

**School of Geography and the Environment**

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*Modelling of Pesticides and POPs in the River Thames System:*

*Potential Impacts of Changes in Climate and Management*

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# Publications

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# Abstract

Due to environmental concerns, most of persistent organic pollutants (POPs) have been eliminated or reduced in production and use; however, due to their great persistency, POPs are expected still to be found in the environment long after their use has ceased. Although, in recent years, POPs have rarely been detected in river water in the United Kingdom (UK), their concentrations in fish (biota) and sediment are expected to be notable due to their lipophilicity and bioaccumulation; however, there is a lack of information and data to understand the current contamination of POPs in catchments and evaluate their potential risk to the environment and ecosystem.

This thesis describes the application of mathematical modelling approaches to (i) predict the current distribution and concentration of POPs in catchments, (ii) evaluate the influence of climate change and extreme weather conditions on the fate of POPs, and (iii) provide guidelines to inform decision-making on managing the potential risks of POPs in river basins. The modelling studies have mainly focussed on polychlorinated biphenyls (PCBs). The River Thames catchment was chosen as the study area. The Fugacity level III model was initially used to describe the general distribution of PCBs between different compartments; it was predicted that the greatest mass of PCBs remain in the soil, but the fish and sediments represent compartments with the highest PCB concentrations. The contamination of PCBs in Thames fish was estimated to exceed the unrestricted consumption thresholds of 5.9  $\mu\text{g}/\text{kg}$  for  $\sum\text{PCBs}$  set by the U.S. Environmental Protection Agency (EPA); no current EU Environmental Quality Standards (EQS) are available for PCBs in fish. It was indicated that the PCBs in fish could be linked to PCB contamination in sediment, which was predicted to be about three times higher than the fish concentrations, but insufficient observed data of

PCBs in Thames fish and sediment are available to validate the results. In order to address this limitation in observed data, fish and sediment sampling and chemical analysis were carried out for the presence of POPs. In addition to PCBs, the measured results for hexachlorobenzene (HCB) and polybrominated diphenyl ethers (PBDEs) in Thames fish and sediment were assessed. Although the observed fish- and sediment concentrations of the chemicals appear quite variable, when normalised to organic carbon the levels in sediment, they were comparable to the fish lipid normalised concentrations. Using the temperature and rainfall data forecasts in the UK Climate Projections 2009 (UKCP09), climate change scenarios were established and assessed in the fugacity modelling. The modelling results suggested a modest influence of climate change on PCB fate over the next 80 years. The most significant result was a tendency, in the Thames catchment, for climate change to enhance the evaporation of PCBs from soil to air.

While the fugacity model successfully simulated the distribution and fate of PCBs, we used greatly simplified representations of climate, hydrology and biogeochemical processes of the catchment: to have a deeper understanding, a newly developed dynamic hydro-biogeochemical transport model—the Integrated Catchment Contaminants model (INCA-Contaminants) was applied. Using additional information about weather, river flows and water chemistry, the INCA-Contaminants model provided new insights into the behaviour of contaminants in the catchment; this led to a better representation of PCB contamination in sediment. In addition, INCA demonstrated the important impact of short-term weather variation on PCB movement through the environment. It was shown that PCBs contamination in Thames sediment was greatly disturbed by the severe flooding that occurred in early 2014.

This thesis presents the application of the INCA model to assess—in addition to POPs—the behaviour of metaldehyde in the River Thames catchment. Metaldehyde is a type of pesticide used mainly to kill snails and slugs. Its application in agricultural areas within the catchment area has in recent years caused severe problems with drinking water supply. The INCA model has proved to be an effective tool for simulating the transport of metaldehyde in the catchment, predicting observed metaldehyde concentrations at multiple locations in the River Thames; this is the first time that a dynamic modelling approach has been used to predict the behaviour of metaldehyde in river basins. Modelling results showed that high concentrations of metaldehyde in the river system are a direct consequence of excessive application rates. In this thesis, a simple decision-support tool was derived from modelling results, based on variable application rates and application areas. This decision-support tool is now being used by Thames Water to help control peak concentrations of metaldehyde at key water supply locations.

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# Chapter 1. Introduction

## 1.1 Background

With the development of modern chemical industry and agriculture, many substances have been produced and applied that do not degrade naturally. Persistent organic pollutants (POPs) are among these substances and posed a great threat to ecosystems and the global environment and (Jones and De Voogt, 1999). Owing to their persistence and semi-volatile properties, POPs can undergo long-range atmospheric transport and tend to disseminate on a global scale. Also, POPs can be deposited into aquatic systems and bio-accumulate in the food chain, which can pose a wide range of risks to river basin ecology and human health (Jones and De Voogt, 1999; Darko *et al.*, 2008). In order to reduce the risk of POPs in the environment, increasing efforts have been put into reduction and cessation of the production and use of POPs; in the UK, this was achieved in the 1970s (Environment Agency, 2007; Lu *et al.*, 2015). POPs are hydrophobic. In recent years, POPs have rarely been detected in water from UK rivers (Environmental Agency WIMS database: <http://discovery.nationalarchives.gov.uk/details/r/C16031>); however, it has been reported that the concentrations of some POPs in fish samples collected from different rivers of the UK remained high (Jürgens, 2015); these are likely to have derived from diffuse and secondary sources in the catchment. With improvements in analytical methods, in addition to POPs, some pesticides that had not previously been detected have regularly been observed at trace levels in surface and groundwater. In the past ten years in the UK, pesticides such as metaldehyde, simazine, isoproturon and mecoprop have regularly been detected in raw waters at levels many times higher than the EU/UK standard of 0.1µg/L (Skinner *et al.*, 1997; Environment Agency, 2009). These pesticides break down very slowly in water and, with

current treatments systems, their eradication cannot be easily achieved. Residual POPs and pesticides in river basins remain a matter of major concern and pose a high level of risk to ecosystems and human health. Constructing strategies to manage this risk is challenging, as very little information on the fate of POPs and pesticides in catchments is available, on both global and local scales.

This thesis addresses this challenge by developing field monitoring programmes and scenario-based modelling that interpret the current contamination of POPs and pesticides and predict their behaviour in a given catchment. The River Thames catchment has been chosen as the study area. Fish and sediment samples were taken from a number of sites along the River Thames and analysed at the Lancaster University Environment Centre for the presence of POPs and pesticides. Polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and metaldehyde have been chosen as the study chemicals. PCBs and PBDEs were listed as POPs under the Stockholm Convention (Stockholm Convention on POPs, last checked Jan 2017), while metaldehyde is a type of molluscicide that is used mainly to control slugs and protect crops (Environment Agency, 2009). Due to analytical complexity and high cost, the frequency of measurements was relatively low.

In order to have a deeper understanding of potential risks of POPs in catchment, mathematical modelling approaches were used to predict the distribution and transport of the contaminants throughout the environment. In this thesis, the fugacity model has been applied to assist in understanding the fate of the chemicals in the River Thames catchment; it is a multi-media mass balance model that employs the concept of fugacity as a thermodynamic equilibrium criterion and treats partitioning of chemicals between different environmental compartments (Mackay, 2001). The approach has been successfully employed in rivers, lakes and other water bodies all over the world and has proved to be an effective tool in the risk

assessment and management of water resources (Thompson *et al.*, 1999; Wodarg *et al.*, 2004; Dalla Valle *et al.*, 2005). The physicochemical properties of POPs and pesticides are temperature-dependent (Dalla Valle *et al.*, 2007). It has been indicated that the fate and transport of POPs and pesticides in a catchment could be influenced by climate change but, so far, very few studies have integrated the climate change issues into the fate assessment of POPs and pesticides in river basin systems. In this thesis, the fugacity model has also been applied to address how climate change might influence the fates of POPs and pesticides in a catchment.

In the River Thames catchment, there is a large degree of spatial heterogeneity in land cover and temporal variation in weather conditions (Jin *et al.*, 2012). As a result, the contamination levels of POPs and pesticides could vary significantly between sub-catchments and change over time. With its greatly simplified representations of climate, hydrology and biogeochemical processes, the fugacity model can only predict general conditions across a region and has limited ability to represent environmental variability (Lu *et al.*, 2016). In response to this limitation, this thesis puts forward a process-based and semi-distribution approach—the INCA-Contaminants model—to simulate the contaminants dynamics in the River Thames catchment. The INCA-Contaminant model, developed by Nizzetto *et al.* (2016), is the newest member of the INCA family (Whitehead *et al.*, 1998). Providing integrated simulations of river flow, dissolved organic carbon (DOC), suspended sediment and contaminant dynamics, it offers an improved representation of contaminant dynamics in a catchment. In this thesis, the INCA model was set up for PCBs (Lu *et al.*, 2016) and metaldehyde. Water quality management scenarios were established and tested with INCA. The modelling approach illustrates the consequences of severe weather conditions, such as flooding. Based on these evaluations, simple management strategies for chemical control in the catchment were developed.

## **1.2 Research objectives**

- To assess the general distribution of POPs and identify the key controls of transport and transformation in the River Thames catchment.
- To understand the current occurrence of the POPs in the Thames fish and sediment.
- To understand the bioaccumulation of these chemicals in Thames fish and assess whether fish and bed-sediment concentrations can be correlated.
- To simulate the concentration dynamics of the POPs and address the potential impact of extreme weather conditions (flooding) on the behaviour of the chemicals in the catchment.
- To apply the INCA-Contaminant model to describe the transport and behaviour of metaldehyde in the catchment.
- To elaborate guidelines for the management of the chemicals on the catchment scale.

## **1.3 Structure of thesis**

This thesis consists of seven chapters; its structure is illustrated in Figure 1.3-1. The first chapter describes current concerns on residual POPs and pesticides in river basins. It provides a brief description of the main contents and demonstrates the importance of the study. Chapter 2 reviews the physico-chemical properties of POPs and pesticides and their behaviours in the environment. It outlines the background information and the conceptualisation description of the fugacity and INCA-Contaminants model, which are used in this work to predict the distribution and transport of POPs and pesticides in catchments.

In Chapter 3, a level III fugacity model was applied to predict the distribution of selected PCB congeners (PCB 52, PCB 118 and PCB 153) in the River Thames catchment. The model also examines the potential influence of climate change on the fate of PCBs in the catchment.

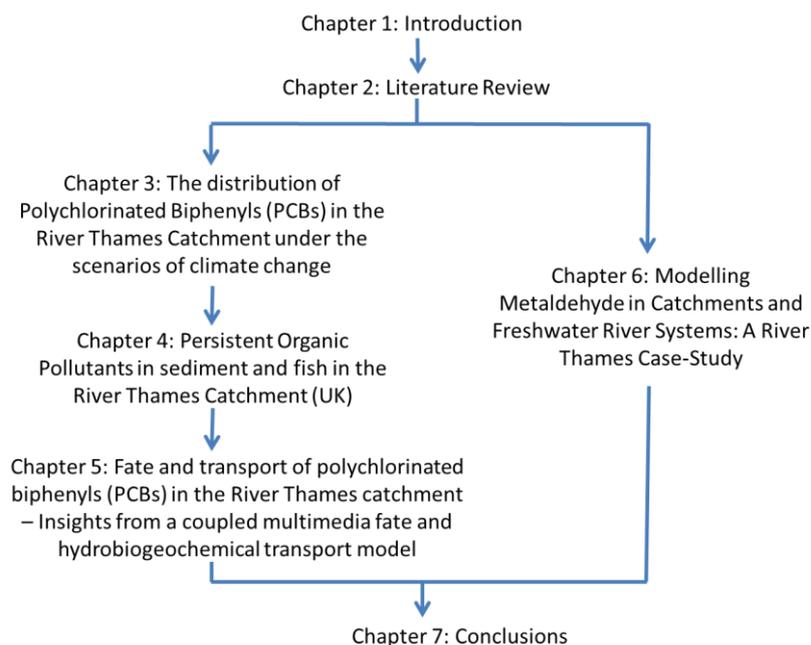


Figure 1.3-1 Structure of this thesis by chapter

Chapter 4 describes the sampling and chemical analysis methods and presents the measured concentrations of PCBs, PBDEs and HCB in both bed sediment and fish in the Thames Basin. In addition, the correlation between bed sediment and fish POP concentrations was assessed.

In Chapter 5, a daily time-step, dynamic-coupled, multimedia fate and hydro-biogeochemical transport model (INCA-Contaminants) was applied to the River Thames catchment. By providing integrated simulations of river flow, dissolved organic carbon, suspended sediment and POP dynamics, the INCA contaminants model leads to a much better representation of the behaviour of POPs in the river system. Chapter 5 also demonstrates the impact of short-term weather variation on the movement of these chemicals in the environment.

Chapter 6 describes the application of the INCA-Contaminants model to simulate metaldehyde transport from areas of application to the aquatic environment. The concentrations of metaldehyde in the River Thames could be a direct consequence of excessive application rates. The assumption was tested in Chapter 6 and, based on the model

results, a simple application control strategy for metaldehyde in the Thames catchment is presented.

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# Chapter 2. Literature review

## 2.1 Persistent organic pollutants (POPs) and pesticides

Persistent organic pollutants (POPs) are a set of organic substances having the characteristics of long-term survival, semi-volatility, bioaccumulation and toxicity. POPs have long half-lives and can persist in the environment for a long period of time (Smaranda and Gavrilesco, 2008). POPs are also noted for their semi-volatility, which allows them to occur either in the vapour phase or adsorbed on to atmospheric particles. Due to this great environmental persistence, coupled with semi-volatile properties, POPs can survive long-range transport between various environmental media (air, water, biomass and so forth) and tend to distribute themselves on a global scale. They have been found and measured on every continent, at sites representing every geographical sector and climatic zone throughout the world—even in isolated regions with no history of their usage or direct emission (Atlas and Giam, 1981; Barrie *et al.*, 1992). POPs also have the property of lipophilicity, which enables them to bio-concentrate into organisms from a surrounding medium. Persistence and lipophilicity give POPs the ability to bio-accumulate and bio-magnify in the food chain, which can present a wide range of risks to the ecology and human health (Ritter *et al.*, 1995).

Although there are natural sources of organochlorines, most POPs originate from anthropogenic sources. According to their different sources and intended purposes, POPs can be divided into three groups: pesticides [such as dichlorophenyltrichloroethane (DDT), hexachlorobenzene (HCB), and hexachlorocyclohexane (HCHs)], industrial chemicals [such as polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and polychlorinated naphthalenes (PCNs)] and chemicals that are accidentally formed and released [such as dioxins, furans, and

certain PCBs, HCBs, and polycyclic aromatic hydrocarbons (PAHs)] (Stockholm Convention on POPs, last checked Jan 2017).

POPs began to appear in the late 19th century (due to the synthesis of DDT in 1873) and were developed and produced for use in the early 20th century (1930s or 1940s). Through the 1950s and 1960s, there was an increasingly widespread use of POPs in developed countries (such as Europe and North America) (Jones and De Voogt, 1999). POPs were widely used both in agriculture and industry and for public health disease vector control. They have been applied to prevent an incipient epidemic of typhus and were used to combat mosquitoes that carried malaria during and after the Second World War. As the application of POPs reached its peak in the 1960s, the general public became aware of their adverse environment impacts; there was increasing concern over their high persistence in the environment and bio-accumulation in the food chain, which resulted in restrictions on usage of POPs in developed countries in the 1970s. Through the 1980s and -90s, most of the dangerous POPs, such as PCBs, had been eliminated or had their usage restricted in Europe and North America (Jones and De Voogt, 1999). In 2001, more than 90 countries had signed the Stockholm Convention on Persistent Organic Pollutants, which initially listed 12 persistent organic pollutants to be eliminated or severely restricted. Since 2009, 10 new chemicals have been added to the list of POPs under the 4th and 5th meetings of the Stockholm Convention (Stockholm Convention on POPs, last checked Jan 2017).

It is very difficult to provide reliable and accurate estimates of the historical or contemporary usage of POPs in the world: most of them have been eliminated; however, current information indicates that some (e.g. DDT and PFOS) are still in use in some developing countries (Stockholm Convention on POPs, last checked Jan 2017). Additionally, there are still many diffuse and secondary sources of POPs in the environment, which are very difficult to estimate (Sweetman *et al.*, 2002). Apart from those in use of agriculture and industry, there are some POPs, such as dioxins and furans, that are accidentally formed and released during combustion

processes. There is very limited information relating to these unintentionally formed POPs. There is still great uncertainty about their sources, emission and deposition discrepancies in various regions (Jones and De Voogt, 1999).

In addition to the recognized POPs, the substances which are used as substitutes can lead to further problems. With the improvement in analytical methods, a number of chemicals which were not previously detected have been regularly observed in bodies of fresh water: for example, some pesticides, including simazine, isoproturon, metaldehyde and so on, have regularly been detected exceeding the European Union's (EU) Water Framework Directive limits of 0.1µg/L in rivers and lakes in England and Wales (the concentrations of pesticides in Thames at Teddington Weir were illustrated as an example, Figure 2.1-1) (Environment Agency, 2012).

