

Article (refereed) - postprint

Lu, Q.; Futter, M.N.; Nizzeto, L.; Bussi, G.; Juergens, M.D.; Whitehead, P.G.
2016. **Fate and transport of polychlorinated biphenyls (PCBs) in the River Thames catchment – insights from a coupled multimedia fate and hydrobiogeochemical transport model.**

© 2016 Published by Elsevier B.V

This manuscript version is made available under the CC-BY-NC-ND 4.0 license <http://creativecommons.org/licenses/by-nc-nd/4.0/>



This version available <http://nora.nerc.ac.uk/513112/>

NERC has developed NORA to enable users to access research outputs wholly or partially funded by NERC. Copyright and other rights for material on this site are retained by the rights owners. Users should read the terms and conditions of use of this material at <http://nora.nerc.ac.uk/policies.html#access>

NOTICE: this is the author's version of a work that was accepted for publication in *Science of the Total Environment*. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in *Science of the Total Environment* (2016), 572. 1461-1470.

[10.1016/j.scitotenv.2016.03.029](https://doi.org/10.1016/j.scitotenv.2016.03.029)

www.elsevier.com/

Contact CEH NORA team at
noraceh@ceh.ac.uk

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

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

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

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

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

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

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

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

11

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

12 **Abstract:**

1
2
3 13 The fate of persistent organic pollutants (POPs) in riverine environments is strongly
4
5 14 influenced by hydrology (including flooding) and fluxes of sediments and organic carbon.
6
7
8 15 Coupling multimedia fate models (MMFM) and hydrobiogeochemical transport models
9
10 16 offers unique opportunities for understanding the environmental behaviour of POPs. While
11
12
13 17 MMFMs are widely used for simulating the fate and transport of legacy and emerging
14
15 18 pollutants, they use greatly simplified representations of climate, hydrology and
16
17
18 19 biogeochemical processes. Using additional information about weather, river flows and water
19
20 20 chemistry in hydrobiogeochemical transport models can lead to new insights about POPs
21
22 21 behaviour in rivers. As most riverine POPs are associated with suspended sediments (SS) or
23
24
25 22 dissolved organic carbon (DOC), coupled models simulating SS and DOC can provide
26
27 23 additional insights about POPs behaviour. Coupled simulations of river flow, DOC, SS and
28
29
30 24 POPs dynamics offer the possibility of improved predictions of contaminant fate and fluxes
31
32 25 by leveraging the additional information in routine water quality time series. Here, we present
33
34
35 26 an application of a daily time step dynamic coupled multimedia fate and
36
37 27 hydrobiogeochemical transport model (The Integrated Catchment (INCA) Contaminants
38
39 28 model) to simulate the behaviour of selected PCB congeners in the River Thames (UK). This
40
41
42 29 is a follow-up to an earlier study where a Level III fugacity model was used to simulate PCB
43
44 30 behaviour in the Thames. While coupled models are more complex to apply, we show that
45
46
47 31 they can lead to much better representation of POPs dynamics. The present study shows the
48
49 32 importance of accurate sediment and organic carbon simulations to successfully predict
50
51
52 33 riverine PCB transport. Furthermore, it demonstrates the important impact of short-term
53
54 34 weather variation on PCB movement through the environment. Specifically, it shows the
55
56
57 35 consequences of the severe flooding, which occurred in early 2014 on sediment PCB
58
59 36 concentrations in the River Thames.
60
61
62
63
64
65

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

63 **1. Introduction:**

64 Persistent Organic Pollutants (POPs) include a wide range of organic compounds
65 characterized by their environmental persistence, toxicity, and potential for long-range
66 transport (Lohmann et al., 2007; Urbaniak, 2007). Many POPs are of concern because they
67 have carcinogenic properties and can be a public health threat (Ross, 2004). POPs can be
68 produced either intentionally through human activity or unintentionally as by-products of
69 human or natural activities. Production of so-called legacy POPs, including polychlorinated
70 biphenyls (PCBs) has either stopped or is severely constrained. Despite great efforts to limit
71 their release, PCBs remain a problem in many parts of the world. In urban areas, PCB
72 contamination can be associated with both point and diffuse sources. Point sources include
73 industrial areas where there have been accidental PCB spills. Diffuse sources include runoff
74 from contaminated sites and atmospheric deposition. PCBs have been widely used as
75 dielectric, petroleum additives and coolant fluids in electrical equipment in the UK between
76 1955 and 1976. The emissions of PCBs to the environment peaked in the early 1970s and
77 dropped rapidly after bans on production and restrictions in their use came into effect in 1977
78 (Sweetman et al., 2002). Prior to this, a voluntary ban on production of PCBs was
79 implemented in the UK by the early 1970s (Schuster et al., 2010).

80 Current sources for PCBs to the aqueous environment in the UK include secondary emissions,
81 contaminated soil, and direct atmospheric inputs or spills from old PCB-containing
82 equipment. Atmospheric PCB concentrations have strongly declined throughout the UK in
83 recent years (Schuster et al., 2010). This decline in concentration should cause a decline in
84 atmospheric deposition. With the decline in atmospheric concentrations, emissions and
85 mobilization from soil is likely to become proportionately more important (Nizzetto et al.,
86 2010). Mass transport due to extreme weather-related events such as flooding may also be an
87 important mechanism for the redistribution and mobilisation of PCBs. Because of their

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

88 hydrophobic nature, many POPs are strongly associated with organic carbon and can
89 accumulate in soils, sediments and biota. These environmental reservoirs can be activated
90 during flooding (Pulkrabová et al., 2008) or other disturbances (Eggleton and Thomas, 2004).
91 Unlike many other environmental parameters, POPs measurements are characterised by their
92 relative infrequency, analytic complexity and high cost. Typically, POPs samples are much
93 less frequent than the routine water quality data monitored by the competent national
94 authority and orders of magnitude less common than hydrological and weather observations.
95 (Figure 1). It is well accepted that the more frequent and less expensive routine water quality
96 and hydrometeorological observations can be used as environmental proxies to provide
97 additional information about POPs fate and transport (Hung et al., 2010). Many hydrophobic
98 compounds associate strongly with suspended sediment (Josefsson et al., 2011) and the
99 relationship between dissolved organic carbon (DOC) and PCB transport is well established
100 (Evans, 1988). DOC and suspended sediment data are routinely collected by many national
101 monitoring agencies (Fölster et al., 2014) and regulatory authorities. Using the information in
102 these routine water quality and hydrometeorological time series can provide additional
103 insights into POPs fate and transport (Figure 1). The cost per sample for POPs analysis
104 (Figure 1; vertical axis) is much higher than costs for water quality (WQ) or
105 hydrometeorological measurements of precipitation, temperature or flow (PTQ). The big
106 difference in sample costs is one reason that POPs measurements are much less frequent than
107 routine water quality measurements (WQ) which are often collected monthly at multiple sites
108 across a river network. WQ samples, in turn, are less frequent than the routine weather and
109 flow observations collected by national agencies. Typically, fugacity models focus solely on
110 POPs data and employ highly simplified representations of the environment. Coupled
111 multimedia fate and hydrobiogeochemical models like INCA-Contaminants (the Integrated
112 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 $\mu\text{g}/\text{kg}$) 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 $\mu\text{g}/\text{kg}$ for PCB 52, 0.20 $\mu\text{g}/\text{kg}$ for PCB
128 118, and 1.70 $\mu\text{g}/\text{kg}$ 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.

149

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).

164

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

186 model has been integrated in the INCA-C/INCA-Sed coupled structure (Nizzetto et al., 2016).

187 All land phase equations are solved for a 1 km² cell and results are pro-rated to sub-

188 catchment area. The processes in the INCA-contaminants model can be described in two

189 main sections: 1) the land phase model simulating the multimedia distribution, transport,

190 storage and transformation of contaminants in soils (Figure SI 1); 2) the in-stream model

191 describing the contaminations fate and transformation in the aquatic system (Figure. SI 2).

192 The major processes of contaminants delivery from the soil compartment to the in-stream

193 system include: 1) surface runoff containing solid organic carbon (SOC) associated

194 contaminants and dissolved contaminants (derived from infiltration excess and saturation

195 excess); and 2) diffuse runoff from the organic and mineral layers of the soil compartment.

