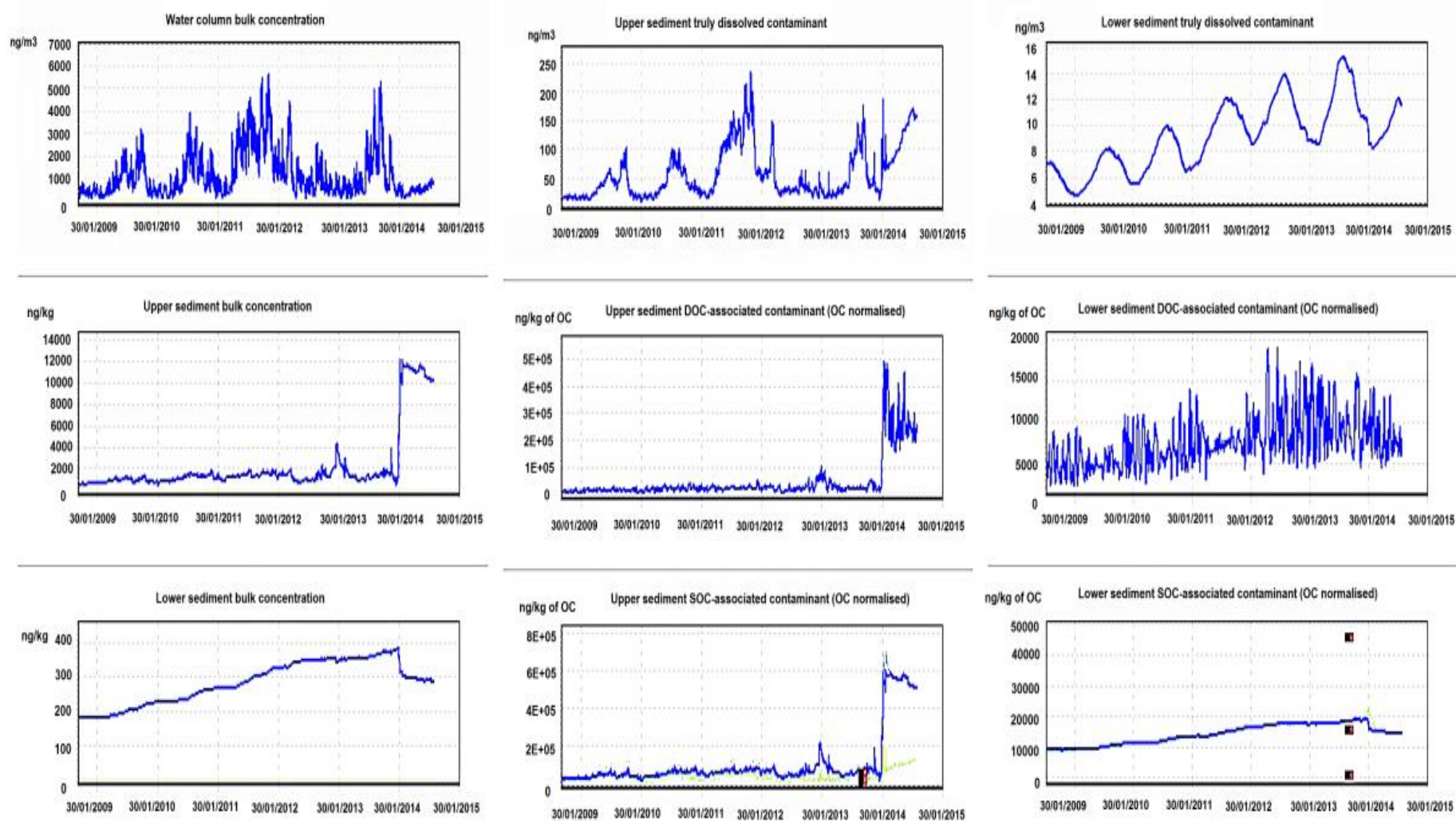


Figure SI 4. The simulated dynamics of PCB 118 in water column, upper sediment and lower sediment layers for Reach 6

4. References

- Ma Y., *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.
- Nizzetto L., *et al.* Assessment of contaminant fate in catchments using a novel integrated hydrobiogeochemical-multimedia fate model. *Science of the Total Environment*, accepted 2016.