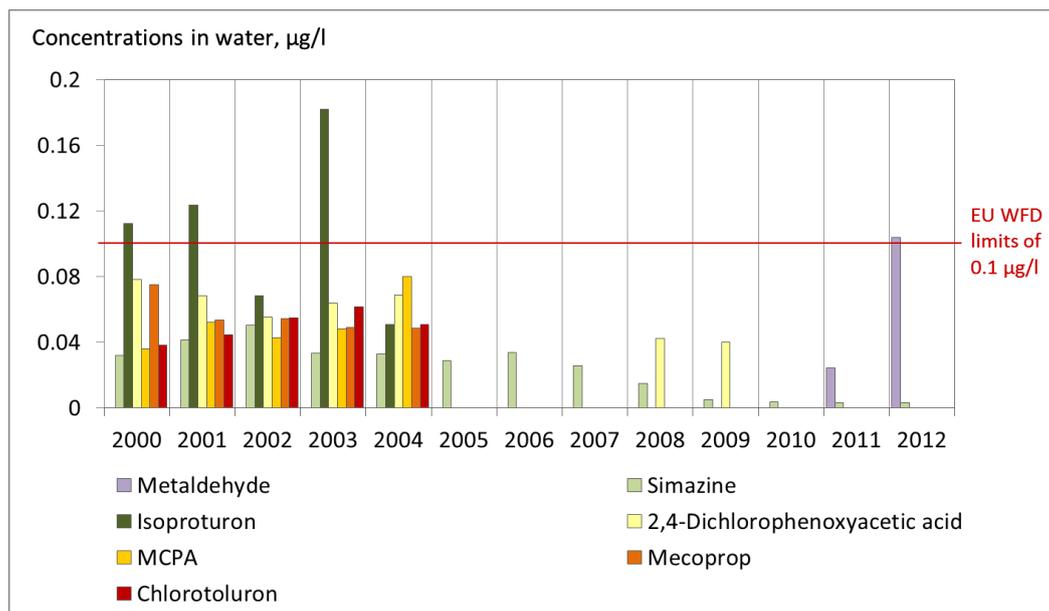


Figure 2.1-1. The contaminations of pesticides in the Thames at Teddington Weir (2000 – 2012) (data source: Environment Agency)

## 2.2 Status of POPs in the environment

Many researchers have looked into atmospheric global transportation of POPs into remote areas; Wania and Mackay (1993) first proposed the hypothesis of global distillation, to explain why relatively high concentrations of POPs have been detected in such remote areas

as the Arctic. Meteorological factors also indicate that the distribution of POPs in the atmosphere is associated with seasonal exchange of temperature. Later, in 1995, Wania and Mackay further demonstrated the ‘grasshopper effect’, which explained the shift of POP transportation according to seasonal temperature changes in mid-latitudes (Wania and Mackay, 1995).

### **2.2.1 POPs in soil**

Due to the strong affinity between POPs and organic matter in soils, POPs are likely to sink and be preserved in soil; hence, soil represents an important global inventory of most types of POPs. The POPs in soil systems can be taken up by plants and animals, washed into bodies of water through run-off, or may leach into deep-layer soils. Additionally, POPs in soils can re-volatilize into the atmosphere, thus become a continuing, diffuse source of atmospheric POPs: the POP burden in soils is therefore a complicated function of balance between inputs and losses (Meijer *et al.*, 2003). Less-volatile POPs are stable in soil profiles, while more-volatile POPs are likely to undergo downward transport to deeper soil layers. The soil-air exchange of more-volatile POPs could therefore be limited as they move downwards from the upper soil layers (Moeckel *et al.*, 2008).

### **2.2.2 POPs in rivers**

POPs are widely distributed in various environments—the atmosphere, soils, rivers, groundwater, oceans and so forth. Of these, the river environment is of the most significance in exposure of humans and ecosystems to POPs. The river environment consists of the water and sediment. The discovery of POPs existing in water and sediment can indicate the extent of POP contamination and their accumulation characteristics in river ecosystems. Fresh water is the most direct medium of exposure to POPs for ordinary people. Due to their property of

hydrophobicity, POPs in water are likely to interact with the organic matter in suspended sediment and, finally, to accumulate into sediments; therefore, their levels in freshwater are normally lower than those in sediment or aquatic biosystems (Sweetman *et al.*, 2002; Bogdal *et al.*, 2010; Lu *et al.*, 2015). In Europe, many POPs have for decades been banned, or their production and use restricted; in recent years, the concentrations of POPs in surface water in the UK have always been detected to be lower than the detection limit (Jürgens, 2015; Jürgens *et al.*, 2015; Lu *et al.*, 2015).

Within the river environment, it is particularly important to consider the sediment layers, containing large amounts of sedimentary organic matter, which can act as an attractive sorbent for POPs; high concentrations of POPs are therefore frequently found in bed sediments (Covaci *et al.*, 2006; Vane *et al.*, 2007; Vane *et al.*, 2010); sediment could be a major sink/source for POPs in river systems. Under particular circumstances, POPs in sediment can be released back into the water. Zeng *et al.* (1999) noticed that the concentration of DDTs in the Palos Verdes Peninsula, California, increased with the depth of sea water, which implied that the contamination came from the surface sediments of the sea floor. Rivers sediments are also one of the main sources of POPs entering the food chain. It has been widely observed that fishes and other aquatic organisms can accumulate high concentrations of POPs through long-term exposure to the contaminated water and sediment, or through the food chain (Van Geest *et al.*, 2011; Lopes *et al.*, 2012; Verhaert *et al.*, 2013); this phenomenon is referred to as bio-concentration, bio-accumulation and bio-magnification (Mackay and Fraser, 2000). Bio-concentration refers to the uptake of POPs by absorption from water only. Of particular concern is bioaccumulation in fishes, which is caused by the retention of POPs as they pass from organism to organism in the food chain, resulting in significantly high concentrations at high trophic levels. Bio-magnification is a special form of bio-accumulation, in which the concentration of POPs exceeds that in the fishes' diet due to

dietary absorption (Mackay and Fraser, 2000). The bio-accumulation levels of POPs in aquatic organisms can be one of the factors in determining the qualities of water and sediment (Mackay and Fraser, 2000; European Union, 2013). Assessing the degree of bioaccumulation is now becoming a component of national and international efforts to identify and control the distribution of POPs and their adverse effects in river ecosystems.

## 2.3 Chemicals of interest

### 2.3.1 Polychlorinated biphenyls (PCBs)

- What are PCBs?

PCBs are a group of man-made, chlorinated, aromatic, organic compounds which have been widely used as dielectric and coolant fluids in industrial and commercial applications including electrical apparatus, heat transfer equipment, plastics and

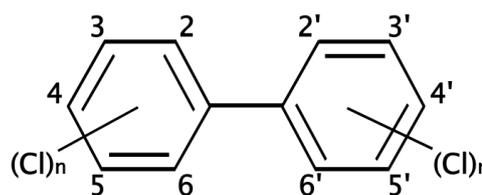


Figure 2.3-1. Structure of PCBs

rubber products and carbonless copy paper. The chemical structure of PCBs is a biphenyl ring with one to ten chlorine atoms attached at different positions ( $C_{12}H_{10-x}Cl_x$ ) (Figure 2.3-1). There can be 209 possible configurations with 1–10 chlorine atoms, and about 130 of these were found in commercial use. The production of PCBs in the UK started in the 1930s and peaked in the early 1970s, before dropping rapidly after a ban was imposed in 1977 (Sweetman *et al.*, 2002). It has been estimated that a total of 66 750 tonnes of PCBs have been produced in the UK. The direct emission of PCBs dropped dramatically after the restriction and ban on their production and use. After the 1970s, the main sources of PCBs entering the environment could be the old PCB-containing equipment or the disposal of such equipment (NAEI, 2011). With the phasing-out of this old equipment, the secondary

emissions from soil and sediment have become significant sources of pollution in recent years (Ghosh *et al.*, 2003; Lu *et al.*, 2015).

- The properties of PCBs

The PCB congeners vary widely in their physico-chemical properties. Among the PCBs, seven congeners (the 'ICES 7': PCBs 28, -52, -101, -118, -138, -153 and -180) were most commonly detected in the environment, so they were often used as indicators for the contamination of PCBs in the environment. The major physico-chemical properties of the ICES 7 PCBs are illustrated in Table 2.3-1. PCBs have low vapour pressure and water solubility; they are very stable in the environment, especially in soil and sediment. The heavier PCBs are more persistent than the lighter ones. PCBs are possible human carcinogens and they can also cause a variety of adverse health effects in animals, including suppression of the immune response, hormone disruption, damage to the nervous system and so on. They can be divided into two groups: 'non dioxin-like PCBs' and 'dioxin-like PCBs', according to their respective mechanisms of toxicity. Dioxin-like PCBs have structure features and toxicological properties that are similar to 2,3,7,8-tetrachloro-dibenzo-dioxin (TCDD) (Jürgens, 2015). Toxicity equivalency factors (TEF) were assigned by the World Health Organization to assess the relative toxicities of dioxin-like PCBs in relation to 2,3,7,8-tetrachloro-dibenzo-dioxin (Ahlborg *et al.*, 1994; Jürgens, 2015; Lu *et al.*, 2015).

Table 2.3-1. Physico-chemical parameters of the selected PCBs (25°) (Sinkkonen and Paasivirta, 2000)

	PCB 28	PCB 52	PCB 101	PCB 118	PCB 138	PCB 153	PCB 180
Molar mass	257.5	292.0	326.4	326.4	360.0	360.9	395.3
Molar volume	247.3	268.2	289.1	289.1	310.0	310.0	330.9
Henry's law constant	29.1	27.2	20.6	10.8	26.6	18.4	7.7
$\Delta H_{OW}$ (kJ/mol) *	-28.4	-37.6	-8.8	-23.0	-17.4	-17.5	-8.3
$\Delta H_{AW}$ (kJ/mol) *	47.2	48.4	71.0	66.9	72.5	71.0	74.1
Log $K_{ow}$	5.7	5.8	6.3	6.7	6.7	6.8	7.2
Half-life in air (day)	25	25	100	120	250	250	500
Half-life in water (day)	1000	1250	2500	2500	5000	5125	10000
Half-life in soil (day)	1083	3650	2300	2300	6875	6875	13750
Half-life in sediment (day)	1083	3650	3650	3650	6875	6875	13750

\*  $\Delta H_{OW}$  - enthalpy of phase transfer between octanol and water;  $\Delta H_{AW}$  - enthalpy of phase transfer between air and water.

- Regulations and environmental quality standards

The production of PCBs ceased in 1976 and the use of PCBs in new products was banned in the UK in 1986. In July 2000, The Environmental Protection (Disposal of Polychlorinated Biphenyls and other Dangerous Substances) (England and Wales) Regulations 2000 provided authority to require reporting of the possession of PCBs or contaminated equipment in the UK (Environment Agency, 2007). PCBs were listed as the initial 12 POPs at the Stockholm Convention 2001 for international action (Stockholm Convention on POPs, last checked Jan 2017).

Although extensive regulatory action and effective bans on their use have been put in place, PCBs still persist in the environment in recent years. The Environmental Quality Standards (EQS) for PCBs in water are not available, as they were always found to be less than the detection limit. There is currently an EU standard of 0.0065  $\mu\text{g}/\text{kg}$  for dioxins and dioxin-like compounds (PCDD + PCDF + DL-PCBs) in fish. No EU standard for non-dioxin-like PCBs has been available, but the U.S. Environmental Protection Agency has proposed an unrestricted consumption threshold of 5.9  $\mu\text{g}/\text{kg}$  for  $\Sigma$  PCBs in fish (U.S. EPA, 2000; Lu *et*

al., 2015). There are no congener-specific quality guidelines for PCBs in freshwater sediment, but Environmental Assessment Criteria (EAC) for the ‘ICES7’ PCBs in marine sediment have been defined by the Oslo and Paris Convention (OSPAR). Detailed information on the EQS for PCBs can be found in Table 2.3-2.

Table 2.3-2. Environmental Quality Standards for PCBs, PBDEs, HCB and Metaldehyde

	PCBs	PBDEs	HCB	Metaldehyde
Water	Not applicable	EU: MAC-EQS <sup>a</sup> 0.14 µg/L for Σ 6 BDEs	EU: MAC-EQS <sup>a</sup> 0.05 µg/L	EU Drinking Water Directive <sup>d</sup> : 0.1 µg/L for each individual pesticide
Biota <sup>c</sup> (fish)	EU: 0.0065 µg/kg TEQ <sup>b</sup> for dioxins and dioxin-like compounds (PCDD + PCDF + DL-PCBs) US EPA unrestricted consumption thresholds: 5.9 µg/kg for Σ PCBs	EU: 0.0085 µg/kg wet weight for Σ 6 BDEs	EU: 10 µg/kg	Not applicable
Sediment	OSPAR EAC <sup>c</sup> (dry weight): 1.7 µg/kg for PCB 28; 2.7 µg/kg for PCB 52; 3.0 µg/kg for PCB 101; 0.6 µg/kg for PCB 118; 7.9 µg/kg for PCB 138; 40 µg/kg for PCB 153; 12 µg/kg for PCB 180.	Not applicable	Not applicable	Not applicable

<sup>a</sup> MAC-EQS: maximum allowable concentration in inland surface waters (European Union, 2013)

<sup>b</sup> TEQ: toxic equivalents according to the World Health Organisation 2005 Toxic Equivalence Factors (Ahlborg *et al.*, 1994)

<sup>c</sup> OSPAR EAC: the Oslo and Paris Convention Environmental Assessment Criteria set up for the use in marine sediment (OSPAR, 2009)

<sup>d</sup> Council Directive 98/83/EC: <http://eur-lex.europa.eu/Legal-content/EN/TXT/PDF/?uri=CELEX:31998L0083&from=EN>

### 2.3.2 Polybrominated diphenyl ethers (PBDEs)

- What are PBDEs?

PBDEs are synthetic compounds that have been used as flame retardants in a wide range of products, including building materials, electronics, textiles, plastics, and wire insulation. Their structure [C<sub>12</sub>H<sub>10</sub>-

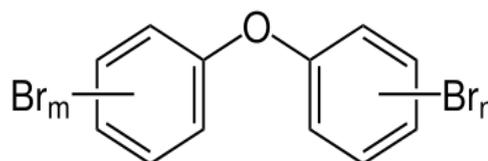


Figure 2.3-2. Structure of PBDEs

<sub>x</sub>Br<sub>x</sub>O (x = 1,2,3,...,10 = m + n)] can be found in Figure 2.3-2. The family of PBDEs

comprises 209 possible configurations, and each of the commercial formulations of PBDEs (e.g. c-pentaBDE, c-octaBDE, c-decaBDE) is a mixture of several PBDE congeners. The commercial mixtures are classified according to their degree of bromination: c-pentaBDE is composed of 24–38% tetra-, 40–60% penta- and 4–8% hexa-BDE congeners (with BDEs 47 and -99 the main congeners); c-octaBDE is composed of 10-12% hexa-, 44% hepta-, 31–35% octa-, 10–11% nona- and 1% deca-BDEs (with BDEs 153 and -183 the main congeners), while c-decaBDE is mainly BDE 209 (97%) (Vane *et al.*, 2010). It is estimated that about 67000 tonnes of PBDEs had been produced in the world in 2001, and c-decaBDE accounts for around 83% of the total PBDE production (Birnbaum and Staskal, 2004).

- The properties of PBDEs

Since the 1990s, major concerns have been raised over the adverse impacts of PBDEs on the environment and human health. Additive flame retardants containing PBDEs are not chemically bound to the product in which they are used and are thus more likely to leach out into the environment. Due to their high resistance to degradation processes and high lipophilicity, PBDEs in river systems are tending to associate with particulate material, accumulate in the organic fractions of sediment, and bioaccumulate in aquatic organisms (Vane *et al.*, 2010). PBDEs also have the potential to biomagnify in food chain (Tomy *et al.*, 2004), and they may cause hormone disruption, permanent changes in behaviour and interruption to the reproductive systems in animals and humans (Vane *et al.*, 2010).

Among the PBDEs, BDEs 28, -47, -99, -100, -153 and -154 have been the most commonly found congeners in the environment generally and are therefore often used as indicators for PBDE contamination. In addition to these six, BDE 209 is the most commonly used congener; it has not often been found in fish, but has been found at the highest concentrations in

sediment (Vane *et al.*, 2010; Jürgens, 2015). BDE 209 is much heavier and larger than other congeners, and thus is more difficult to mobilise. The properties of the 6 most common BDEs and BDE 209 are set out in Table 2.3-3.

Table 2.3-3. Physico-chemical parameters of the selected PBDEs (25°)  
(Wania and Dugani, 2003; Cetin and Odabasi, 2005)

	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	BDE 209
Molar mass	406.9	485.8	564.7	564.7	643.6	643.6	959.2
Henry's law constant (Pa m <sup>3</sup> /mol) <sup>a</sup>	4.8	0.85	0.60	0.24	0.26	0.08	0.02
$\Delta H_{OW}$ (kJ/mol) <sup>* b</sup>	-20	-20	-20	-20	-20	-20	-20
$\Delta H_{AW}$ (kJ/mol) <sup>* b</sup>	59.2	58.4	55	70.8	62.1	-	63.2
Log K <sub>ow</sub> <sup>b</sup>	5.9	6.8	7.3	7.2	7.9	7.8	10.0
Half-life in air (day) <sup>b</sup>	5.3	10.7	14.9	19.5	46.3	-	317.5
Half-life in water (day) <sup>b</sup>	60.0	150	150	150	150	150	150
Half-life in soil (day) <sup>b</sup>	60.0	150	150	150	150	150	150
Half-life in sediment (day) <sup>b</sup>	240	600	600	600	600	600	600

\*  $\Delta H_{OW}$  - enthalpy of phase transfer between octanol and water;  $\Delta H_{AW}$  - enthalpy of phase transfer between air and water.

<sup>a</sup> Source: (Cetin and Odabasi, 2005).

<sup>b</sup> Source: (Wania and Dugani, 2003).

- Regulations and Environmental Quality Standards

The production of penta- and octa-BDE was banned in the EU in 2004, but deca-BDE is still allowed. Voluntary restrictions on its production and use have been put in place and, in 2008, a decision was made by the European Court of Justice that deca-BDE could no longer be used in electrical and electronic compounds (<http://www.ebfrip.org/main-nav/european-regulatory-centre>). Penta- and octa-BDE were added to the list of POPs under the Stockholm Convention in 2009 (Stockholm Convention on POPs, last checked Jan 2017).