196 The contaminant fluxes were computed by multiplying the contaminant concentrations by the

197 velocity components of the water and organic matter exchange in, between and out of the soil

198 compartment, which were calculated using the equations adopted in the INCA-C and INCA-

199 Sed models.

200 In INCA-contaminants, the soil is represented as two vertically stacked boxes, which can be

201 conceptualised as a superficial organic layer and an underlying mineral layer (Figure. SI 1).

202 The SOC within each box is divided into easily accessible (SOC_{ea}) and potentially accessible

203 (SOC_{pa}) fractions to simulate contaminant and SOC pools with different breakdown rates

204 and different degrees of connectivity to soil water. Soil water (including DOC and a truly

205 dissolved phase) and soil air are included in each of the layers. The fraction of pore space is a

206 model parameter and the relative volumes of air and water are determined dynamically based

207 on soil moisture. The model also allows fixed or time varying contaminant inputs including

208 wet and dry atmospheric deposition, litterfall associated pollutant inputs and accidental spills.

209 All relevant model parameters can vary on a sub-catchment basis and according to soil and

210 land use type. This degree of flexibility in the model allows the process rates, hydrological

1 211 pathways and the mass of contaminants in soil to vary spatially across a catchment or region.

2 212 Although the fugacity notation was not used in the mathematical formalism of INCA-

3 213 contaminants, the diffusive exchange that controls the distribution of contaminants between

4 214 different phases and soil layers was predicted using the thermodynamic equations derived

5 215 from the fugacity models (Eq. SI 1-SI 15, Supporting Information). Contaminant

6 216 concentrations in each phase of the soil layers were calculated based on the thermodynamic

7 217 equilibrium partitioning coefficients including Henry's law constant (H), enthalpy of phase

8 218 transfer between air and water, octanol-water equilibrium partitioning coefficients, enthalpy

9 219 of phase transfer between water and octanol, and the scaling from octanol-water to SOC-

10 220 water and DOC-water equilibrium partitioning coefficients.

11 221 The in-stream sub-model consists of a series of reaches (or stream segments). Each reach is

12 222 comprised of a water column and underlying sediments. Within the water column,

13 223 contaminants can be present in a truly dissolved phase (TPD), associated with DOC, and with

14 224 an arbitrary number i of suspended solid classes ranked by their size (SUS i). The underlying

15 225 sediment consists of two vertically stacked layers. Only the upper layer undergoes material

16 226 exchange with the overlying water column. The depth of the upper sediment layer is

17 227 dynamically calculated depending on the deposition and erosion of sediment. The sediment

18 228 exchange processes in the stream system could be dominant affecting the fate of

19 229 contaminants in the sediment layers. When deposition becomes the dominant dynamic

20 230 processes, the contaminants associated with SUS i in the water column would accumulate into

21 231 the upper sediment layer. In contrast, the contaminants in the lower bed sediment would re-

22 232 integrate into the upper sediment layer and become available for dynamically enhanced

23 233 exchange with the water column if erosion of sediment dominates the processes.

24 234 Within each sediment compartment, contaminants are present in TDP, DOC-associated and

25 235 SOC-associated sub-phases (Figure. SI 2). In addition to delivery from the surrounding

236 catchment, inputs of contaminants to the in-stream phase include wet or dry atmospheric
237 deposition, possible point sources, and diffusive air-water exchange (Eq. SI 20). The
238 influence of wind speed on the air-water exchange is included in the calculations (Eq. SI 16-
239 SI 20). The reach mass balance of SUSi in the water column includes upstream inputs,
240 entrainment associated with soil, flow erosion of the channel bank, bed sediment erosion,
241 downstream advection and settling of suspended sediment. The distribution of contaminants
242 across different phases in the water column is calculated using a similar approach to that used
243 for the computing of the partitioning within the soil compartment. More detailed information
244 of the processes and equations of the INCA-Contaminants model is given in Nizzetto et al.
245 (2016).

247 2.3. Model set up

248 To model the behaviour of selected PCB congeners in the River Thames catchment, the
249 current version of INCA-contaminants (version 1.0) was applied. Simulations were
250 performed for the period of 1st Jan 2009 - 30th Sep 2014. The Thames system was divided
251 into 8 reaches and sub-catchments from Cricklade to its tidal limit at Teddington (Figure 2,
252 Table 1) based on Futter et al. (2014). Four types of land use were used in the INCA-
253 contaminants model: arable, pasture, forest and urban (Table 1). The reach length, sub-
254 catchment area and proportion of land cover in each sub-catchment were derived from
255 previous studies (Futter et al., 2014; Jin et al., 2012) (Table 1). Suspended grain size could be
256 important in influencing the contaminant transport. In the INCA-contaminants model, five
257 sediment size classes were used representing clay, silt, fine, medium and coarse sand.

258 The INCA-contaminants application presented here simulates the behaviour of six PCB
259 congeners at eight points along the main stem of the Thames above the tidal limit. The

260 selected congeners are six out of the seven PCBs representing a range of chlorination levels,
261 that are most commonly monitored in the environment (ICES7 PCBs), including: the tri-
262 chlorinated PCB 28, tetra-chlorinated PCB 52, penta-chlorinated PCB 101 and PCB 118
263 (dioxinlike), hexa-chlorinated PCB 153 and hepta-chlorinated PCB 180. For brevity of
264 presentation, we focus on three PCB congeners (PCB 52, PCB 118 and PCB 153) and give
265 only brief summary information about the others. Wet and dry atmospheric deposition were
266 considered to be the major external inputs of PCBs to the catchment in the INCA-
267 contaminants modelling. The input data of the dry and wet deposition were calculated based
268 on estimates of deposition fluxes from Sweetman and Jones (2000). Primary sources of PCBs
269 in the catchment were not included because PCBs are no longer used. Initial concentrations
270 of the three PCBs in the soil compartment were estimated according to recent measurements
271 and predictions reported by the Environment Agency (2007), Vane et al. (2014) and Lu et al.
272 (2015). The initial sediment concentrations for the PCBs were estimated with recent
273 measurements at seven sites in the River Thames and its tributaries (samples analysed at the
274 Lancaster University Environment Centre) (Lu et al., in preparations, see supporting
275 information). The physical-chemical properties of the PCB congeners are important in
276 determining the fate of these chemicals in the catchment. The octanol-water partition
277 coefficient (K_{ow}) and half-lives of PCBs in each compartments were taken from the previous
278 fugacity modelling study (Lu et al., 2015; Sinkkonen and Paasivirta, 2000; Sweetman et al.,
279 2002). Other parameters of physical-chemical properties were mainly collected from
280 Schenker et al. (2005).

281 The application of INCA-contaminants requires an input of daily time series of precipitation,
282 air temperature, hydrologically effective rainfall (HER), soil moisture deficit (SMD) and
283 wind speed as driving data (Crossman et al., 2013). The daily precipitation and temperature
284 data were provided by the UK Met Office. In particular, time series of daily precipitation,

1 285 minimum daily air temperature and maximum daily air temperature from 1st Jan 2009 to 30th
2 286 Sep 2014 were obtained for all available meteorological stations within the Thames
3
4 287 catchment, and a spatial average over the catchment was computed for all these variables.
5
6
7 288 Mean daily air temperature was computed as the average of minimum and maximum daily
8
9 289 values. The time series of wind speed data came from the Meteorological Station at CEH
10
11
12 290 Wallingford. The other two data series (HER and SMD) were generated using the
13
14 291 Precipitation, Evapotranspiration and Runoff Simulator for Solute Transport (PERSiST)
15
16 292 model. PERSiST is conceptual watershed-scale rainfall-runoff model that is designed
17
18
19 293 primarily to provide input data series to the INCA models (Futter et al., 2014). The
20
21
22 294 underlying geology could also be an important factor influencing the hydrologic response
23
24 295 across the catchment (Futter et al., 2014). This is accounted for in the PERSiST simulation
25
26 296 which divided the catchment into chalk bedrock, non-chalk bedrock and Quaternary sand, slit
27
28
29 297 and clay (Futter et al., 2014). The water discharge simulated by PERSiST was calibrated
30
31
32 298 against the observed daily flows at different sites of the River Thames by manually adjusting
33
34 299 the model parameters within a recommended range. More information about the PERSiST
35
36 300 application on the River Thames can be found in Futter et al. (2014). Measured flows were
37
38
39 301 obtained from the CEH National River Flow Archive (<http://nrfa.ceh.ac.uk>). The INCA-
40
41 302 Contaminants model was calibrated against a time series of observed water quality data. The
42
43
44 303 number of available data points for each of the sub-catchments is summarized in table 2.
45
46 304 Dissolved organic carbon (DOC) and suspended sediments (SS) observations were obtained
47
48
49 305 from the CEH Thames Initiative ([http://www.ceh.ac.uk/our-science/projects/river-thames-](http://www.ceh.ac.uk/our-science/projects/river-thames-initiative)
50
51 306 initiative) routine sampling (1-2 times a week over the modelled period), which covered four
52
53
54 307 of the eight sub-catchments (Reach 1, Reach 2, Reach 5 and Reach 6) (Table 2). Limited
55
56 308 PCB measurement data was available for the Thames river system for recent years. A
57
58 309 sampling campaign was conducted in 2013 to characterize sediment concentrations of a range
59
60
61
62
63
64
65

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

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

2.3. Sensitivity analysis

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

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

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

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

339 **3. Results and Discussion**

340 **3.1. Model performance**

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

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

1 358 sediment layers were available for three Thames reaches (Reach 3, Reach 5 and Reach 6)
2
3 359 (Table 2). There is a large variance within the observed values due to the spatial and
4
5 360 geological differences in sampling locations. Model predictions within the minimum and
6
7 361 maximum range of the observed data were considered as acceptable, valued as '0' in Table 5.
8
9
10 362 Values outside of the range were described as the ratio of a over b (a/b), where 'b' is the
11
12 363 range between the minimum and maximum observed values and 'a' is the distance of the
13
14 364 outlier to the closest boundary of the range. The 'a/b' values above 0 indicated the predictions
15
16 365 for PCB contaminations to be over the maximum values of the observed data. The model
17
18 366 generated very good predictions for Reach 6 (Figure SI 3, Figure SI 4, Figure 4), with all the
19
20 367 values set to 0. There were a few outliers in Reach 3 and Reach 5, but they were close to the
21
22 368 boundary of the acceptable range. Only in one case (PCB 52 in lower sediment of Reach 5),
23
24 369 the predicted values were a factor of 6-8 higher than the average measured values (Table 5).
25
26
27 370 The model performed better for heavier PCB congeners (Table 5). Given the complexity of
28
29 371 the INCA-contaminants modelling, in integrating so many different factors, the simulation
30
31 372 for PCB contaminations in the Thames system was deemed acceptable.
32
33
34

35
36
37 373 The sensitivity analysis showed that model predictions were influenced by PCB physico-
38
39 374 chemical properties, simulated atmospheric inputs and parameters related to land-phase
40
41 375 sediment mobilisation (Table 6). Simulations were sensitive to octanol:water partition
42
43 376 coefficients and estimated in-soil degradation rates. PCB 153 was the only congener sensitive
44
45 377 to simulated atmospheric deposition rates. The sensitivity to groundwater time constants is
46
47 378 linked to the effect of that parameter on in-stream suspended sediment dynamics.
48
49
50

51 379 3.2. The dynamics of PCB concentrations in the River Thames system

52
53

54
55 380 In the INCA modelling, the predicted bulk water concentrations of the PCBs showed
56
57 381 pronounced seasonality. The modelling results for concentrations of PCB 52 (Figure SI 3),
58
59 382 PCB 118 (Figure SI 4), and PCB 153 (Figure 4) in different phases for Reach 6 are presented
60
61
62
63
64
65

1 383 as examples. The highest concentrations are simulated during summer low flow periods. Low
2 384 concentrations are simulated during winter high flow periods, indicating that the water
3
4 385 concentrations of PCBs are affected by the dilution of river flow. For the majority of the time,
5
6
7 386 the PCB concentrations in Thames water were estimated to be below the Environment
8
9 387 Agency monitoring programme detection limit of 1000 ng/m³
10
11 [\(http://www.geostore.com/environment-agency/\)](http://www.geostore.com/environment-agency/). In some extreme low flow conditions, the
12 388
13
14 389 contaminations in water could be 2- to 6-fold above the detection limit (Figure 4). The
15
16 390 simulated increase in PCB concentrations during summer low flow periods is consistent with
17
18 391 observations made in a northern English river (Meharg et al., 2003), where a 2-order of
19
20 392 magnitude rise in total PCB concentrations was observed during summer. While this increase
21
22 393 is much higher than that obtained in our simulations, it does lend credence to the simulated
23
24 394 temporal dynamics or riverine PCB concentrations. The model also predicted similar seasonal
25
26 395 pattern for upper and lower sediment truly dissolved contaminants, with high levels in
27
28 396 summer and low levels in winter. However, the pattern is not as clear as that of the water bulk
29
30 397 concentrations. There was little difference between the studied PCB congeners in the
31
32 398 simulation of concentration dynamics.
33
34
35
36
37
38

39 399 The model predicted the concentrations of the studied PCB congeners in the upper sediment
40
41 400 layer of the River Thames (SOC associated) to range from around 10 to 100 µg/kg of OC
42
43 401 between early 2009 and late 2013. Afterwards in the winter 2013/2014, sharp increases in the
44
45 402 PCB concentrations in the upper sediment were predicted. The rapid increases were most
46
47 403 remarkable for the lower sub-catchments (Reach 6, Reach 7, and Reach 8) and heavier PCB
48
49 404 congeners. The upper sediment SOC associated concentration for PCB 52 in Reach 6 was
50
51 405 modelled to increase 24- fold, while those for PCB 118 and PCB 153 increased 26- fold and
52
53 406 32-fold respectively in winter 2013/2014 (Figures 4, SI 3 and SI 4). However, this could not
54
55 407 be verified with measured data due to lack of observed data concerning the PCBs behaviour
56
57
58
59
60
61
62
63
64
65

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

408 in the period of the sharp increase. Both modelled data and observed flow indicated that
409 extreme flooding has happened in the River Thames Catchment during the winter 2013/2014.
410 Both large increases (Pulkrabová et al., 2008) and decreases (Barber and Writer, 1998) in
411 sediment PCB concentrations have been reported after flooding. The model predictions
412 presented here suggest that large increases in upper sediment PCB concentrations occurred
413 after the severe floods of 2014. This hypothesis of increased concentrations of PCBs in
414 sediment is consistent with what is known about low pre-flood concentrations of bulk
415 sediment PCBs measured in 2013 (see supporting information), which are well below the
416 concentrations reported elsewhere in catchment soils (Vane et al., 2014). The extremely high
417 flows during winter 2013/2014 could have mobilized a large amount of contaminated soil
418 within the catchment and deposited it in the river sediment. The high flows during winter
419 2013/2014 were quite unusual for the Thames (Huntingford et al., 2014). Previous studies
420 found much higher PCB concentrations in urban soils than that in rural soils in England
421 (Environment Agency, 2007; Lu et al., 2015). The lower sub-catchments of Reach 6, 7 and 8
422 are characterised by urban land use. Moreover, with higher flows in the lower catchments,
423 more contaminated soil would be washed off to the river, thus could lead to remarkable
424 increases in the PCB concentrations. The model also represented a slow change of the PCB
425 concentrations (SOC associated) in the lower sediment layer of the River Thames during the
426 simulation period (Figures 4, SI 3 and SI 4). It could be a reflection of the long residence time
427 of the pore water in lower bed sediments.

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

1 433 with the responsibility for water quality monitoring are under increasing pressure to
2
3 434 rationalize or cut monitoring. Given the importance of long time series for the sustainable
4
5 435 management of water quality in the Thames (Howden et al., 2010), the UK (Battarbee et al.,
6
7 436 2014) and elsewhere (Fölster et al., 2014), there is a pressing need to derive the maximum
8
9
10 437 information possible from existing monitoring programs and to ensure their continuity. Given
11
12 438 these pressures, it is unlikely that monitoring agencies will be able to devote significant new
13
14
15 439 resources to low level analysis of environmental contaminants.

16
17 440 Models such as INCA-Contaminants can play an important role in maximizing the value of
18
19
20 441 agency monitoring data. The fate and transport of PCBs and other POPs is connected to the
21
22 442 cycling of DOC and suspended sediments in rivers and their catchments. Coupling these
23
24
25 443 cycles in modelling frameworks can lead to new insights about the environmental behaviour
26
27 444 of POPs and pose new hypotheses about their eventual fate. Using routine agency monitoring
28
29
30 445 data to augment the information obtained during POPs sampling campaigns can reduce the
31
32 446 predictive uncertainties about contaminant fate and transport and help to ensure the longevity
33
34
35 447 of monitoring programs by demonstrating their multi-functional nature.