In 2013, Directive 2013/39/EU (European Union, 2013) was published to replace the previous version of the Priority Substances Directive. A biota-based EQS was added, of

0.0086 µg/kg wet weight and a maximum concentration of 0.14 µg/L for inland surface waters for Σ 6 BDEs.

### 2.3.3 Hexachlorobenzene (HCB)

- What is HCB?

HCB is a type of organochlorine pesticide (OCP) with the molecular formula C<sub>6</sub>Cl<sub>6</sub> (Figure 2.3-3). It has been widely used as a fungicide for seed treatment (e.g. to control the fungal disease ‘bunt’ on wheat). HCB was commercially available in the USA as wettable powder, liquid and dust, which contained

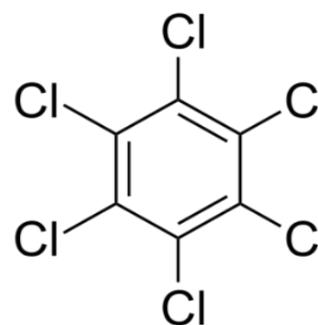


Figure 2.3-3. Structure of HCB

about 98% hexachlorobenzene, 1.8% pentachlorobenzene and 0.2% 1,2,4,5-tetrachlorobenzene (IARC, 1979). Sources of HCB in the general environment also include the manufacture of fireworks, ammunition, rubber, aluminium, and dyes, and in wood preservation. In addition, HCB can be formed as a by-product during the manufacture of certain chemicals (e.g. solvents, pesticides, and other chlorine-containing compounds), or during the combustion of municipal waste (Stockholm Convention on POPs, last checked Jan 2017). The production of HCB has been halted in most countries, but a considerable amount of it has been created as inadvertent by-product. Estimates by the US Environmental Protection Agency (EPA) indicated that around 18 tonnes of HCB were generated as a waste product in the US in 1997. It was also estimated that, in the 1990s, up to 4000 tonnes/year of HCB were produced in Europe as a byproduct (WHO, 1997).

- The properties of HCB

HCB is a persistent pesticide with very low volatility. Its rate of degradation in soil is very slow, with a half-life measured in decades (Table 2.3-4). It is hydrophobic and thus likely to accumulate in sediment with rich organic carbon content in the aquatic system. HCB is toxic to animals and human, and it can bioaccumulate in the food chain. High levels of bioconcentration factors (BCFs) of HCB (ranging between 300 and 35 000) were reported by Euro Chlor (2002) for organisms from three trophic levels in the North Sea. At low levels, HCB has endocrine effects on organisms; for example it increases estradiol in female crucian carp and reduces 11-keto-testosterone in males. In higher doses, it is lethal to animals, including humans. It is reported that people who ate HCB-treated seed grain in eastern Turkey between 1954 and 1969, developed a variety of symptoms, such as photosensitive skin lesions, colic, debilitation and metabolic disorders, and 14% died (Stockholm Convention on POPs, last checked Jan 2017).

Table 2.3-4. Physico-chemical parameters of the selected PCBs (25°)

	HCB
Molar mass	284.8
Henry's law constant (Pa m <sup>3</sup> /mol) <sup>a</sup>	35
Log K <sub>ow</sub> <sup>b</sup>	5.5 - 6.2
Half-life in air (yr) <sup>c</sup>	0.5 – 4.2
Half-life in water (yr) <sup>c</sup>	2.7 - 5.7
Half-life in soil (yr) <sup>c</sup>	3.0 – 6.0
Half-life in sediment (yr) <sup>c</sup>	7

<sup>a</sup> (Jantunen and Bidleman, 2006);

<sup>b</sup> (Verschueren, 1985);

<sup>c</sup> (ATSDR, 2013)

- Regulations and Environmental Quality Standards

The production and use of HCB has been discontinued in many countries due to the concerns about their risks to human health and to the environment. In the UK, HCB is considered as a 'red list substance', highlighting that it is of particular concern to human health and the environment. The use of HCB as a pesticide has been banned since 1975. Internationally, HCB has been banned under the Stockholm Convention on Persistent Organic Pollutants, which was adopted in May 2001 and came into force in May 2004 (Jürgens, 2015). In 1993, the WHO recommended a guideline limit of 1 µg/L for HCB in drinking water. In the EU, a biota EQS of 10 µg/kg for HCB was set out in Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 (European Union, 2013).

#### 2.3.4 Metaldehyde

- What is metaldehyde?

Metaldehyde is the cyclic tetramer of acetaldehyde ( $\text{CH}_3\text{CHO}$ )<sub>4</sub>; see Figure 2.3-4. The compound is a white or colourless solid with a melting point between 110– 120°C and boiling point of 246°C (Environment Agency, 2009). It is mainly used as a contact molluscicide, applied in the form of slug

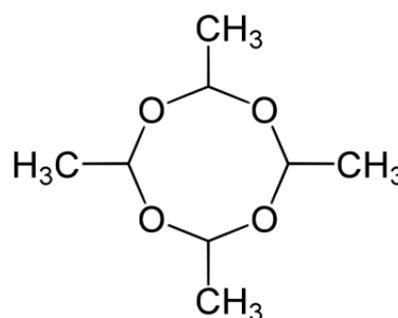


Figure 2.3-4. Structure of Metaldehyde

pellets to protect crops and control slugs. It is estimated that metaldehyde has been applied to more than 8% of the arable cultivation area in the UK (mainly to wheat, potatoes and oil-seed rape). Metaldehyde is also applied by members of the public to kill the pests in their gardens and allotments, although little information is available on this. In addition, it is used as a camping fuel, solid fuel in lamps, and for military purposes.

- The properties of metaldehyde

Metaldehyde is flammable and soluble in water. It undergoes rapid hydrolysis to acetaldehyde and has a half-life limited to several days in soil (Environment Agency, 2009). Due to its low persistence, metaldehyde is not a significant threat to groundwater. Metaldehyde is weakly sorbed to organic matter and clay particles, and thus is less likely to accumulate in the sediment. The physico-chemical properties of metaldehyde are presented in Table 2.3-5. Metaldehyde is classified as a Class II ‘moderately hazardous’ pesticide by the WHO (WHO, 2010). It does not pose a direct risk to the environment or human health, but it is dangerous to all organisms that ingest it. Seventeen metaldehyde poisoning incidents involving cats and dogs were recorded by the Wildlife Incident Investigation Scheme (WIIS) in 1998 (Fletcher *et al.*, 1999). It poses dangers to hedgehogs that are very likely to eat poisoned molluscs, resulting in serious internal damage (Jawad *et al.*). In addition, metaldehyde has a very slow rate of breakdown in water and it is very difficult to effectively remove by conventional water treatment processes (Environment Agency, 2009). In the UK, following heavy/sustained periods of rainfall in the years 2011, 2012, and 2013, metaldehyde levels in some surface waters were found to be many times higher than set out in the drinking water quality standard of 0.1 µg/L. Whilst the levels of metaldehyde detected are not a risk to human health, they fail to comply with drinking water standards.

Table 2.3-5. Physical properties of metaldehyde (EFSA, 2010)

Molar mass (g/mol)	176.2
Molar volume (cm <sup>3</sup> /mol)	186
Henry’s law constant (25 °) (Pa m <sup>3</sup> /mol)	3.8
Kow	1.318
Half-life in water (days)	200
Half-life in soil (days)	30
Half-life in sediment (days)	1000

- Regulations and Environmental Quality Standards

Currently, there is no particular EQS for metaldehyde, but the drinking water quality regulation limit of 0.1 µg/L was set up for individual pesticides in the EU. To avoid contaminating water courses and to protect drinking water supplies, guidelines on metaldehyde application were introduced. Farmers are allowed to apply a maximum total dose of 700 g active substance/ha/year; however, different metaldehyde products have different concentrations of actual metaldehyde in them (usually 3%, but sometimes 1.5%) so farmers have to calculate how much product they can apply without exceeding this application limit. Guidelines for farmers are that a maximum single application should not exceed 210 g active substance/ha. For the protection of water, some advisors may recommend 160 g active substance/ha. In addition, between 1st August and 31st December annually, farmers are advised to use a maximum total dose of 210 g active substance/ha, as this is the period of highest risk for metaldehyde getting into water. They are advised to leave a 6 m 'no spread zone' adjacent to water courses.

## **2.4 The River Thames catchment**

Starting as a small trickle from Thames Head in Gloucestershire, the River Thames flows over 346 km through some of the most historic towns in England, right into the centre of the capital city, London (where the river is deep and navigable to ships) and, eventually, into the North Sea via the Thames Estuary. It is the longest river in England and the second longest river in the UK. The River Thames catchment covers an area of about 10 000 square kilometres, which comprises less than 10% of the total area of England and Wales; however, it includes the most heavily urbanised area (Greater London), which houses nearly 25% of the population of these countries—about 14 million people (Crossman *et al.*, 2013; Lu *et al.*, 2015). The major tributaries and sub-catchments of the River Thames catchment are

illustrated in Figure 2.4-1. Heavily abstracted for drinking water, the discharge of the Thames is low considering its length and breadth and it varies significantly with the seasons. The river flow is relatively high in winter but much lower in summer: average flow ranges from around 1.5 m<sup>3</sup>/s at the source at Cricklade, to about 37.5 m<sup>3</sup>/s at Caversham and up to 65.5 m<sup>3</sup>/s at Teddington (Lu *et al.*, 2015). There are 13 sewage treatment plants in the catchment, which discharge into the main stream of the River Thames.

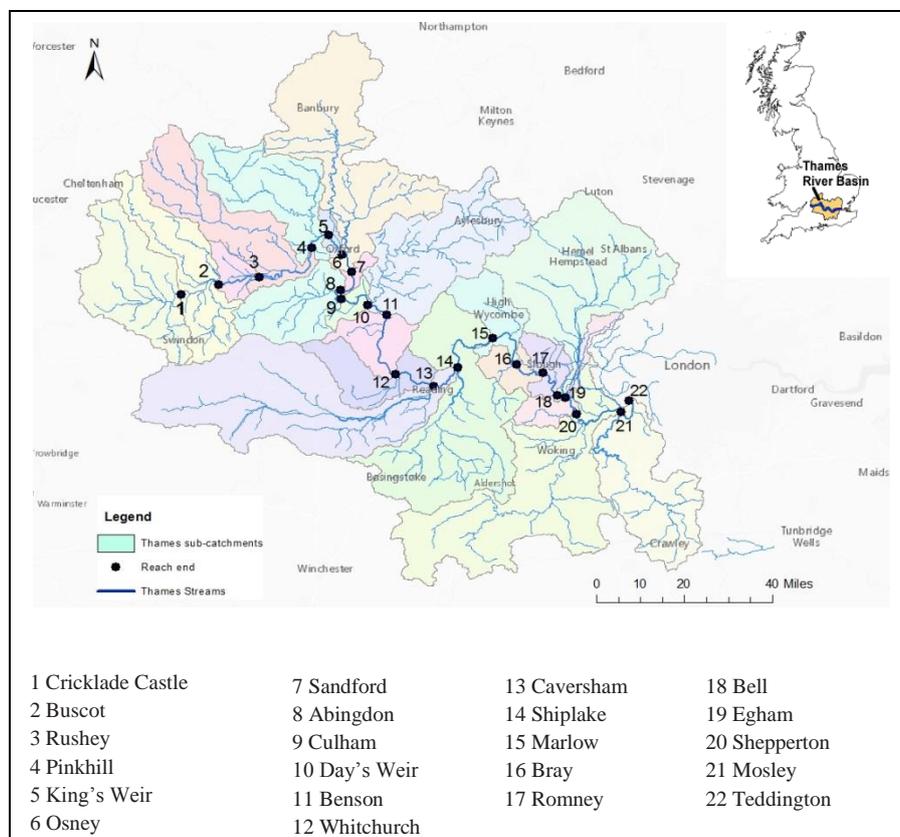


Figure 2.4-1. Location map of the non-tidal River Thames catchment, showing the major tributaries and sub-catchments (Crossman *et al.*, 2013; Lu *et al.*, 2015)

POPs have been used in the River Thames catchment for many years and have been widely distributed in the environment. Multiple types of POP have been detected in sediment cores from the river itself. Taking the Thames at Tilbury Basin as their study site, Scrimshaw and Lester (1997) looked into the historical inputs and contamination levels of some common

POPs, based on sediment records. The average concentrations of total PCBs and DDTs in the upper sections of sediment cores were 39  $\mu\text{g}/\text{kg}$  and 47  $\mu\text{g}/\text{kg}$ , respectively, while those in the lower section were 309  $\mu\text{g}/\text{kg}$  and 87  $\mu\text{g}/\text{kg}$ . A difference in the concentration of total PCBs was measured between higher levels sampled from a depth of 5.82 m and lower levels sampled from a depth of 4.65 m. This difference suggests a reduction in rates of pollution over time. It has been suggested that the decrease over time was attributed to the reduction in use and production of POPs and earlier improvements in waste water treatment technologies (Scrimshaw and Lester, 1997). The distribution of DDTs in the sediment cores was similar to that of PCBs; HCB, HCHs and endrin levels were constant at around 1  $\mu\text{g}/\text{kg}$ .

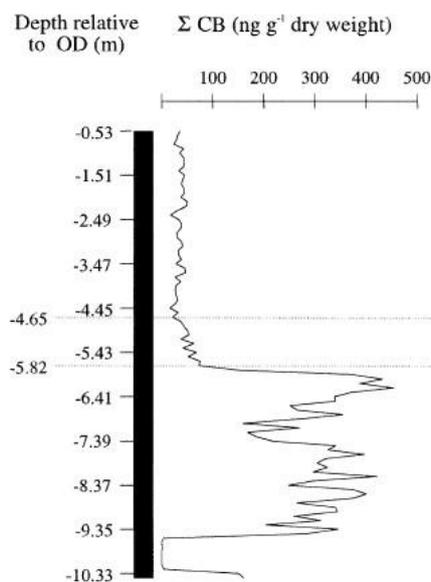


Figure 2.4-2. Distribution of PCBs within sediment cores from the River Thames at Tilbury Basin (Scrimshaw and Lester, 1997)

With growing concern over the impacts of POPs, more and more effort has been put into the reduction and elimination of their production and use; this has kept contamination at low levels in fresh water ecosystems. In recent years, some POPs (e.g. PCBs, HCHs, HCB, and PBDE) have hardly been detected in Thames water, which leads to the presumption that they may no longer be there at all. However, due to the lipophilicity of POPs, they are likely to

accumulate in sediment and bio-accumulate in biotas. High levels of PBDEs, HCB and DDTs have been detected in Thames fish in recent years (Jürgens, 2015; Jürgens *et al.*, 2015). In addition, recent studies point out that some pesticides, such as metaldehyde, have regularly exceeded the EU drinking water standards of 1 µg/L; high concentrations in the Thames have occurred in recent years following heavy rainfall. In particular, in the autumn of 2012 following heavy rainfall, the metaldehyde concentrations in the Thames were generally many times greater than the EU standard (Environment Agency, 2009). There is still concern over the risks presented by POPs and pesticides in the River Thames catchment.

## **2.5 Understanding the behaviour of POPs and pesticides in catchment through modelling**

POPs and pesticide residues in river environments may contaminate the water and cause adverse effects in aquatic organisms and human health. It is of great importance to understand their distribution and behaviour under different conditions. A major challenge associated with describing the behaviour of POPs in river basins is that they are multi-compartment chemicals. Different compartments of river systems contain differing amounts of POP residues. They are reversibly exchanged between various compartments of the environment, implying that their distribution in river basins is influenced by various transformation and transportation processes occurring in or between the compartments. In order to understand the complex systems which are not fully accessible, there is a need for mathematical modelling which can depict the distribution characteristics of POPs in river basins and that such models are now available. Numerous models, such as GLEAMS (Ground Water Loading Effects of Agricultural Systems) (Leonard *et al.*, 1987), fugacity-based models (Mackay, 2001), SWAT (Brown and Hollis, 1996), MAPPE (Vizcaíno and Pistocchi, 2010) and others have been developed to predict the chemical fate of POPs in the

environment. Most recently, Nizzetto *et al.* (2016) have developed an integrated catchment model for organic contaminants (INCA-contaminants Model), which could quantitatively characterize the distribution and fate of POPs and pesticides in large river basins under complex scenarios with a mixture of drivers.

### **2.5.1 The fugacity approach**

The fugacity approach was formulated by using the concept of fugacity as a thermodynamic equilibrium criterion applied to chemical fate in environmental systems (Mackay, 2001). It is one of the most widely used models and, due to its versatility, has proved to be very effective in describing the distribution of chemicals in multimedia environments.

- Principles of fugacity

Fugacity is a convenient technique for describing the ‘escaping’ or ‘fleeing’ tendencies by which chemicals diffuse or migrate between different compartments. In many respects, fugacity plays the same role as temperature in the case of heat transfer (Mackay and Fraser, 2000; Mackay, 2001). Fugacity is expressed as Pascals (Pa), a unit of pressure, and is essentially partial pressure. It is logarithmically related to chemical potential and linearly or near-linearly related to concentration. By expressing the quantity as fugacity, instead of concentration, this directly conveys the equilibrium status and the likely direction of the diverse diffusive transfer between phases (Mackay *et al.*, 2009). The nature of migration of chemicals in a multimedia environment is that they are seeking a balance of fugacity in different phases; in general, they diffuse from high to low fugacity (Mackay, 2001; Mackay *et al.*, 2009).