36
37 448 Despite a ban on their production and significant clean-up efforts, PCBs and other legacy
38
39
40 449 POPs remain a problem in the Thames catchment and elsewhere. As atmospheric deposition
41
42 450 continues to decline, mobilisation from contaminated soils will become an ever more
43
44
45 451 important vector for POPs transport to the river. This problem is likely to become worse if
46
47 452 climate change leads to increased flooding, and may contribute to ongoing contamination of
48
49
50 453 the Thames ecosystem and delay achievement of Water Framework Directive good
51
52 454 ecological status. The sensitivity of POPs releases from soils on SOC ageing is also a factor,
53
54
55 455 which deserves further attention.

56
57 456
58
59
60
61
62
63
64
65

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.

481 **Acknowledgements**

1
2
3 482 The river flow data and the wind speed data were provided by CEH Wallingford. The authors
4
5 483 would also like to thank Mike Bowes for the DOC and suspended sediment data. The lead
6
7
8 484 author is grateful to Karl Davis and Wolfson College (Oxford) for providing the Steward
9
10 485 Award to support the academic visit to Swedish University of Agricultural Science (SLU).
11
12
13 486 MNF was supported by the Swedish Research Council, FORMAS.
14
15

16 487

18 488

21
22 489 **References**

23
24
25 490 Barber L.B., Writer J.H. Impact of the 1993 flood on the distribution of organic contaminants
26 491 in bed sediments of the upper Mississippi River. *Environmental Science &*
27 492 *Technology* 1998; 32: 2077-2083. doi: 10.1021/es970795i.

28
29
30 493 Battarbee R.W., *et al.* Recovery of acidified surface waters from acidification in the United
31 494 Kingdom after twenty years of chemical and biological monitoring (1988–2008).
32 495 *Ecological Indicators* 2014; 37: 267-273. doi: 10.1016/j.ecolind.2013.10.011.

33
34 496 Crooks S., Davies H. Assessment of land use change in the Thames catchment and its effect
35 497 on the flood regime of the river. *Physics and Chemistry of the Earth, Part B:*
36 498 *Hydrology, Oceans and Atmosphere* 2001; 26: 583-591. doi: 10.1016/S1464-
37 499 1909(01)00053-3.

38
39
40 500 Crossman J., *et al.* The interactive responses of water quality and hydrology to changes in
41 501 multiple stressors, and implications for the long-term effective management of
42 502 phosphorus. *Science of the Total Environment* 2013; 454: 230-244. doi:
43 503 10.1016/j.scitotenv.2013.02.033.

44
45
46 504 Dalla Valle M., *et al.* Reconstruction of historical trends of PCDD/Fs and PCBs in the Venice
47 505 Lagoon, Italy. *Environment International* 2005; 31: 1047-1052. doi:
48 506 10.1016/j.envint.2005.05.015.

49
50
51 507 Eggleton J., Thomas K.V. A review of factors affecting the release and bioavailability of
52 508 contaminants during sediment disturbance events. *Environment international* 2004;
53 509 30: 973-980. doi: 10.1016/j.envint.2004.03.001.

54
55
56 510 Environment Agency. UKHSH Report No. 8: Environmental concentrations of
57 511 polychlorinated biphenyls (PCBs) in UK soil and herbage, NO. 8. Bristol:
58 512 Environment Agency, Uk Soil And Herbage Pollutant Survey, [www.environment-](http://www.environment-agency.gov.uk)
59 513 [agency.gov.uk](http://www.environment-agency.gov.uk), 2007.

60
61
62
63
64
65

- 514 Evans H.E. The binding of three PCB congeners to dissolved organic carbon in freshwaters.
1 515 Chemosphere 1988; 17: 2325-2338. doi: 10.1016/0045-6535(88)90143-9.
2
- 3 516 Fölster J., *et al.* The Swedish monitoring of surface waters: 50 years of adaptive monitoring.
4 517 Ambio 2014; 43: 3-18. doi: 10.1007/s13280-014-0558-z.
5
6
- 7 518 Futter M.N., *et al.* Modeling the mechanisms that control in-stream dissolved organic carbon
8 519 dynamics in upland and forested catchments. Water Resources Research 2007; 43:
9 520 W02424, 16 pp. doi: 10.1029/2006wr004960.
10
- 11 521 Futter M.N., *et al.* PERSiST: a flexible rainfall-runoff modelling toolkit for use with the
12 522 INCA family of models. Hydrology and Earth System Sciences 2014; 18: 855-873.
13 523 doi: 10.5194/hess-18-855-2014.
14
15
- 16 524 Hope B.K. A model for the presence of polychlorinated biphenyls (PCBs) in the Willamette
17 525 River Basin (Oregon). Environmental Science & Technology 2008; 42: 5998-6006.
18 526 doi: 10.1021/es8000213.
19
20
- 21 527 Howden N., *et al.* Nitrate concentrations and fluxes in the River Thames over 140 years
22 528 (1868–2008): are increases irreversible? Hydrological Processes 2010; 24: 2657-
23 529 2662. doi: 10.1002/hyp.7835.
24
- 25 530 Hung C.-C., *et al.* Relationships between persistent organic pollutants and carbonaceous
26 531 materials in aquatic sediments of Taiwan. Marine Pollution Bulletin 2010; 60: 1010-
27 532 1017. doi: 10.1016/j.marpolbul.2010.01.026.
28
29
- 30 533 Huntingford C., *et al.* Potential influences on the United Kingdom's floods of winter 2013/14.
31 534 Nature Climate Change 2014; 4: 769-777. doi: 10.1038/Nclimate2314.
32
33
- 34 535 Jin L., *et al.* Modelling phosphorus in Lake Simcoe and its subcatchments: scenario analysis
35 536 to assess alternative management strategies. Inland Waters 2013; 3: 207-220. doi:
36 537 10.5268/Iw-3.2.520.
37
- 38 538 Jin L., *et al.* Modelling the impacts of climate change on flow and nitrate in the River
39 539 Thames: assessing potential adaptation strategies. Hydrology Research 2012; 43: 902-
40 540 916. doi: 10.2166/nh.2011.080.
41
42
- 43 541 Josefsson S., *et al.* Structure-related distribution of PCDD/Fs, PCBs and HCB in a river–sea
44 542 system. Chemosphere 2011; 83: 85-94. doi: 10.1016/j.chemosphere.2011.01.019.
45
46
- 47 543 Jürgens M.D., *et al.* PCB and organochlorine pesticide burden in eels in the lower Thames
48 544 river (UK) Chemosphere 2015; 118: 103-111. doi:
49 545 10.1016/j.chemosphere.2014.06.088.
50
- 51 546 Lazar A.N., *et al.* An assessment of the fine sediment dynamics in an upland river system:
52 547 INCA-Sed modifications and implications for fisheries. Science of the Total
53 548 Environment 2010; 408: 2555-2566. doi: 10.1016/j.scitotenv.2010.02.030.
54
55
- 56 549 Lohmann R., *et al.* Global fate of POPs: Current and future research directions.
57 550 Environmental Pollution 2007; 150: 150-165. doi: 10.1016/j.envpol.2007.06.051.
58
59
60
61
62
63
64
65