Fugacity and concentration are related by the constant Z, which is termed as ‘fugacity capacity’ with a unit of mol/m<sup>3</sup>Pa. Their relationship can be postulated in the following formula:

$$C = Zf \quad (\text{Eq. 2.5-1})$$

The constant Z is specific to the nature of chemical, phase composition and temperature. It can be defined in thermodynamic terms (Table. 2.5-1). Another important constant is the partition coefficient known as K. An equilibrium partition coefficient  $K_{12}$  is the ratio of concentrations in the two phases ( $C_1/C_2$ ), and is then ‘ $Z_1f_1/Z_2f_2$ ’. The fugacities ‘ $f_1$ ’ and ‘ $f_2$ ’ convey the equilibrium status, and ‘ $f_1 - f_2$ ’ expresses the driving force of diffusive transfer between two phases (Mackay *et al.*, 2009). When it reaches equilibrium, ‘ $f_1$ ’ would be equal to ‘ $f_2$ ’, and thus ‘ $K_{12} = Z_1/Z_2$ ’. Full details of the relationships between partition coefficients (K) and fugacity capacity (Z) between different compartments are illustrated in Table 2.5-1.

Table 2.5-1. Fugacity capacities (Z) in multi-compartments (Mackay, 2001)

Compartments	Z	Comments
Air	1/RT	R = 8.314 (J/mol K) T: Temperature (K)
Water	1/H or C <sub>s</sub> /P <sub>s</sub>	H: Henry’s Law constant (J/mol) C <sub>s</sub> : Solubility (mol/m <sup>3</sup> ) P <sub>s</sub> : Vapour pressure (Pa)
Soil/sediment	ρ <sub>s</sub> K <sub>p</sub> /H	ρ <sub>s</sub> : Density of solid (kg/L) K <sub>p</sub> : Solid-water partition coefficient (l/kg)
Biota	ρ <sub>B</sub> K <sub>BW</sub> /H	ρ <sub>B</sub> : Density of biota(usually assumed to be 1.0 kg/L) K <sub>BW</sub> : Biota-water partition coefficient (l/kg)
Pure solute	1/P <sub>v</sub> <sup>S</sup>	V: Solute molar volume (m <sup>3</sup> /mol)

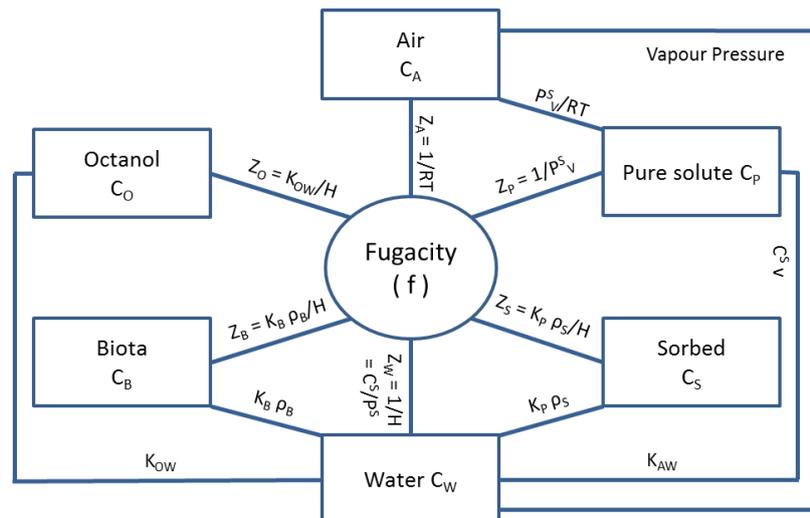


Figure 2.5-1. Relationships between fugacity capacity and partition coefficients between different compartments (Mackay, 2001)

- Fugacity models

Four fugacity-based models have been developed (Mackay, 2001; Mackay *et al.*, 2009). The simplest Level I model simulates the situation in which a constant chemical achieves equilibrium in a closed environment. It is assumed that the chemical is conserved: that it can neither degrade by reactions, nor be added into or conveyed out of the environment. The level I model is widely used as a first indication of where a chemical is likely to partition; however, it is too simple to be capable of estimating the chemical fate and assess the impact of chemical emissions. The more realistic Level II model describes the situation in which a non-conserved chemical is continuously discharged, at a constant rate, into an open environment at a steady state. In the Level II model, the rates of chemical degradation and advection are introduced, which enables the calculation of their environmental persistence; however, the inter-phase transport processes are still not quantified. The model assumes that all the environmental phases are in equilibrium, which is rarely the case in the real environment. The Level III model also describes the distribution of a non-conserved chemical discharged into an open environment, but it assumes that equilibrium exists within—but not between—compartments; thus, it is more realistic and complex than the Level II model. Unlike Level II,

a Level III model not only applies a mass balance to the system as a whole, but separately to each environmental phase (air, water, soil, and sediment). The inter-phase transfer rates are calculated using the constant D (Figure 2.5-2), which contains information on mass transfer coefficients, areas, deposition and re-suspension rates, diffusion rates, and soil run-off rates. The Level IV model extends Level III to cover unsteady state conditions. The Level IV model involves the solution of differential mass balance equations and can be used to describe the time-dependent or dynamic behaviours of chemicals although it is very complex and not easy to use.

Table 2.5-2. Level III fugacity model calculation: interphase transfer D value equations  
(adapted from Mackay, 2001; Lu *et al.*, 2015)

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

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

### 2.5.2 The Integrated Catchment Model (INCA) approach

The INCA model is a process-based model that represents soil, groundwater components and in-stream biogeochemical and hydrological dynamics. It was initially established to investigate the distribution and fate of nitrogen in catchments (Whitehead *et al.*, 1998). It is dynamic, stochastic, and semi-distributed. The INCA model is easy and fast to use and can provide very good outputs, including:

- Daily contaminant fluxes for all transformation processes within the land phase
- Daily time series of flows and contaminant concentrations at selected sites along the river and at selected periods of time
- Cumulative frequency distributions of flow and contaminant concentrations at selected sites
- Tables of statistics for all sites.

The INCA model can also be used to address the impacts of a wide range of issues, such as climate change, land use change, and environmental management practices. Whitehead *et al.* (2006) have applied the INCA model to investigate the impacts of climate change on in-stream nitrogen distribution in the River Kennet system. Adaptation strategies were appraised using the model and it was suggested that changing the land use or reducing fertiliser use could be the most effective strategy. After that, Whitehead *et al.* (2009b) studied the impacts of climate change on water quality across the UK by applying the INCA model to six UK rivers. The output data have provided helpful information for catchment management. It has been proved that INCA is a very effective tool for providing guidelines for decision-making. Based on the INCA concept, new integrated models have been developed to predict the distribution of various substances in catchments, such as INCA for phosphorus (Crossman *et al.*, 2013), sediments (Lazar *et al.*, 2010), chlorides (Jin *et al.*, 2011), carbon (Futter *et al.*, 2007), metals (Whitehead *et al.*, 2009a) and pathogens (Rankinen *et al.*). These models have

been widely used in assessing the concentration dynamic of particular substances in catchments, and have proved to be effective in most cases.

The INCA Contaminants Model is the newest member of the INCA family, developed by Nizzetto *et al.* (2016) to investigate the fate of organic contaminants in catchments. It combines two different modelling approaches:

- a) the hydrology-based catchment model approaches used for carbon and sediment (INCA-C and INCA-Sediment Models) and
- b) the multi-media fate models typically used for POPs, which describe the partitioning of compounds between environmental compartments, based on physical-chemical properties.

The processes in the INCA-contaminants model are driven by daily-input time series of precipitation, hydrologically effective rainfall (HER), soil moisture deficit (SMD), temperature and wind speed. In the INCA-Contaminants model, a daily time-step dynamic multimedia box model has been integrated in the INCA-C/INCA-Sediment coupled structure (Lu *et al.*, 2016; Nizzetto *et al.*, 2016). The processes in the INCA-Contaminants model can be described in two main sections: (i) the land-phase model, simulating the multimedia distribution, transport, storage and transformation of contaminants in soils (Figure. 2.5-2) and (ii) the in-stream model, describing the chemical fate and transformation of contaminants in the aquatic system (Figure. 2.5-3).

In the land-phase model, the soil has been divided into two layers: a superficial organic layer and an underlying mineral layer. Each contains soil air, soil water (which includes the fractions of dissolved organic carbon (DOC), and soil organic carbon (SOC)). Major transport processes taken into account in the land-phase model include: -

- wet and dry atmospheric depositions

- inputs from application of fertilizers or accidental spills
- partitioning among sub-phases of the soil compartment (e.g. SOC, DOC, soil water and soil air)
- diffusion through 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 layers
- losses due to surface- and diffuse run-off from the upper layer and diffuse run-off from the lower layer
- degradation of contaminants.

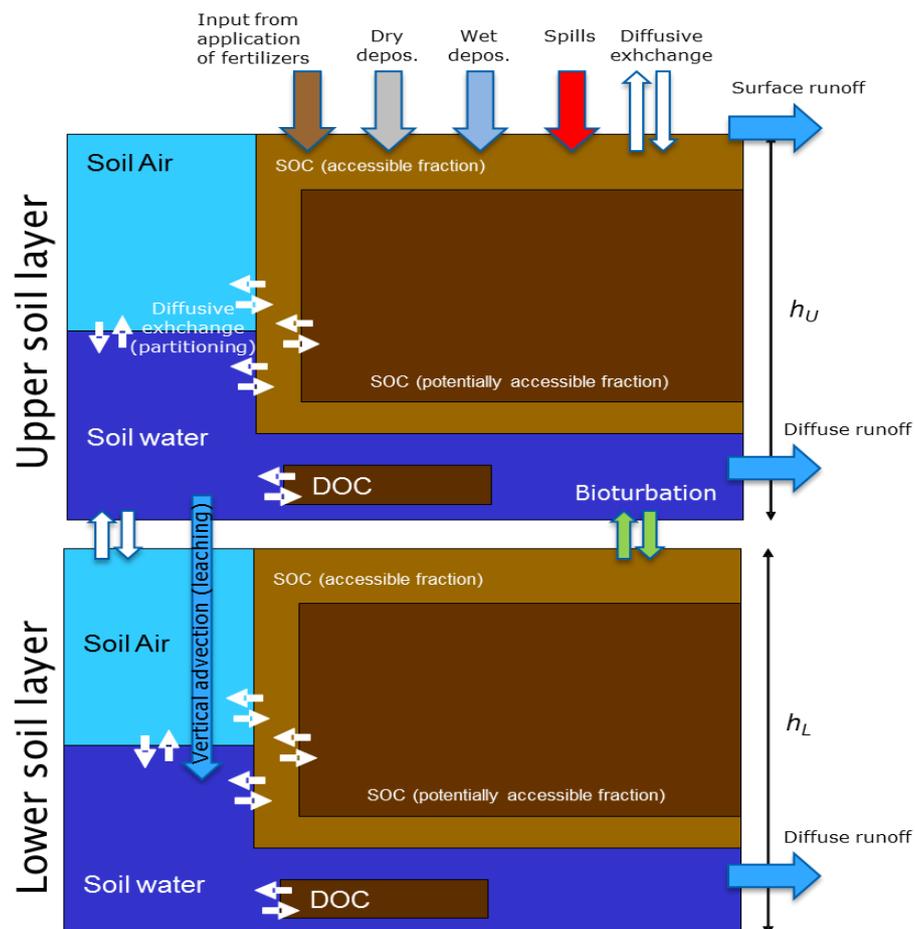


Figure 2.5-2. Structure of the soil compartment, adapted from (Nizzetto *et al.*, 2016)

The main processes in the in-stream phase modelling 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 re-suspension fluxes associated with sediment dynamics;
- bioturbation;
- diffusive exchange between superficial and deep-bed sediments;
- downstream advection;

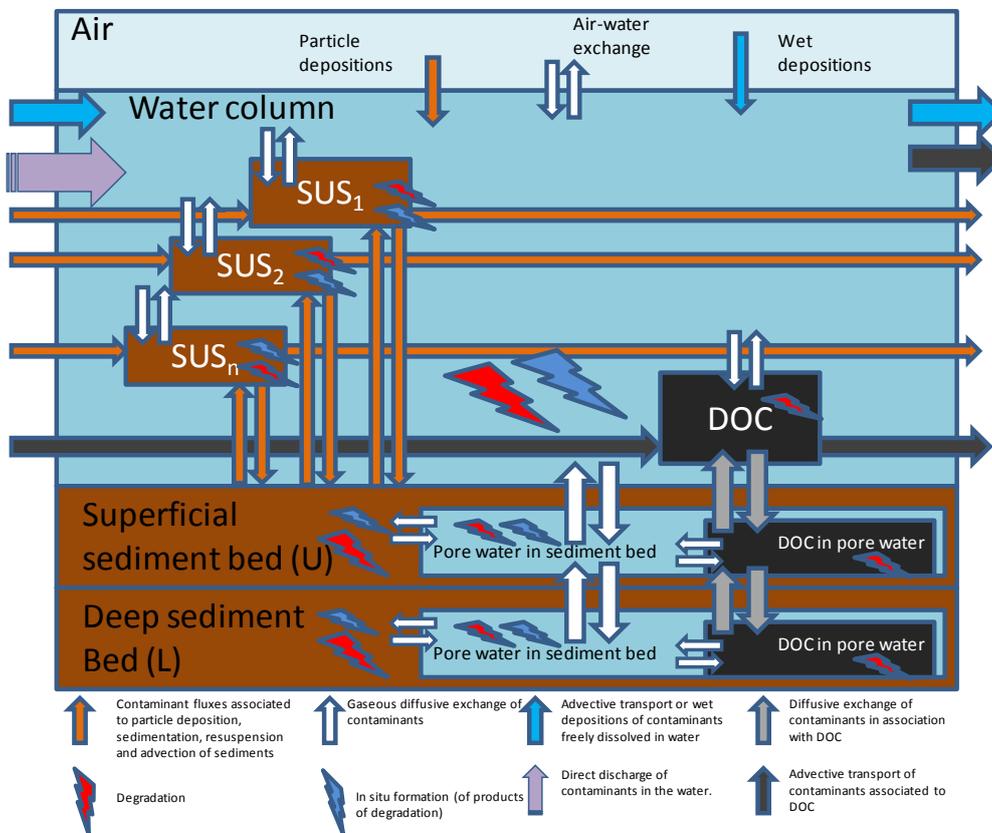


Figure. 2.5-3 Structure of the in-stream compartment, adapted from (Nizzetto *et al.*, 2016)

In INCA-Contaminants modelling, the contaminant fluxes are computed by multiplying their concentrations by the velocity components of the water and organic matter exchange. The fugacity notation was not used in the mathematical formalism of INCA-Contaminants, but the diffusive exchange that controls the distribution of contaminants between different phases was predicted using the thermodynamic equations derived from the fugacity models. The contaminant concentrations in each phase were calculated based on the temperature dependent thermodynamic equilibrium partitioning coefficients (Lu *et al.*, 2016; Nizzetto *et al.*, 2016):

*Air–water partitioning coefficient*

$$\text{Log}H_T = \text{Log}H_{25^0} - \frac{(10^3 \cdot \Delta U_{AW} + R \cdot 298.15)}{\ln(10) \cdot R} \cdot \left( \frac{1}{T} - \frac{1}{298.15} \right) \quad (\text{Eq.2.5-2})$$

$$K_{AW} = \frac{H_T}{R \cdot T} \quad (\text{Eq. 2.5-3})$$

Where:  $H_T$  is the Henry's law constant;  $\Delta U_{AW}$  is the enthalpy of phase transfer between air and water;  $R$  is the ideal gas constant (8.314 J/K/mol),  $T$  is water temperature (K); and  $K_{AW}$  is the air–water equilibrium partitioning coefficient.

*Water–SOC partitioning coefficient*

$$\text{Log}K_{OWT} = \text{Log}K_{OAW25^0} - \frac{(10^3 \cdot \Delta U_{AO})}{\ln(10) \cdot R} \cdot \left( \frac{1}{T} - \frac{1}{298.15} \right) \quad (\text{Eq. 2.5-4})$$

$$K_{W-SOC} = K_{OC} = K_{OWT} \cdot r_{OC} \cdot \frac{1}{\rho_{OC}} \quad (\text{Eq. 2.5-5})$$

Where:  $K_{OW}$  is the octanol–water equilibrium partitioning coefficient;  $\Delta U_{OA}$  is the enthalpy of phase transfer between octanol and air;  $K_{OA}$  is the octanol–air equilibrium partitioning coefficient;  $K_{W-SOC}$  is the temperature-corrected SOC-water equilibrium partitioning coefficient;  $K_{OC}$  is the water–organic carbon partitioning coefficient;  $r_{OC}$  represents the empirical coefficient; and  $\rho_{OC}$  is the density of solid organic carbon;

*Water–DOC partitioning coefficient*

$$K_{W-DOC} = \frac{10^{(0.93 \cdot \text{Log}K_{owT} - 0.45)}}{\rho_{DOC}} \quad (\text{Eq. 2.5-6})$$

Where:  $K_{W-DOC}$  is the temperature-corrected DOC–water equilibrium partition coefficient.

The density of DOC was assumed to be  $\rho_{OC} = 1100 \text{ kg m}^{-3}$ . The coefficient parameterization was taken from Poerschman and Kopinke (Poerschmann and Kopinke, 2001). The constants 0.93 (a), -0.45 (b) are the regression data of  $\text{Log } K_{DOM} = a \text{ Log } K_{OW} + b$ .

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# **Chapter 3. The distribution of Polychlorinated Biphenyls (PCBs) in the River Thames Catchment under the scenarios of climate change**



# The distribution of Polychlorinated Biphenyls (PCBs) in the River Thames Catchment under the scenarios of climate change



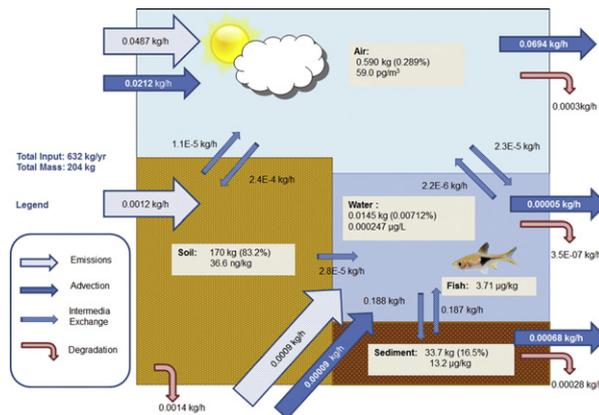
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## HIGHLIGHTS

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

## GRAPHICAL ABSTRACT



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## ABSTRACT

Measurements have shown low levels of PCBs in water but relatively high concentrations in the resident fish of the River Thames (UK). To better understand the distribution and behaviour of PCBs in the Thames river basin and their potential risks, a level III fugacity model was applied to selected PCB congeners (PCB 52, PCB 118 and PCB 153). The modelling results indicated that fish and sediments represent environmental compartments with the highest PCB concentrations; but the greatest mass of PCBs (over 70%) is likely to remain in the soil. As emissions decline, soil could then act as a significant secondary source of PCBs with the river bed-sediment functioning as a long-term reservoir of PCBs. The predicted changes in temperature and rainfall forecast in the UK Climate Projections 2009 (UKCP09) over the next 80 years had only a modest influence on PCB fate in the model. The most significant result was a tendency for climate change to enhance the evaporation of PCBs from soil to air in the Thames catchment.

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## 1. Introduction

Polychlorinated Biphenyls (PCBs) are industrial chemicals whose main application was heat exchange fluids in electrical equipment. An estimated 1.3 million tonnes of PCBs were manufactured globally between 1990 and 1993; and approximately 66,500 tonnes of PCBs were produced in the UK between 1954 and 1977 (Breivik et al., 2002). PCBs are considered to be amongst the most persistent, bio-accumulative, and toxic of organic chemicals listed as Persistent Organic Pollutants (POPs) under the Stockholm Convention. The production and usage of PCBs have been banned and regulated in the UK since 1976 (EA, 2007). However, emissions of the contaminants continued due to losses from old PCB-containing equipment that is still in use or from their disposal. With the phasing out of the old equipment in recent decades, the emissions of PCBs have dropped significantly in the UK (from 6698 kg/a in 1990 to 906 kg/a in 2009, approximately) (NAEI, 2011). However, due to the persistence of PCBs, they continue to exert their influence on the environment and transfer freely between different environmental compartments. Because of the lipophilicity of PCBs, they are likely to bio-accumulate and bio-magnify in aquatic food chains (Elskus et al., 1994; Koenig et al., 2012). In the River Thames Catchment, the concentrations of PCBs in water are almost always found to be lower than the level of EU EQS, but the PCB levels in Thames fishes suggested by recent studies (Jürgens, 2015; Jürgens et al., 2015) exceed the unrestricted consumption thresholds (5.9 µg/kg for  $\sum$  PCBs) which was proposed by the U.S. Environmental Protection Agency (U.S. EPA, 2000). The burden of PCBs in the sediments has the potential to be bioavailable for Thames fish (OSPAR, 2009b). Although limited sediment data is available for non-tidal section of Thames, a recent study suggested that the sediment concentrations of PCBs in the Thames estuary observed in 2011 significantly exceeded the Ecotoxicological Assessment Criteria derived by the Oslo and Paris Convention (OSPAR) (Nicolaus et al. (in preparation); Scrimshaw and Lester, 2001).

To predict the potential risks of PCBs, information on their distribution, transport and ultimate sinks in the catchment is essential. However, addressing temporal and spatial distribution of PCBs by chemical analysis is both a time-consuming and expensive activity. Mass balance models can assist in predicting the transport and distribution of PCBs throughout the environment. Recently, this approach has been successfully employed in lakes and rivers, such as the Great Lakes on the Canada–United States border (Thompson et al., 1999) and the Altamaha River and the Willamette River in the US (Kilic and Aral, 2009). Studies in Europe exist for the western Baltic Sea (Wodarg et al., 2004) and the Venice Lagoon (Dalla Valle et al., 2005). Sweetman et al. (2002) applied a level IV fugacity model to assess the historical emissions and distribution of PCBs over the whole of the UK over the last 60 years, but only discussed their fate in river systems to a small extent. Estimates on the levels of PCBs in the biosphere (fish) were not included in any of these studies.

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

knowledge on the interactions of fish with PCBs and with climate change issues.

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

The aims of this study were: 1) To understand the distribution of PCBs throughout the Thames catchment through the use of a multi-media fate model, 2) corroborate the model predictions using field measurements or nearest literature reported values for three test PCB congeners (52, 118, 153), and finally 3) estimate the extent to which climate change might alter the fate of PCBs in the River Thames Catchment and so affect environmental and human exposure.

## 2. Materials and methods

### 2.1. The Thames Catchment

The River Thames is the longest river that sits entirely within England with a total length of 346 km (255 km are non-tidal, Fig. 1). It flows through the capital city London to the North Sea. The catchment covers an area of approximately 10,000 km<sup>2</sup>, which comprises less than 10% of the area of England and Wales. However, it includes the most heavily urbanised area which houses nearly a quarter of the population of England and Wales (supporting about 14 million people) (Crossman et al., 2013). There are 352 sewage treatment plants in the Thames Region which discharge into the River Thames and its tributaries (Williams et al., 2009). The bedrock of the Thames is mainly high permeable chalk, although there are also some reaches of low permeability clays (Crossman et al., 2013). The climate in the River Thames Catchment is close to a typical temperate maritime climate, with modest rainfall (716.9 mm mean annual precipitation between 2000 and 2008), warm summers and mild winters (average 17 °C in summer and 5.56 °C in winter between 2000 and 2008) (Crossman et al., 2013). The discharge in the River Thames varies significantly between seasons, with relatively high flows in winter and lower flows in summer (Crossman et al., 2013). On average, the flow ranges from around 1.5 m<sup>3</sup>/s at the source at Cricklade, to about 37.5 m<sup>3</sup>/s at Caversham and up to 65.5 m<sup>3</sup>/s at Teddington (Jin et al., 2010; Johnson, 2010). Jin et al. (2012) have divided the Thames system into 22 reaches and sub-catchments (Fig. 1), and have applied the INCA model to predict their vulnerability to climate change. It has been suggested that climate change could affect the river flows and could exacerbate water quality problems (nitrogen, phosphorus) of the Thames (Jin et al., 2012).

### 2.2. The level III fugacity model

The fugacity model is a multi-media mass balance model that employs the concept of fugacity as a thermodynamic equilibrium criterion and treats partitioning of chemicals between different environmental compartments (Mackay, 2001). There are basically four levels of fugacity models. A level III fugacity model has been applied in this study. The level III model provides a more realistic description of the chemicals' fate including emissions, advective inflows, degradation, advective losses and intermedia exchange processes, as shown in Fig. SI1 in the Supporting Information. The four bulk environmental compartments considered in the level III fugacity model are air, soil, water and sediment. These compartments contain varying proportions of sub-compartments (e.g. air, water, solid and biota). The model runs in

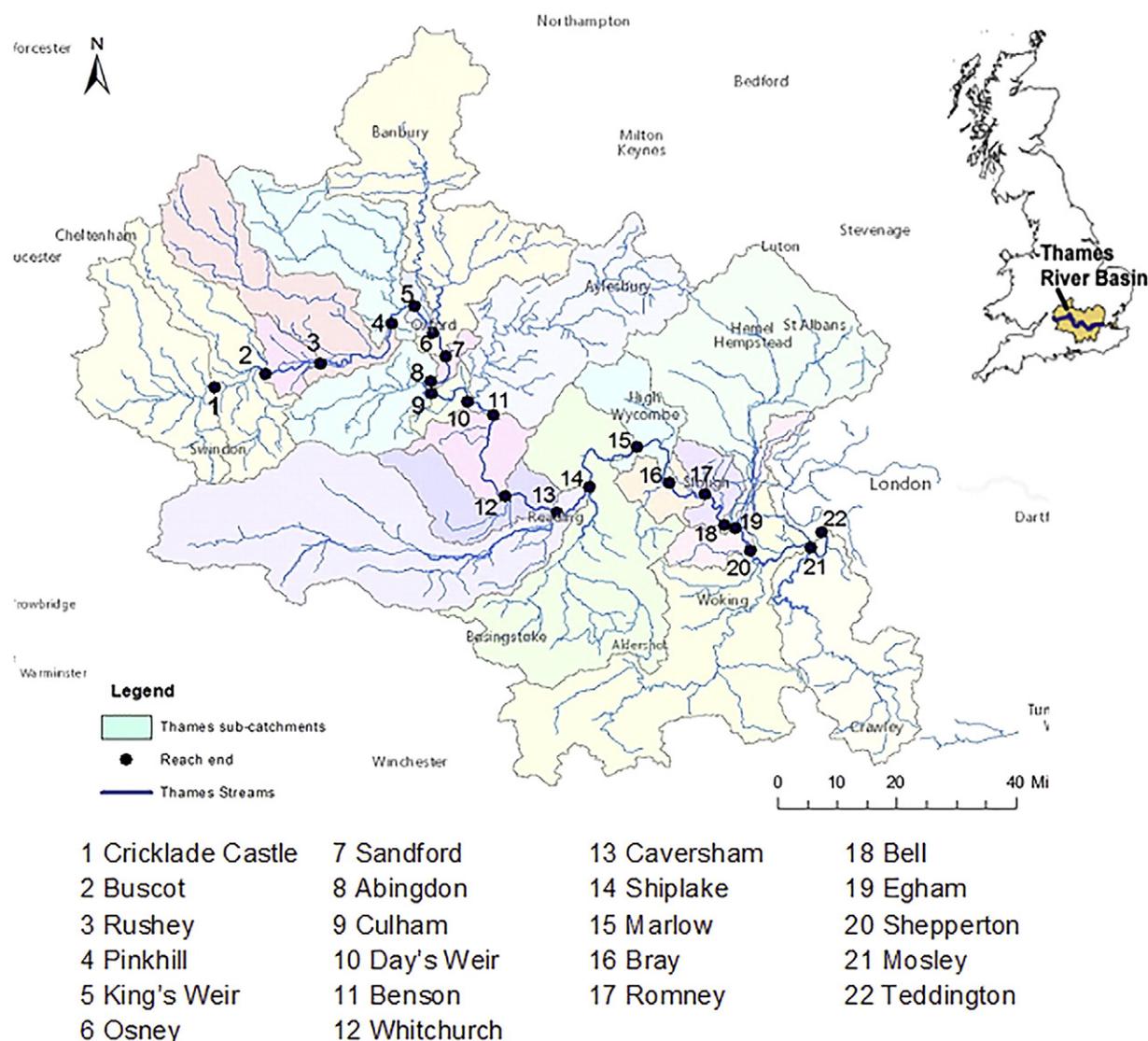


Fig. 1. Location map of the non-tidal River Thames Catchment showing the major tributaries and sub-catchments.

steady-state conditions and assumes that equilibrium exists within (i.e. between sub-compartments), but not between bulk compartments. The rates of intermedia transport and transformation are calculated using the constant  $D$  (Table S11). More detailed information on the level III fugacity model are provided elsewhere (Mackay, 2001; MacLeod et al., 2002).

### 2.3. Model set-up

In this study, of four bulk compartments (air, soil, water, and sediment) a sub-compartment in water (fish) was included. Whilst a fish compartment may only account for a small part of the overall pool, concentrations could be high and of environmental significance (Jürgens et al., 2015). The level III fugacity model for the River Thames relies on two major sets of parameters: the physico-chemical properties of the selected chemicals (Table S12) and environmental properties of the study area (Table S13). The values for vapour pressure, water solubility and half-lives have been adjusted for the annual average temperature of the River Thames Catchment (11.07 °C). Detailed information on the environmental and landscape properties of the River Thames Catchment was obtained from the Meteorological Office in England and Wales, the Environment Agency, or from similar environments taken from literature and adjusted for the study area as deemed appropriate.

### 2.4. Model evaluation

To evaluate the performance of the fugacity level III modelling, a range of measured data of PCBs in different environmental compartments was needed. However, only a limited number of observed datasets were available (Table 2). Although hundreds of water samples in the River Thames have been examined by the Environment Agency, very few of them exceeded the detection limit of 0.001 µg/L. To the best of our knowledge, no PCB congener-specific measurements in River Thames sediments have been carried out in recent years. The pollutant levels of PCBs in soil were collected from the UK Soil and Herbage Pollutant Survey (UKSHS) Report (EA, 2007) and a previous monitoring study (Vane et al., 2014). In the UKSHS Report, only average values for rural and urban areas of England were reported (EA, 2007). The observed air concentrations of the studied PCBs have been collected from the results of Toxic Organic Micro-Pollutants (TOMPS) programme (Schuster et al., 2010). The PCB values in Thames fish were collected both from previous work carried out as part of the CEH (Centre of Ecology and Hydrology) Fish Archive Project (Jürgens, 2015; Jürgens et al., 2015; Rose et al., 2015). The observed data were for different fish species, including roach, perch, bream, bleak and eel. The PCB burden of eels is likely to be slightly higher than for other fish (Jürgens et al.,

2015), but average values for all fish species were used to evaluate the model performance.

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

### 2.5.1. Emissions over time

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

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

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

### 2.5.2. Change in climate with time

In order to estimate the influence of climate change on the fate of PCBs in the River Thames catchment, two different scenarios (A and B) were tested. Scenario A assumes the climate to be constant in the period of simulation. In Scenario B, the outcomes of UKCP09 and its medium emission scenario (IPCC SRES A1B) dataset were used. UKCP09 is the latest regional climate model for the UK that provides probabilistic projections for a number of variables (temperature, rainfall, etc.) under three future emission scenarios (low, medium and high emissions). For each scenario, the full UKCP09 sampled data consists of 10,000 variants, which capture all the possible combinations, for each 25 km grid square and aggregated region (Murphy et al., 2009). From a random sample of 100 variants, Jin et al. (2010) illustrated the ranges of temperature and precipitation projections under the medium emission scenario in the 2020s and 2080s for the Thames catchment. The river flows were simulated with the Integrated Nitrogen Catchment Model (INCA) by using driving data derived from the random samples of the UKCP09 database (Jin et al., 2010). In this study, the average temperature, precipitation rate and river flows in the 2020s and 2080s were obtained from the predictions by Jin et al. (2010) (Table 1). These suggest some reduction in river flow with warmer temperatures and higher evaporation rates playing an important role (Jin et al., 2012). The current temperature and precipitation rate were supplied by the Meteorological Office and the mean observed flows by the Environment Agency.

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

		Temperature (°C)	Rain rate (mm/d)	Mean flow (m <sup>3</sup> /s)	Water residence time (h) <sup>a</sup>
Scenario A	2000s	11.07	1.86	65.0	324
	2020s	11.07	1.86	65.0	324
	2080s	11.07	1.86	65.0	324
Scenario B	2000s	11.07	1.86	65.0	324
	2020s	11.5	2.03	59.0	333
	2080s	13.6	2.03	58.8	334

<sup>a</sup> Annual average.

The water residence time was estimated from the mean flow and from available values for the Thames estimated by Johnson et al. (2009) with a general relationship developed by Round et al. (1998) (Table 1). The future changes in wind speed and snow and ice cover were not addressed. Therefore, these factors were assumed to be constant in the simulation of Scenario B. The seasonal effects of climate change have been addressed by modelling PCB 52 (which is expected to be most affected) for 2080s summer climate conditions.

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

## 3. Results and discussion

### 3.1. Comparison of predicted values against observed data

The predicted values were compared with observed concentrations of PCBs in different environmental compartments to evaluate the performance of the model. There have been few reported detections of PCBs in the river water column in the Thames (LOD 0.001 µg/L) by the UK Environment Agency. However, this model would predict that water concentrations of PCB 52, 118 and 153 would be 0.00012–0.00025 µg/L which would be well below that detection limit (Table 2). Schuster et al. (2010) have presented the measured values of PCBs in ambient air of six sites in England (London, Manchester, Middlesbrough, Hazelrigg, High Muffles and Stoke Ferry). In this study, the predicted air concentrations were compared to the average values for London and Stoke Ferry, which are within or close to the Thames catchment. The estimates for PCB 118 and PCB 153 were in good agreement with the observed values. But the model estimates of PCB 52 in air exceeded the observed values by a factor of 4.0 (Table 2). The lower than expected measured air concentrations of PCB 52 might be attributed to lower emissions than PCB 118 and PCB 153. The observed soil data collected from previous studies were grouped into rural and urban domains (Table 2). The reported average values for urban soils of England in the UKSHS report were much lower than the data for the site in London. The survey area in London has a long history of urban and industrial activity, and may therefore be a contaminant hot spot (Vane et al., 2014). The model estimates of soil concentrations were compared to the average values of England generated from the UKSHS report. The predicted value for PCB 52 fell between the average measured values for soil in rural and urban areas (Table 2), whilst the values for PCBs 118 and 153 fell within the expected range although about half the measured average for rural areas.