- 551 Lu Q., *et al.* The distribution of Polychlorinated Biphenyls (PCBs) in the River Thames
1 552 Catchment under the scenarios of climate change. *Science of the Total Environment*
2 553 2015; 533: 187-195. doi: 10.1016/j.scitotenv.2015.06.084.
3
- 4 554 Lu Q., *et al.* The current occurrence of organic chemicals in river Thames fish and sediment.
5 555 in preparations.
6
- 7
8 556 Ma Y., *et al.* Persistent organic pollutants in ocean sediments from the North Pacific to the
9 557 Arctic Ocean. *Journal of Geophysical Research: Oceans* 2015; 120: 2723-2735. doi:
10 558 10.1002/2014jc010651.
11
- 12 559 Meharg A.A., *et al.* PCB congener dynamics in a heavily industrialized river catchment.
13 560 *Science of the Total Environment* 2003; 314: 439-450. doi: 10.1016/S0048-
14 561 9697(03)00067-6.
15
- 16 562 Nash J., Sutcliffe J.V. River flow forecasting through conceptual models part I—A discussion
17 563 of principles. *Journal of Hydrology* 1970; 10: 282-290. doi: 10.1016/0022-
18 564 1694(70)90255-6.
19
- 20 565 Nizzetto L., *et al.* Assessment of contaminant fate in catchments using a novel integrated
21 566 hydrobiogeochemical-multimedia fate model. *Science of the Total Environment* 2016;
22 567 544: 553-563. doi: 10.1016/j.scitotenv.2015.11.087.
23
- 24 568 Nizzetto L., *et al.* Past, Present, and Future Controls on Levels of Persistent Organic
25 569 Pollutants in the Global Environment. *Environmental Science & Technology* 2010;
26 570 44: 6526-6531. doi: 10.1021/es100178f.
27
- 28 571 Pulkrabová J., *et al.* Organic pollutants in areas impacted by flooding in 2002: A 4-year
29 572 survey. *Bulletin of environmental contamination and toxicology* 2008; 81: 299-304.
30 573 doi: 10.1007/s00128-008-9486-6.
31
- 32 574 Ross G. The public health implications of polychlorinated biphenyls (PCBs) in the
33 575 environment. *Ecotoxicology and Environmental Safety* 2004; 59: 275-291. doi:
34 576 10.1016/j.ecoenv.2004.06.003.
35
- 36 577 Schenker U., *et al.* Improving data quality for environmental fate models: A least-squares
37 578 adjustment procedure for harmonizing physicochemical properties of organic
38 579 compounds. *Environmental Science & Technology* 2005; 39: 8434-8441. doi:
39 580 10.1021/es0502526.
40
- 41 581 Schuster J.K., *et al.* Temporal trends and controlling factors for polychlorinated biphenyls in
42 582 the UK atmosphere (1991-2008). *Environmental Science & Technology* 2010; 44:
43 583 8068-8074. doi: 10.1021/es102134d.
44
- 45 584 Sinkkonen S., Paasivirta J. Degradation half-life times of PCDDs, PCDFs and PCBs for
46 585 environmental fate modeling. *Chemosphere* 2000; 40: 943-949. doi: 10.1016/S0045-
47 586 6535(99)00337-9.
48
- 49 587 Sweetman A.J., *et al.* A dynamic level IV multimedia environmental model: Application to
50 588 the fate of polychlorinated biphenyls in the United Kingdom over a 60-year period.
51 589 *Environmental Toxicology and Chemistry* 2002; 21: 930-940. doi:
52 590 10.1002/etc.5620210507.
53
54
55
56
57
58
59
60
61
62
63
64
65

591 Sweetman A.J., Jones K.C. Declining PCB concentrations in the UK atmosphere: Evidence
1 592 and possible causes. *Environmental Science & Technology* 2000; 34: 863-869. doi:
2 593 10.1021/es9906296.
3
4 594 Urbaniak M. Polychlorinated biphenyls: sources, distribution and transformation in the
5 595 environment—a literature review. *Acta Toxicologica* 2007; 15: 83-93.
6
7
8 596 Vane C.H., *et al.* Polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls
9 597 (PCB) in urban soils of Greater London, UK. *Applied Geochemistry* 2014; 51: 303-
10 598 314. doi: 10.1016/j.apgeochem.2014.09.013.
11
12
13 599 Whitehead P.G., *et al.* An INCA model for pathogens in rivers and catchments: Model
14 600 structure, sensitivity analysis and application to the River Thames catchment, UK.
15 601 *Science of The Total Environment* 2016. doi:
16 602 <http://dx.doi.org/10.1016/j.scitotenv.2016.01.128>.
17
18
19 603 Whitehead P.G., *et al.* A semi-distributed Integrated Nitrogen model for multiple source
20 604 assessment in Catchments (INCA): Part I - Model structure and process equations.
21 605 *Science of the Total Environment* 1998; 210-211: 547-558. doi: 10.1016/S0048-
22 606 9697(98)00037-0.
23
24 607
25
26 608
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

609 **Table Captions List:**

610 Table 1. Sub-catchment information of the Thames system (according to LCM2000 land coverage map (CEH),

611 see also Figure. 2 for a map of the sub-catchments)

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

613 Table 3. Data sources for the INCA-contaminants modelling

614 Table 4. Model parameter values (min-max)

615 Table 5. The model performance for predictions of upper and lower sediment SOC associated PCB

616 concentrations based on initial manual calibration

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

618

619 **List of Figure Captions**

1
2 620 Figure 1. Conceptual figure showing the relationship between (i) different data sources useful for understanding
3
4 621 POPs fate in the environment and (ii) multi-media fate and hydrobiogeochemical modelling frameworks. –POPs
5
6 622 samples are typically expensive and infrequent. The additional information in water quality (WQ) and
7
8 623 hydrometeorological (PTQ: precipitation, temperature and flow) time series can augment and contextualize the
9
10 624 information in POPs measurements, thereby reducing the uncertainties in POPs fate and transport estimates.
11
12 625 Fugacity models require less information inputs and mainly focus on POPs data, but employ highly simplified
13
14 626 representation of environmental parameters and have high uncertainties; INCA models make use of POPs data
15
16 627 as well as the more frequent and less expensive WQ and flow PTQ data, thus it is possible to obtain additional
17
18 628 insights and reduce uncertainty.

20
21 629 Figure 2. Map of the River Thames Catchment showing the points where flow, water chemistry and sediment
22
23 630 PCB concentrations were simulated.

24
25
26 631 Figure 3. (a) Observed and simulated flow for reach 6 (Caversham - Shepperton); (b) Observed and simulated
27
28 632 suspended sediment data for reach 6; (c) Observed and simulated DOC data for reach 2 (Pinkhill - Osney).

29
30 633 Figure 4. The simulated dynamics concentrations of PCB 153 in water column, upper sediment and lower
31
32 634 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 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 |
| | Atmospheric wet deposition | 2.0E+05 | 2.0E+07 | ng/day/km ² |
| PCB 118 | 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 |
| | 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 |
| PCB 153 | 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