The predicted sediment concentrations of the PCBs in the Thames were 9–13 µg/kg. Unfortunately, there appears to be no recent congener-specific monitoring data for PCBs in sediments of the Thames catchment. The most relevant data that exists is only for PCB as Aroclor-1248 in salt marsh sediment of Two Tree Island in the Thames estuary where a mean value of 34.4 µg/kg was reported (1990–1995) (Scrimshaw and Lester, 2001). Much lower values have been reported for the same congeners in the River Willamette (located in northwestern Oregon, US) and Lake Thun (situated in the Bernese Oberland, Switzerland) (Bogdal et al., 2010; Hope, 2008) but these are both very rural areas (>90%). The predicted sediment concentrations for the studied PCBs were about 6 times higher than the monitored data for

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

Media	PCB 52		PCB 118		PCB 153	
	Observed (min–max, mean)	Estimated	Observed (min–max, mean)	Estimated	Observed (min–max, mean)	Estimated
Air (pg/m <sup>3</sup> ) <sup>a</sup>	2000–2008: n = 50 0.01–71, 14.77	59.0	2000–2008: n = 50 0.2–56, 5.46	5.44	2000–2008: n = 50 0.02–37, 7.15	7.90
Soil (ng/kg) <sup>b</sup>	2001–2002: Rural, n = 183: 0.1–505, 28.6 Urban, n = 42: 7.1–322, 75.2	36.6	2001–2002: Rural, n = 183: 2.12–6350, 129 Urban, n = 42: 58.6–3220, 436	80.1	2001–2002: Rural, n = 183: 24.8–782, 336 Urban, n = 42: 153–9310, 906	163
	2009: Urban (London), n = 74: 0–1.2E+8, 3.0E+6		2009: Urban (London), n = 74: 1.0E+5–7.7E+7, 2.2E+6		2009: Urban (London), n = 74: 1E+5–1.6E+8, 5.2E+6	
Water (µg/L) <sup>c</sup>	2000–2006: n = 181 <0.001	0.000247	2000–2006: n = 179 <0.001	0.000149	2000–2006: n = 179 <0.001	0.000122
Fish (µg/kg) <sup>d</sup>	2007–2012: n = 50 0.16–15.90, 3.02	3.71	2007–2012: n = 50 0.15–12.35, 2.58	3.16	2007–2012: n = 32 0.10–9.52, 2.34	2.64
Sediment (µg/kg) <sup>e</sup>	–	13.2	–	11.3	–	9.43

<sup>a</sup> (Schuster et al., 2010).

<sup>b</sup> (EA, 2007; Vane et al., 2014).

<sup>c</sup> Environment Agency WIMS database.

<sup>d</sup> (Jürgens, 2015; Jürgens et al., 2015; Rose et al., 2015).

<sup>e</sup> Data only for PCB as Aroclor-1248 in the Thames estuary with a mean value of 34.4 µg/kg (Scrimshaw and Lester, 2001).

sediments from the Mersey Estuary (Vane et al., 2007b), but were within the ranges of the reported values for sediment from the Clyde Estuary located in the conurbation of Glasgow (Vane et al., 2007a). There are no congeners specific quality guidelines for PCBs in freshwater sediment, but Environmental Assessment Criteria (EAC) for ICES7 CBs in marine sediment have been set up within OSPAR (OSPAR, 2009b). The predicted sediment values for PCB 52 and PCB 118 significantly exceeded the EAC of 2.7 µg/kg for PCB 52 and of 0.6 µg/kg for PCB 118 (Nicolaus et al. (in preparation); OSPAR, 2009b), indicating a potential threat to the aquatic environment. But the concentration for PCB 153 was predicted to be lower than the EAC of 40 µg/kg for PCB153.

In the river system, the fugacity level III model indicated likely relative concentrations between water, fish and sediment. Here the fish compartment in the model represents the inclusion of all fish species. Average values of the observed concentrations for different fish species (roach, perch, bream, bleak and eel) were calculated for comparison with the modelled data (Table 2). For the three studied PCBs in Thames fish, the predicted concentrations (2.64–3.71 µg/kg) were in good agreement with their observed values (Table 2). The sum concentration of the three modelled PCBs in fish tissue was predicted to be 9.51 µg/kg in 2000–2010, which would exceed the U.S. EPA unrestricted consumption thresholds (5.9 µg/kg) for ΣPCBs. PCB 118 belongs to a group of ‘dioxin like’ PCBs. The estimated value of PCB 118 in the fish compartment (3.04 µg/kg) would translate to 0.0001 µg/kg toxic 2,3,7,8-TCDD equivalents (Van den Berg et al., 2006). The newly established EU Environmental Quality Standard for dioxin and dioxin-like compounds is 0.0065 µg/kg (European Union, 2013). The levels of PCBs in Thames fish will be linked to the PCBs in surrounding water and sediment via the food chain (Mackay, 2001). The modelled bioconcentration factors (BCFs, Supporting Information Eq. (SI7)) for the studied PCBs ranged from 15,020 to 21,640, which were much higher than the Canadian criteria for very bioaccumulative (BCF ≥ 5000) (Gobas et al., 2009). The biota-sediment accumulation factors (BSAFs, Supporting Information Eq. (SI8)) were calculated to be around 0.6, which were a bit lower than measured data from some laboratory and field studies (0.5–2.8) (Nowell et al., 1999; Weisbrod et al., 2007). While there is a small tendency for the model to underestimate the concentrations of PCBs in soil, the results for the Thames catchment could be considered acceptable since they fall within an order of magnitude from the observed data for each of the four compartments (Hope, 2008). Whether the differences are attributable to underestimated loadings of PCBs or an overestimated degradation rate constant in soil is not clear.

### 3.2. Sensitivity and uncertainty analysis

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

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

where  $\partial Y$  is the change of output value while  $\partial X_i$  is the variance in input parameter.

For PCB 52, 118 and 153 temperature appeared to be the most important parameter that determined its fate in the catchment (Tables 3, SI4 and SI5). The influence of other parameters was only evident on one or two compartments. Air residence time was the most influential parameter for air concentrations. Soil concentration was found to be mainly influenced by temperature followed by degradation rate. In the river water, the most sensitive parameters were sediment deposition and re-suspension. Sediment deposition and re-suspension also have the biggest influence on the concentrations in fish, degradation in sediment being the most important parameter for the sediment concentration. For PCB 118 and PCB 153, the concentration variations obtained for each compartment were much less than for the lower chlorinated PCB 52. This would reflect the lower volatility/mobility and biodegradability of the heavier PCBs.

In addition to the sensitivity analysis, it is also important to communicate the uncertainty associated with the fate modelling. The analytical approach presented by MacLeod et al. (2002) has been applied to weigh the contributions of the most sensitive variables to uncertainty in the model outputs. The 95% confidence factors (Cfs) (the extent to which the values might diverge from the medians) for the input variables were estimated from reported values (Lamon et al., 2012; MacLeod et al., 2002; Sweetman et al., 2002) (Table 3). The corresponding confidence factors in the outputs ( $Cf_{output}$ ) of each compartment associated with the most sensitive variables were assessed (Supporting Information, Figs. SI2–SI4). The  $Cf_{output}$  were calculated with the following equation (Eq. (3)):

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

where  $|S|$  is the partial derivative of the sensitivity equation (Eq. (2)). Using this approach, the sensitivity was calculated with 0.1% variation

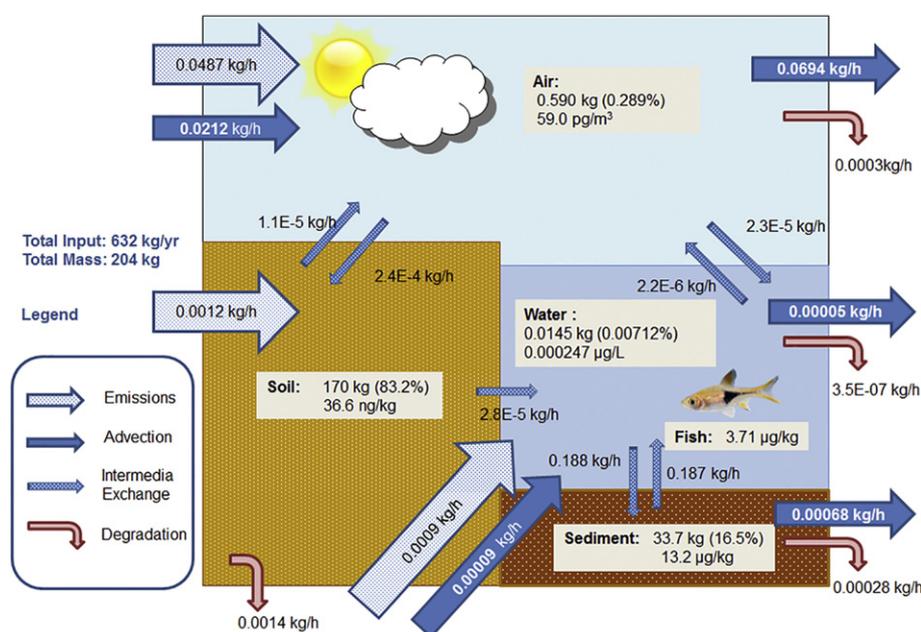
**Table 3**  
Sensitivity analysis for PCB 52 in the different compartments (similar tables for PCBs 118 and 153 can be found in the supporting information).

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

for each individual input parameter (MacLeod et al., 2002). The graphic analyses of the contribution of the most sensitive parameters to uncertainty of outputs in different compartments for the studied PCBs are presented in Supporting Information Figs. SI2–SI4. For PCB 52, air residence time was the most important parameter in terms of contribution to uncertainty in the modelling output in the air compartment. In soil, temperature played the most important role in determining the uncertainty associated with the modelling results, whereas soil degradation was the most important source of uncertainty for sediment. In water and fish, sediment re-suspension, sediment deposition and sediment degradation are the most influential parameters in determining the confidence factors in outputs. For the higher chlorinated PCBs 118 and 153, temperature played a more important role in determining the uncertainty in the modelled results in air, whereas air residence time was less important. The parameters that contributed most to the model outputs in water and fish were sediment deposition and resuspension. In soil, temperature and soil degradation were the most important parameters in determining the results for PCB 118 and PCB 153.

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

PCBs are no longer produced and are progressively being eliminated from use in the UK. In the Thames river catchment, there is no evidence of significant point sources or accidental spillage. Therefore, it is suspected that the closed and open usage of PCB-containing equipment in the Thames catchment serves as the main (diverse) source of the pollutants (EA, 2007). The total inputs of PCB 52, PCB 118 and PCB 153 to the whole system were estimated to be approximately 631.5 kg/yr, 103.7 kg/yr and 115.9 kg/yr respectively for the period between 2000 and 2008. The total mass of PCBs stored in the catchment system was then 204 kg for PCB 52, 401 kg for PCB 118, and 781 kg for PCB 153. These totals were distributed throughout the environmental compartments. In the case for PCB 52, the estimated amount in the environment was 0.59 kg in air, 170 kg in soil, 0.015 kg in water and 33.7 kg in sediment (Fig. 2). The corresponding capacities of each compartment for the chemical (VZ) were  $4.3E+9$  mol/Pa,  $1.38E+12$  mol/Pa,  $8.1E+6$



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

mol/Pa and  $1.8E+9$  mol/Pa. The modelled distributions of PCB 118 and PCB 153 in the Thames Catchment in the 2000s are shown in Supporting Information in Figs. S15 and S16. The soil compartment was identified as the major sink/source for the transfer of PCBs in the Thames catchment (accounting for 83.2% of PCB 52, 92.8% of PCB 118, and 96.9% of PCB 153) (Table 4). The largest mass of PCBs being deposited in soil is due to its large volume (capacity), with this compartment covering about 99.8% of the catchment area.

The river bed-sediment was predicted to be the most important sink/source within the river. PCBs are hydrophobic, and PCBs that are released into the water would be expected to partition strongly to suspended sediment which would subsequently fall out of suspension to become bed-sediment. River bed-sediment is predicted to be responsible for 3–17% of total PCB in the catchment (Table 4). The model estimates the highest concentration and fugacity for the three PCB congeners to reside in the sediment compartment; where fugacity is a function of the escape tendency of chemicals and implies a higher tendency for PCB congeners to transfer from the sediment to other phases in the aquatic environment – indicating that the sediment could act as a significant secondary source of PCBs in the River Thames. The percentage of PCBs in fish would be only a tiny fraction of that within the catchment as a whole.

The major contributors to the loss of PCBs from the catchment include advective (loss by air and water outflows) and degradation. The advective outflows accounted for about 74–97% of the total losses of the chemicals while degradation in different compartments accounted for the rest. To reveal the response of the catchment system to changing input, the corresponding characteristic time  $VZ/D$  was evaluated, where  $D$  is the transfer coefficient (Mackay, 2001; Sweetman et al., 2002). The output pathways for PCBs in the soil compartment include soil to air evaporation, soil runoff to water and degradation. For PCB 52, the corresponding time for evaporation to air was 1280 years, for runoff to water was 700 years and for degradation in soil was 14 years. Therefore, degradation is the most important loss process for the chemical in soil. Similar calculations have been done for the other compartments. Advective outflow dominates the loss of PCBs in air and with a response time of 8.5 h. Sediment deposition and re-suspension are the key transfer processes between water and sediment. The characteristic times are short in both directions (0.08 h for deposition and 7.5 d for re-suspension). Therefore, the exchange is rapid and the chemicals will approach equilibrium within a short time (Sweetman et al., 2002). The response times for PCB 52 in the catchment system were 0.35 d in air, 4964 d in soil, 0.04 d in water and 7.5 d in sediment. Similar analyses have also been done for PCB 118 and PCB 153. The response times for PCB 118 were 0.34 d in air, 5413 d in soil, 0.002 d in water and 7.5 d in sediment, whereas those

for PCB 153 were 0.33 d in air, 9175 d in soil, 0.002 d in water and 7.5 d in sediment.

### 3.4. The impacts of climate change and future trend

The trend over the simulation periods was for a net loss of all the studied PCBs from the catchment (Fig. 3). The major factor influencing the changing flux of PCBs in the catchment was the dramatic drop in the primary emissions. As the primary emissions decline, the re-volatilisation of PCBs in the soil compartments becomes another source. There is a tendency for the residue percentage of PCBs in the soil compartment to decrease and for that of air, water and mainly sediment to increase (Table 4). The sediment compartment is likely to act as the reservoir of PCBs in the Thames aquatic environment and could become a more important sink and secondary source in the future. For PCB 52, the total mass in Thames catchment soil was predicted to drop from 170 kg (83.3%) in 2000s to 12.2 kg (75.5%) in 2020s and to 8.5 kg (72.4%) in 2080s. Although the mass of PCB 52 in sediment was predicted to drop from 33.7 kg to 3.76 kg in the 2020s and 3.07 kg in the 2080s, the proportion of that held in the catchment was predicted to increase from 16.5% to 23.3% in the 2020s and to 26% in the 2080s.

The overall influence of climate change on PCB fate does not appear to be dramatic (Fig. 3). The largest influence was on concentrations in soil, probably due to the faster evaporation and degradation rates with the influence of increased temperatures (Harner et al., 1995) (Table 5). As the concentration and percentage in air increases, the potential for the long range transportation of the PCBs is slightly enhanced by climate change (Dalla Valle et al., 2007). Compared to the predictions for annual average climate conditions in the 2080s (Table 5), the values for season variations have only been enhanced by another 5–10% for PCB 52 in summer (summer has the most significant variations in temperature, precipitation and river flow). The difference for other PCBs is expected to be less because, in the sensitivity analysis, PCB 52 was the most sensitive to changes in environmental parameters. A confounding factor not considered here was the possible effect of higher temperature on the emission rates. With rising temperature, both the primary and secondary emissions of PCBs will be enhanced through the increased volatility. Moreover, the potential secondary effects of climate change on the catchment, such as wind speed change and land use change, were also not considered.

The contamination of PCBs in fish is a concern as fish are relevant to human and ecosystem health. The modelling results indicate a significant drop of the PCB concentrations in fish over the next decades (Fig. 3). The sum concentration of the studied PCBs in fish tissue is expected to drop from 9.51 ng/g in 2000–2010 to 1.32 ng/g in the 2020s which would now place it below the U.S. EPA unrestricted consumption thresholds (5.9 ng/g) for  $\Sigma$ PCBs. This decline has also been detected for marine fish in recent years (1998–2007) (OSPAR, 2009a). However, besides the three studied PCBs, significant levels of many other PCB congeners have also been detected in Thames fish (Jürgens, 2015; Jürgens et al., 2015). The influence of climate change on the fish concentrations of the studied PCBs was limited, with only 3–6% decrease in scenario B compared to scenario A.