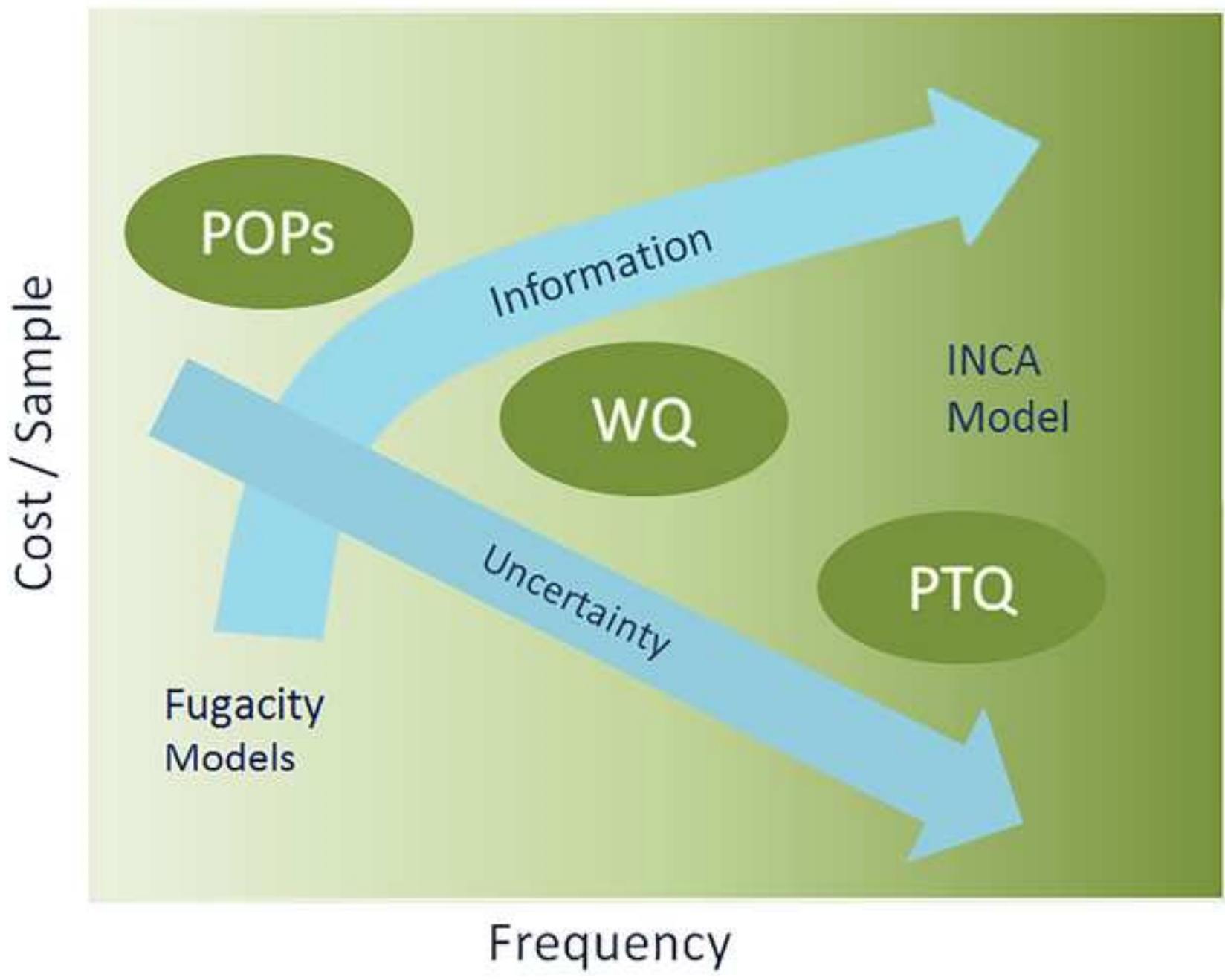
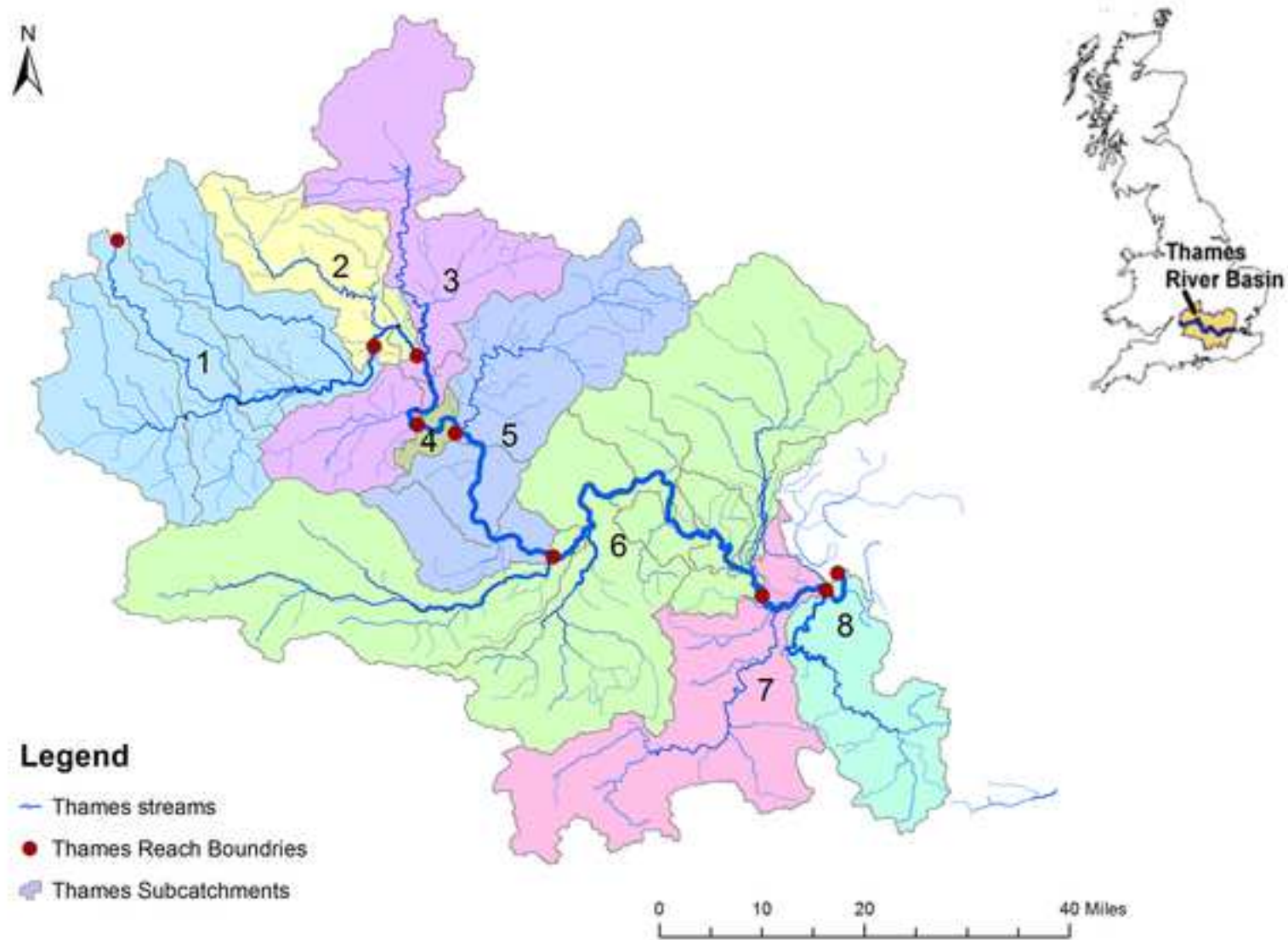