### 3.5. Influence of differing congener properties on their fate

The predicted fate of the PCBs in the Thames catchment varied between the congeners. The studied PCBs belong to three different congener groups. Hexa-PCB 153 and penta-PCB 118 have higher octanol-water partition coefficients ( $K_{ow}$ ) than tetra-PCB 52, therefore, are more likely to accumulate in the organic-rich soil. This was reflected in the percentage residing in the soil compartment of the Thames catchment: tetra-PCB 52 (83.7%), penta-PCB 118 (92.8%) and hexa-PCB 153 (97%) (Table 4). As the primary emissions decline, soil becomes an important secondary source for PCBs in the catchment. The re-volatilisation for PCB 52 in the soil exceeds the others due to its higher

**Table 4**  
The distribution of PCBs under various climate scenarios.

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

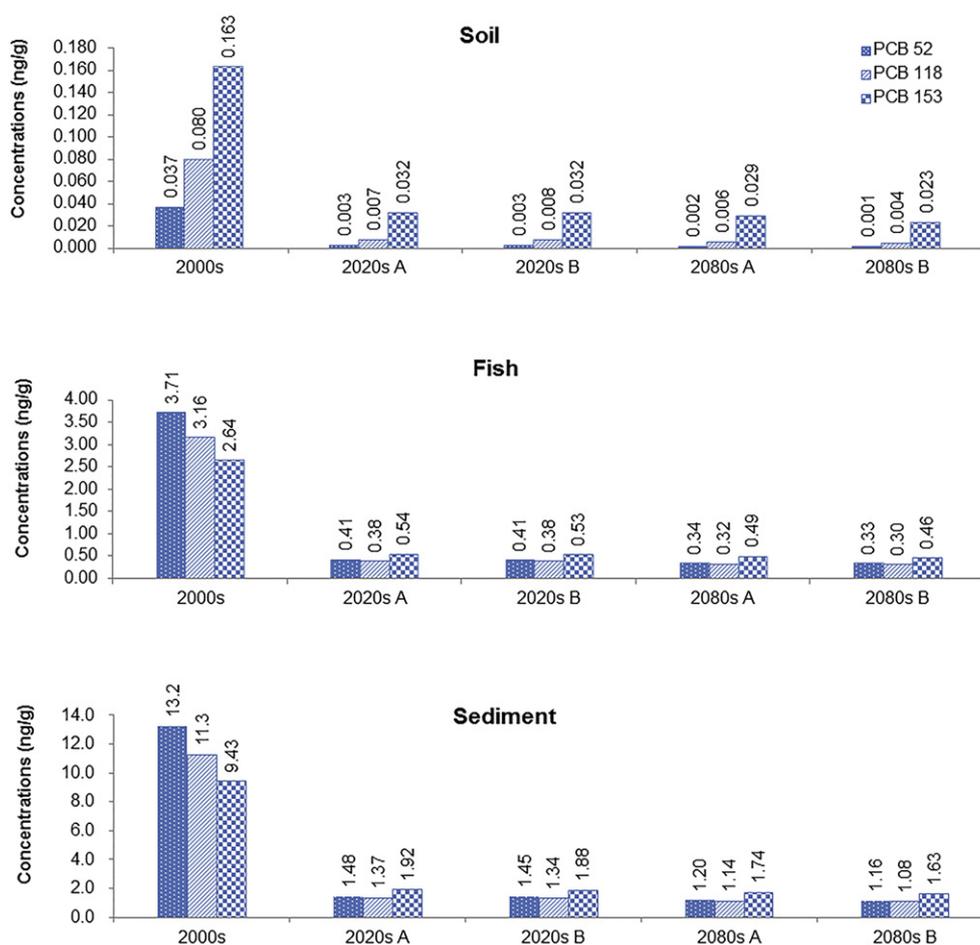


Fig. 3. The predicted concentrations of selected PCBs in soil, fish and sediment of River Thames Catchment under different climate scenarios.

vapour pressure. The concentration of PCB 153 was predicted to decline slower than that of other congeners, which would be related to its slower degradation rate. The heavier PCBs could stay longer than the lower congeners in the soil compartment. With the influences of climate change, the evaporation of PCBs from soil to other compartments will be slightly enhanced due to the increased volatilisation of the PCB congeners because of increased temperatures. The trend is more noticeable for PCB 52 and PCB 118 as they are more volatile and are more sensitive to the temperature increase than PCB 153.

#### 4. Conclusion

The fugacity level III model offers a helpful approach to predict the distribution and long term fate of PCBs in the River Thames Catchment. The modelled results suggest that the majority of the PCBs in the catchment will reside in the soil, whilst the highest concentrations of PCBs were predicted to lie in the sediment compartment. However, little recent observed sediment data is available for comparison. Over the next 80 years, we expect little transfer of PCBs between different

compartments, especially for the heavier PCB congeners, but, a significant overall drop in PCB concentrations in all compartments is expected. The rates of decrease were led by the decreasing trends of the assumed emission rates. With the decline in primary emissions, the soil compartment would become a significant ongoing secondary source of PCBs for the catchment environment. For the water environment the sediment serves as the major reservoir and would become a more important sink for PCBs in the system over time. In line with the other compartments, the modelling also forecast a drop in PCB concentrations in fish over the next decades. To inform decision making, additional measurements of the different congeners in sediment from different sites in the Thames would be recommended. With the influence of climate change, the evaporation of PCBs in soil was predicted to increase. Therefore, the mass and concentrations of PCBs in soil would drop faster than in the other compartments. The trend is the most noticeable for light (PCB 52) and less for heavier congeners (PCB 118, PCB 153).

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2015.06.084>.

**Table 5**  
Comparison between the predicted concentrations of selected PCBs under scenario B compared to scenario A in the 2080s.

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

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## Supporting Information to:

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

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### 1. Level III Fugacity Model

Figure S11 shows the processes taken into account in the fugacity level III model. The intermedia transport and transformation rates are described with the constant D. The equations of the interphase transfer calculation are presented in Table S11. More detailed information about the level III fugacity calculation is discussed in previous work carried out by Mackay (2001).

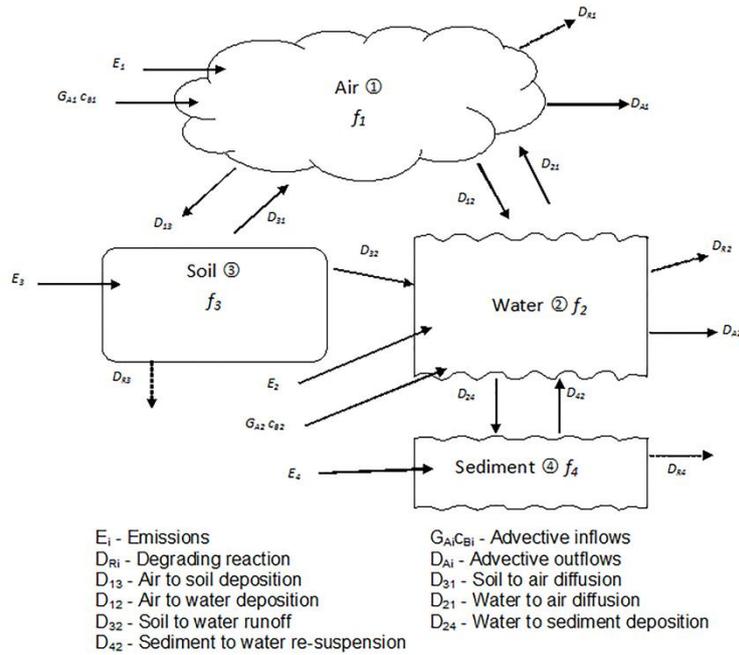


Fig.S11. Level III fugacity model schematic diagram (adapted from Mackay, 2001).

Table S11. Level III fugacity model calculation – Interphase Transfer D Value Equations (adapted from Mackay, 2001).

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

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

## 2. Input Parameters

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

Table SI2. Physico-chemical parameters of the selected PCBs

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

<sup>a</sup> Mackay et al. (1992);

<sup>b</sup> Dalla Valle et al. (2007); Paasivirta et al. (1999);

<sup>c</sup> Enthalpy of vaporization (Bamford et al., 2000; Kong et al., 2013);

<sup>d</sup> Activation energy for degradation of PCBs in air (Kong et al., 2013);

<sup>e</sup> Sinkkonen and Paasivirta (2000); Sweetman et al. (2002)

Table SI3. Environmental Properties of the River Thames Catchment

Parameter	Value	Data Sources
Temperature (°C)	11.07	Meteorological Office
Total catchment area (m <sup>2</sup> )	1.00E+10	Crossman et al. (2013)
Water surface area (m <sup>2</sup> )	1.96E+07	Crossman et al. (2013)
Depth of river (m)	3	—
Organic carbon in soil (g/g)	0.02	Hiederer and Kochy (2012)
Organic carbon in sediment (g/g)	0.1	Sweetman et al. (2002)
Lipid in fish (g/g)	0.05	Experiment data
Residence time in air (annual average) (h)	8.5	—
Residence time in water (annual average) (h)	324	Johnson et al. (2009)
Rain rate (m/h)	1.03E-04	Sweetman et al. (2002)
Average precipitation (mm)	1.88	Meteorological Office
Average wind speed (m/s)	3.28	Meteorological Office
Atmosphere height (m)	1000	Mackay (2001)
Density of air (kg/m <sup>3</sup> )	1.86	Mackay (2001)
Density of water (kg/m <sup>3</sup> )	1000	—
Depth of soil (m)	0.3	—
Depth of sediment (m)	0.1	—
Volume fraction of aerosol in air	1.30E-11	Sweetman et al. (2002)
Density of aerosol (kg/m <sup>3</sup> )	2.50E+03	Mackay (2001)
Volume fraction of suspended particles in water	5.00E-06	Sweetman et al. (2002)
Density of suspended particles(kg/m <sup>3</sup> )	2.50E+03	Mackay (2001)
Volume fraction of fish	1.00E-06	Sweetman et al. (2002)
Density of fish (kg/m <sup>3</sup> )	1.08E+03	Mackay (2001)
Volume fraction of air in soil	0.2	Sweetman et al. (2002)
Volume fraction of water in soil	0.3	Sweetman et al. (2002)
Volume fraction of solids in soil	0.5	Sweetman et al. (2002)
Volume fraction of water in sediment	0.63	Sweetman et al. (2002)
Volume fraction of solids in sediment	0.37	Sweetman et al. (2002)
Organic carbon in suspended particles (g/g)	0.2	—
Residence time in sediment (h)	5.00E+04	Mackay (2001)
Air side air-water MTC* (m/h)	3	Sweetman et al. (2002)
Water side air-water MTC (m/h)	0.03	Sweetman et al. (2002)
Aerosol dry deposition velocity (m/h)	10.8	Swackhamer et al. (1988); Sweetman et al. (2002)
Soil air phase diffusion MTC (m/h)	0.02	—
Soil water phase diffusion MTC (m/h)	1.00E-05	—
Soil air boundary layer MTC (m/h)	1	Sweetman et al. (2002)
Sediment-water MTC (m/h)	0.01	Lamon et al. (2012)
Sediment deposition velocity (m/h)	5.84E-04	Gevao et al. (1997); Sweetman et al. (2002)
Sediment re-suspension velocity (m/h)	1.11E-04	Gevao et al. (1997); Sweetman et al. (2002)
Soil water runoff rate (m/h)	3.00E-05	Gevao et al. (1997); Sweetman et al. (2002)
Soil solids runoff rate (m/h)	2.30E-08	Sweetman et al. (2002)
Scavenging ratio	2.00E+05	Sweetman et al. (2002)

\*MTC – Mass transfer coefficient

### 3. Change in Parameters with Temperature

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

$$\log P_s = A_{PS} - B_{PS}/T \quad (\text{SI1})$$

$$\log S_s = A_{SS} - B_{SS}/T \quad (\text{SI2})$$

$$\log S_l = A_{SL} - B_{SL}/T \quad (\text{SI3})$$

$$\log H = A_H - B_H/T \quad (\text{SI4})$$

$$\log K_{ow} = A_Z - B_Z \log S_l \quad (\text{SI5})$$

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

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

$$k = A e^{\frac{-E_a}{RT}} \quad (\text{SI6})$$

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

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

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

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

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

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

$$\text{BSAF} = \frac{C_f/f_t}{C_s/f_{soc}} \quad (\text{SI8}),$$

where  $C_f$ ,  $C_s$  are the chemical concentrations in fish and sediment,  $f_t$  stands for the fraction of lipid in fish, and  $f_{soc}$  is the organic carbon content in sediment.

## 5. Sensitivity and Uncertainty Analysis

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

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

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

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

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

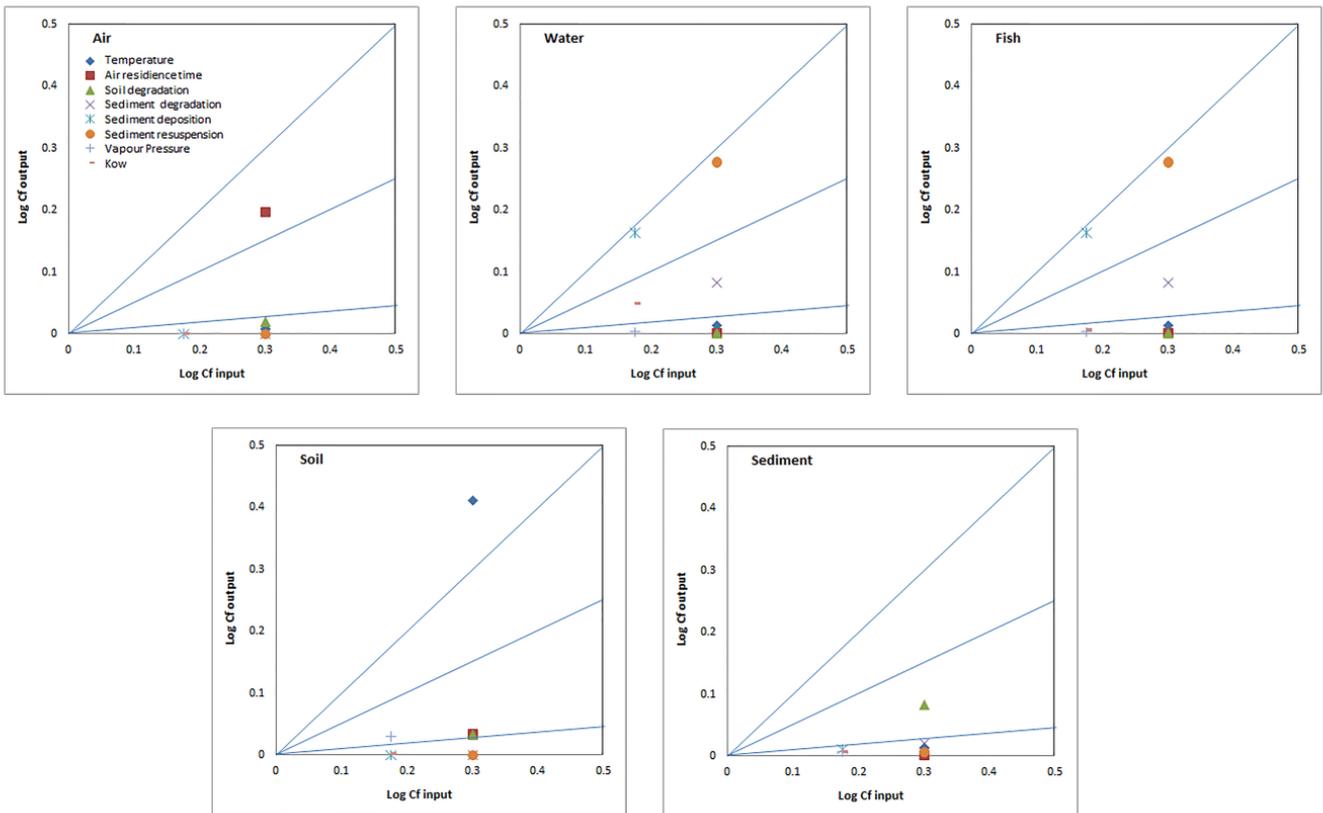


Fig. SI2. Graphic analysis of the contribution of the most sensitive parameters to modelling outputs in the compartments of air, soil, water, fish and sediment for PCB 52.

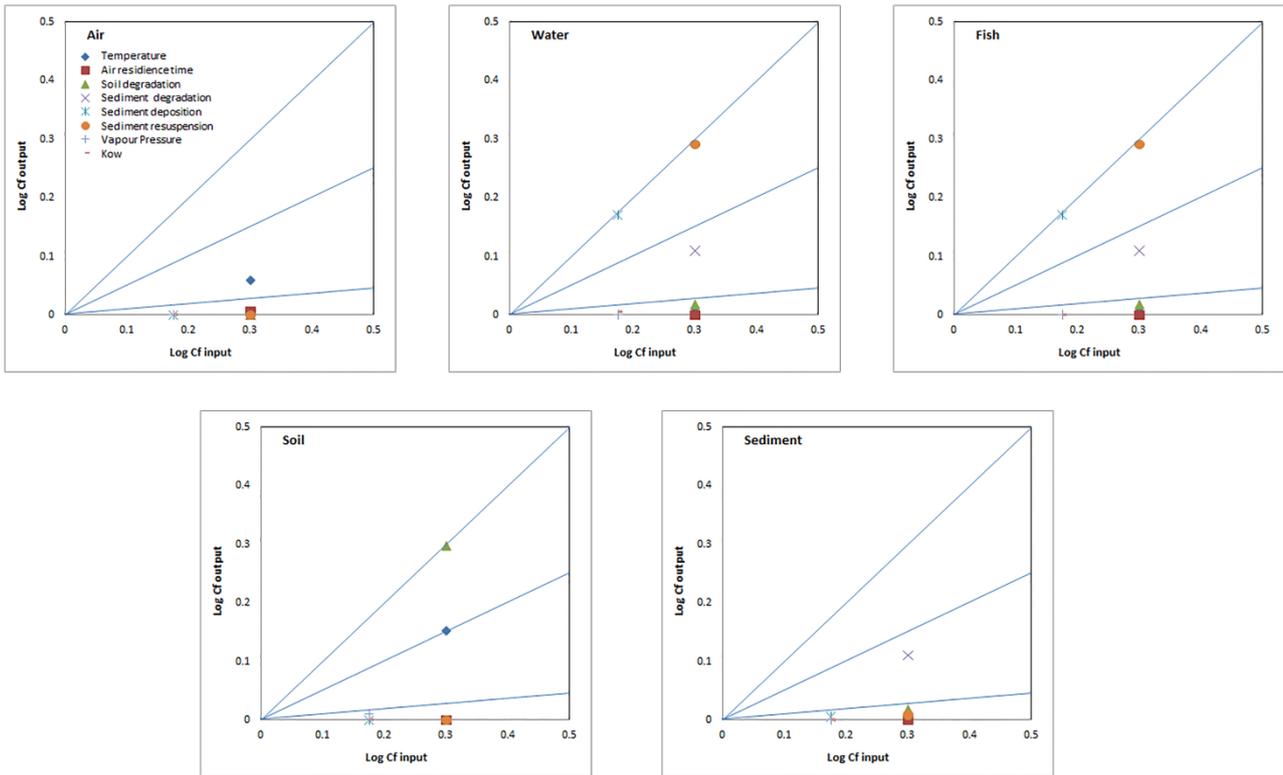


Fig. S13. Graphic analysis of the contribution of the most sensitive parameters to modelling outputs in the compartments of air, soil, water, fish and sediment for PCB 118.