Figure 2



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

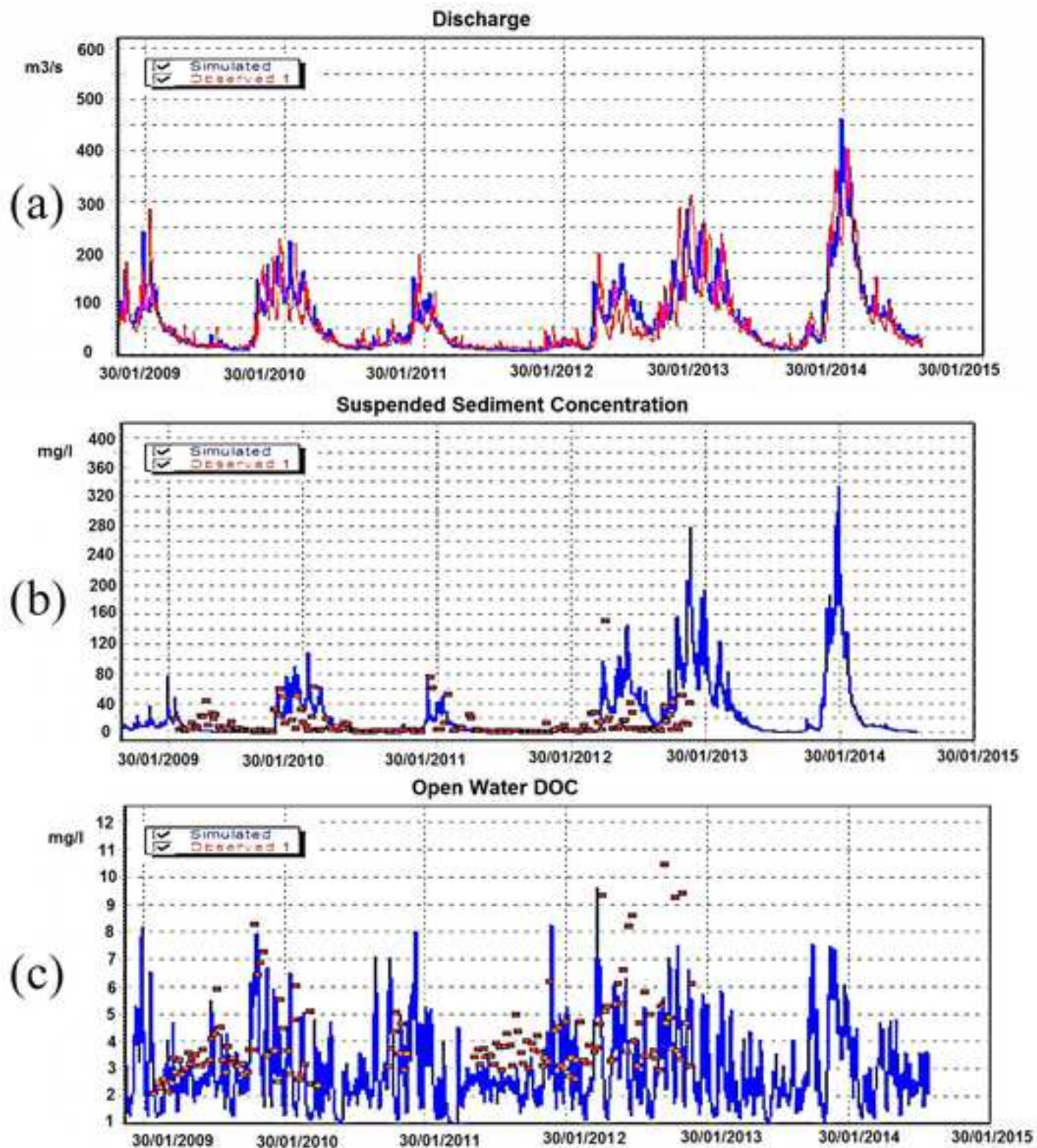
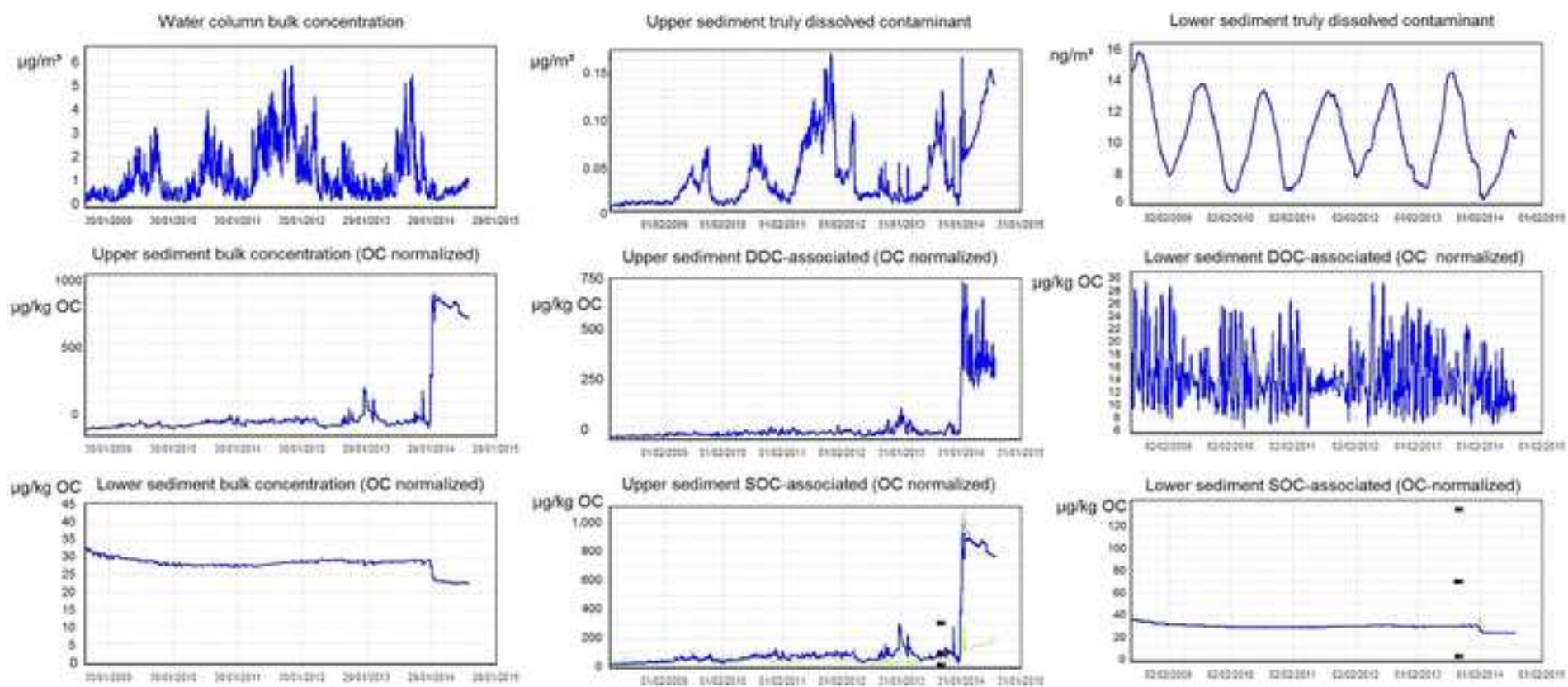


Figure 4



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

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

Contents

| | |
|---|---|
| 1. The INCA-Contaminants Model | 2 |
| 2. Measured Sediment Concentrations..... | 5 |
| 3. Predicted PCB Dynamics in the Thames System..... | 6 |
| 4. References..... | 9 |

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;

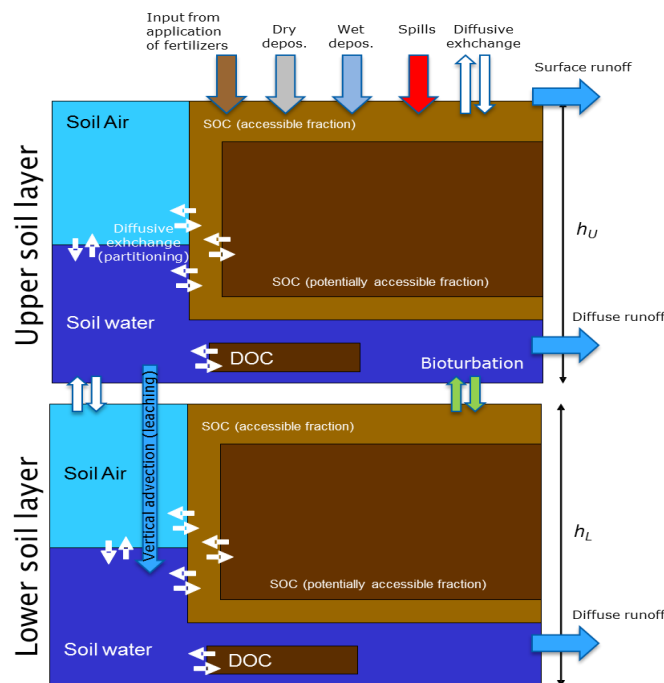


Figure. SI 1 Structure of the soil compartment, adapted from Nizzetto et al. (2016)

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

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

The mass of potentially accessible SOC in upper soil

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

Air-water partitioning coefficient

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

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

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.

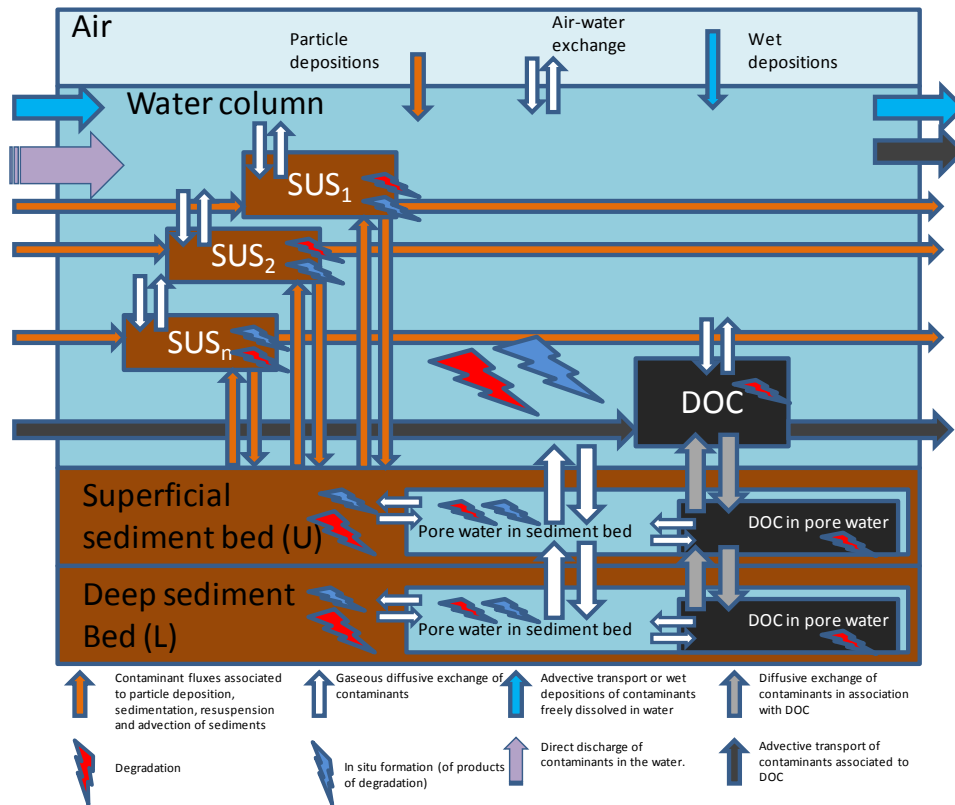


Figure. SI 2 Structure of the in-stream compartment, adapted from Nizzetto et al. (2016)

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):

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

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

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

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

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

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.

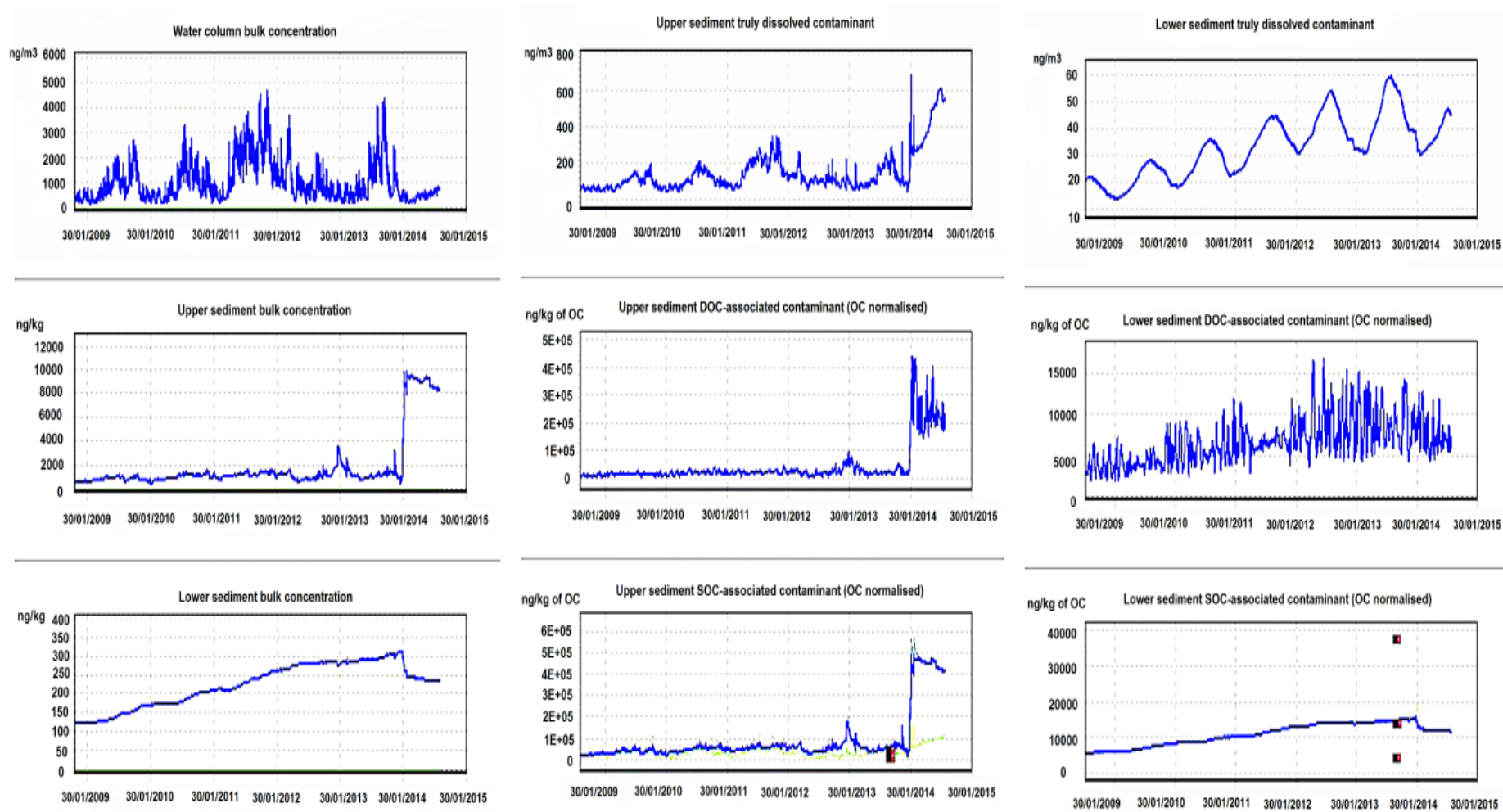


Figure SI 3. The simulated dynamics of PCB 52 in water column, upper sediment and lower sediment layers for Reach 6

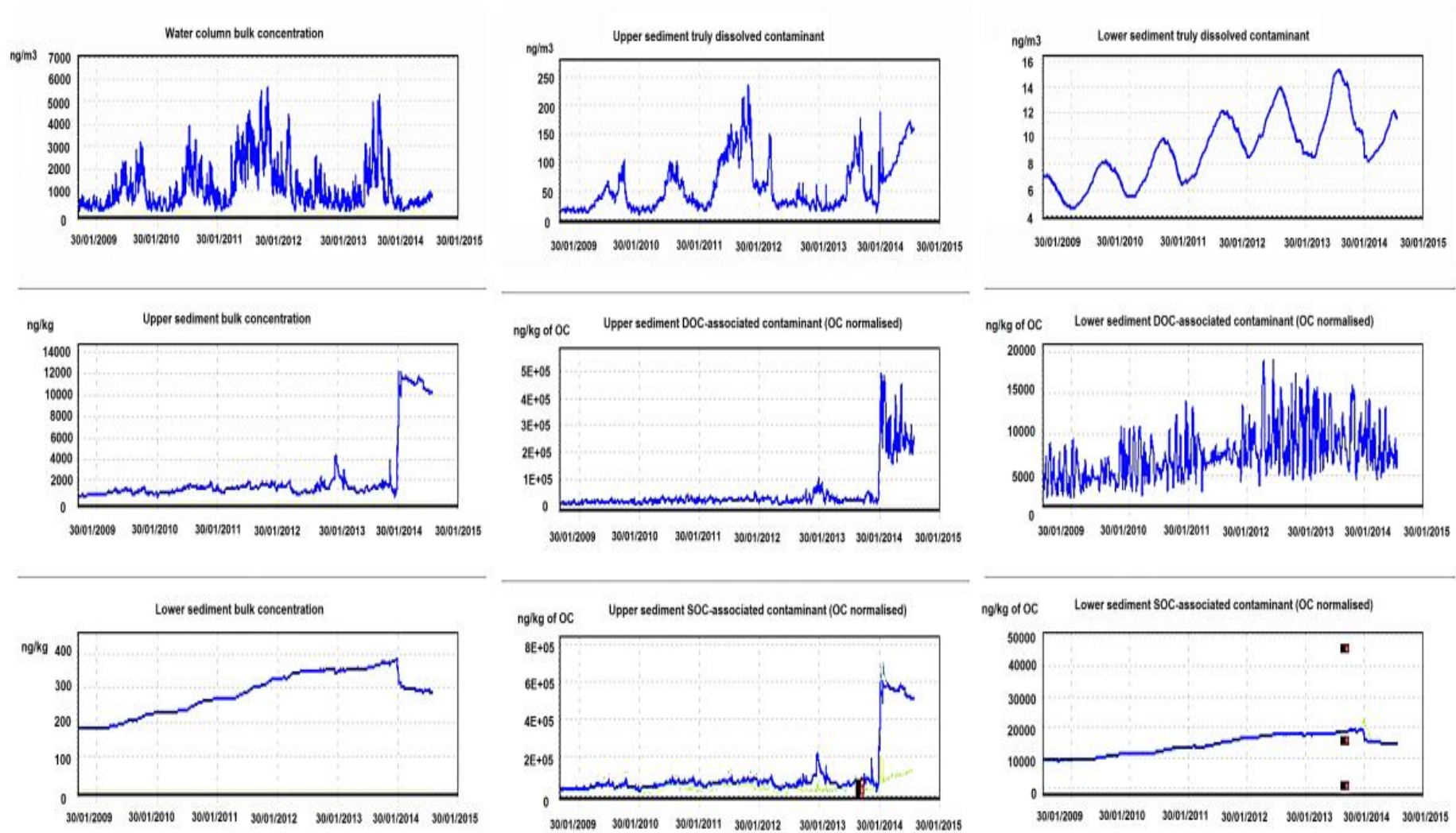


Figure SI 4. The simulated dynamics of PCB 118 in water column, upper sediment and lower sediment layers for Reach 6

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.