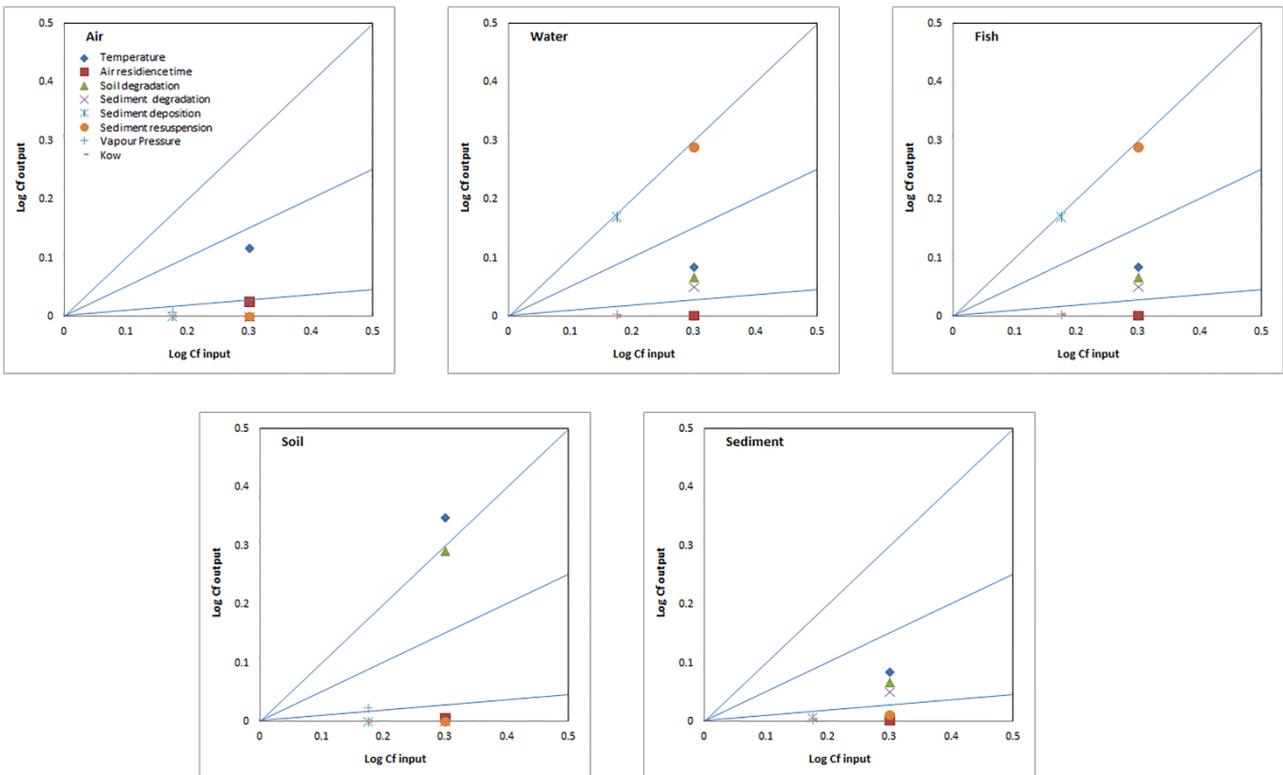


Fig. S14. Graphic analysis of the contribution of the most sensitive parameters to modelling outputs in the compartments of air, soil, water, fish and sediment for PCB 153.

## 6. The Fate of PCBs in the Catchment

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

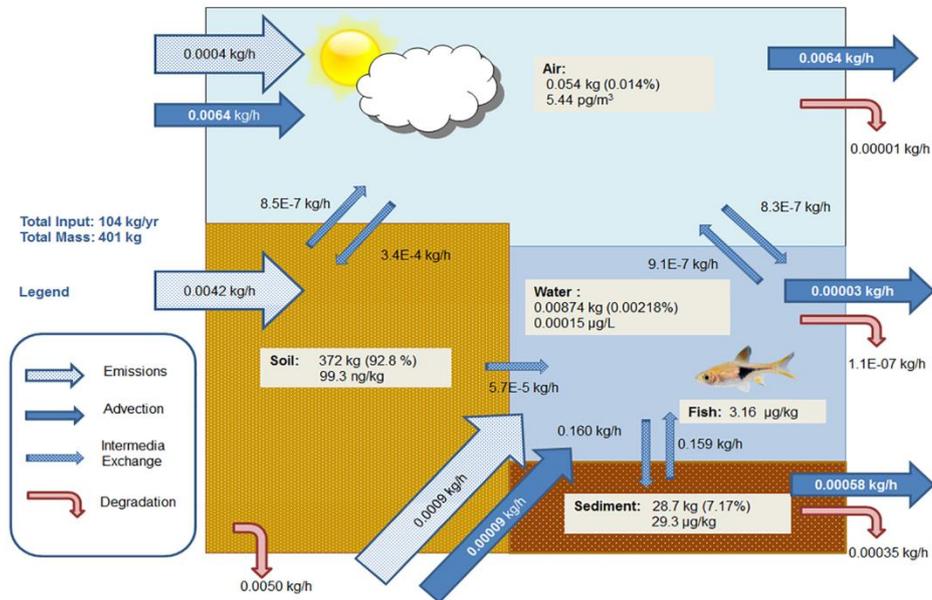


Fig. SI5. The modelled distribution of PCB 118 in the River Thames catchment in the 2000s

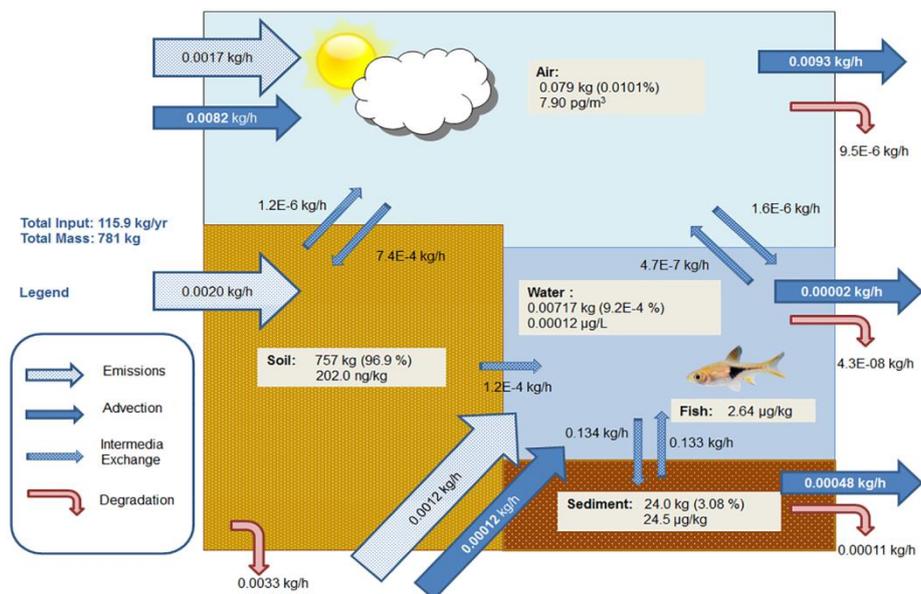


Fig. SI6. The modelled distribution of PCB 153 in the River Thames catchment in the 2000s

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## **Chapter 4. Persistent Organic Pollutants in sediment and fish in the River Thames Catchment (UK)**



## Persistent Organic Pollutants in sediment and fish in the River Thames Catchment (UK)



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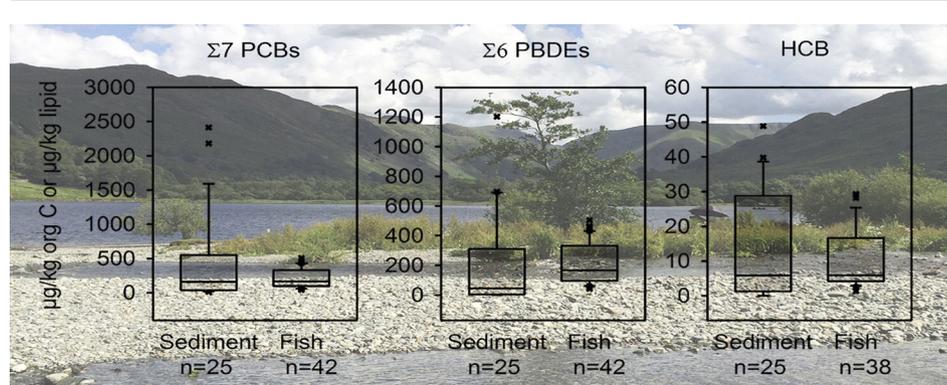
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### HIGHLIGHTS

- The mean PBDEs concentrations in fish exceeded the proposed European standards.
- The highest sediment POPs values were found in an urbanised tributary of the Thames.
- A higher dw concentration of POPs was found in the fish compared to the sediment.
- When normalised to OC/lipid, a similar POPs level in sediment and fish can be seen.
- The data suggests the contaminations of sediment and fish by POPs are connected.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Some organic pollutants including polychlorinated biphenyls (PCBs), polybrominated diphenylethers (PBDEs) and hexachlorobenzene (HCB) have been banned from production and use in the UK for >30 years but due to their toxicity and persistence are still of concern. However, due to their hydrophobicity they are present at very low concentrations and are difficult to measure in water, and so other matrices need to be sampled in order to best assess contamination. This study measured concentrations of ΣICES 7 PCBs (PCB congeners 28, 52, 101, 118, 138, 153 and 180) and Σ6 PBDEs (PBDE congeners 28, 47, 99, 100, 153, 154) and HCB in both bed-sediments and wild roach (a common pelagic fish) in the Thames Basin. The highest sediment concentrations were detected in an urbanised tributary of the Thames, The Cut at Bracknell (HCB: 0.03–0.40 µg/kg dw; ICES 7 PCBs: 4.83–7.42 µg/kg dw; 6 BDEs: 5.82–23.10 µg/kg dw). When concentrations were expressed on a dry weight basis, the fish were much more contaminated than the sediments, but when sediment concentrations were normalised to organic carbon concentration they were comparable to the fish lipid normalised concentrations. Thus, despite the variability in the system, both sediments and wild fish can be considered suitable for representing the level of POPs contamination of the river system given sufficient sample numbers.

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## 1. Introduction

Due to their persistence, bioaccumulation potential and toxicity many Persistent Organic Pollutants (POPs) remain of concern and are prominent in environmental legislation (Vonderheide et al., 2008; Kuzyk et al., 2010; Nicolaus et al., 2015). These compounds of concern, which include organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs), have been eliminated or severely reduced in production and use due to environmental concerns. This study focuses on PCBs and hexachlorobenzene (HCB), a fungicide, for which an environmental quality standard for biota has been set in the first version of the EU Priority Substances Directive (European Union, 2008) which were both banned in the EU >30 years ago, as well as PBDE flame retardants most of which have been banned since 2004.

Normally, chemical pollutants in rivers are monitored by regular sampling of the water column, but here there is a problem, because in the UK in recent years, HCB, PBDEs and PCBs concentrations are close to or lower than the detection limits for current methods. For example, between 2000 and 2015 only six out of 4373 Environment Agency HCB measurements from the non-tidal Thames and its tributaries were above the detection limit of 1 ng/l (<http://environment.data.gov.uk/water-quality>).

The chemicals in the current study have log  $K_{ow}$  values between 5 and 8 (Schenker et al., 2005; Rowe, 2009) so they tend to partition much more favourably to organic matrices than water. However, natural water bodies contain suspended sediments which may be partly or wholly composed of organic matter which can act as an important sorbent for POPs (Katagi, 2002). These suspended sediments will ultimately become bed-sediments and consequently, high concentrations of POPs can be found in bed-sediments of rivers (e.g. up to 4 or 5 µg/kg dry weight for BDE 99 and BDE 47 respectively in River Viskan, Sweden 1995 (Sellström et al., 1998); 105–400 µg/kg dw for the sum of 27 PCBs (ICES 7 PCBs<sup>1</sup> contributed about half of that) and up to 272 µg/kg dw for the sum of 10 tri- to hexa-BDEs (including the 6 commonly monitored ones) in the Scheldt river, Belgium (Covaci et al., 2005; Vane et al., 2007). In the UK, high levels organic pollutants have been observed in the Mersey, Clyde, and Tyne estuaries (Vane et al., 2007; Vane et al., 2010; Nicolaus et al., 2015). The concentrations of PCBs in some sediment samples from the Thames estuary were recently reported to have exceeded the Ecotoxicological Assessment Criteria (EACs) derived by the Oslo and Paris Convention (OSPAR) by up to 218 fold (Nicolaus et al., 2015). The difficulty with bed-sediment sampling, however, is that the distribution of fine organic rich sediments can be very variable across a river, even over distances of a few metres (Hedges and Keil, 1995; Bianchi et al., 2007; Wakeham and Canuel, 2016).

An alternative is examining the presence of POPs in wildlife, known as biomonitoring. Monitoring aquatic wildlife for the presence of POPs is attractive for two reasons, firstly they are another potential organic sorbent and secondly they represent what we want to protect in the first place. There has been some use of macroinvertebrates, such as *Gammarus* species, but this has been most used in connection with metals (Lebrun et al., 2015). However, short-lived species low down the food web such as these are not ideal for monitoring low levels of POPs. Molluscs have been used for biomonitoring but there are some indications that their accumulation does not correlate well with sediments for some POPs (Bervoets et al., 2005). This may be related to their low position in the food web (grazer). Fish are higher in the food web and so are more connected to their whole environment through their diet. High concentrations of POPs can be found in fish through long-term exposure to a contaminated water environment (MacKay and Fraser, 2000; Fujii et al., 2007; Deribe et al., 2011). Assessing the

degree of contamination of priority organic pollutants in fish is now becoming a component of national and international efforts to monitor the distribution of organic pollutants and their adverse effects in river ecosystems (European Union, 2008, 2013). In the UK, a fish archive has been established by CEH (Centre for Ecology and Hydrology, Wallingford) (<http://www.ceh.ac.uk/our-science/projects/national-fish-tissue-archive>) to investigate the occurrence of pollutants in fish (mainly roach, *Rutilus rutilus*) from English rivers. Since 2007, about 200–300 fish have been caught per year from different river sites in England and stored at –80 °C as a resource for monitoring chemical pollution or other aspects of fish and environmental health (Jürgens et al., 2013). Roach offer a number of advantages for biomonitoring in lowland rivers as they are abundant, do not roam far, typically no >300 m (Baade and Fredrich, 1998; Penczak, 2006; Bolland et al., 2009) and they have a broad diet. Their food sources include invertebrates, such as the larvae of many insects, molluscs, algae and plant remains (Mann, 1973).

This study had the following objectives:

- To examine if, and to what extent, the freshwater River Thames bed-sediments are contaminated with HCB, 7 PCBs and 6 PBDEs;
- To assess whether this contamination can be linked to local sewage effluent discharge;
- To examine whether POPs contamination can be correlated to the depth of the sediment sample;
- To examine if and to what extent the roach fish of the River Thames are contaminated;
- To assess whether bed-sediment and fish POPs concentrations can be correlated.

## 2. Materials and methods

### 2.1. Sediment sampling

The sediment samples were collected in 2013 using 28 mm diameter copper tubes filled with dry ice to freeze the sediment to the core, which was then pulled up allowing the collection of undisturbed sediment layers (Jürgens et al., 2014 and Supporting Information Fig. SI 1). The sediment samples were collected from seven sites in the River Thames and its tributaries (Littlemore Brook, a very small tributary impacted by a large sewage treatment works, both upstream and downstream of the sewage discharge, the river Thames at Wallingford Bridge and Winterbrook, The Cut, an urbanised river downstream of the town of Bracknell, and two rivers with relatively little urban impact, the river Kennet in Newbury, and the river Ock upstream of Abingdon) (Fig. 1). One or two sediment cores from each site were used for determining the sediment contamination of organic pollutants in this study. The samples were removed from the tubes by filling hot water into the cores until the frozen cores slipped off. These sediment samples were left to defrost overnight and then sliced into 5–8 layers. Generally divisions were made where the appearance (e.g. colour, grain size etc.) changed, with the exception of the Ock sample which appeared uniform throughout and was therefore cut at 5 cm intervals (Supporting Information, Table SI 1). Large pieces of wood and stones were removed during the segmentation process. The divided sediment samples were added to small plastic vessels for storage and were kept frozen at –20 °C. All 5 layers of one sediment core collected from the Littlemore Brook upstream site were analysed. However, for the other sediment cores, only the surface and second layers were examined for POPs contamination in this study (Table SI 1).

### 2.2. Fish Tissue Archive project (fish collecting)

CEH Wallingford has been building up a sample base for fish from UK rivers since 2007 (The Fish Tissue Archive). Whole fish samples have

<sup>1</sup> ICES 7 PCBs are recommended by International Council for Exploration of Sea (ICES) for marine environment monitoring, includes PCB congeners 28, 52, 101, 118, 138, 153 and 180.

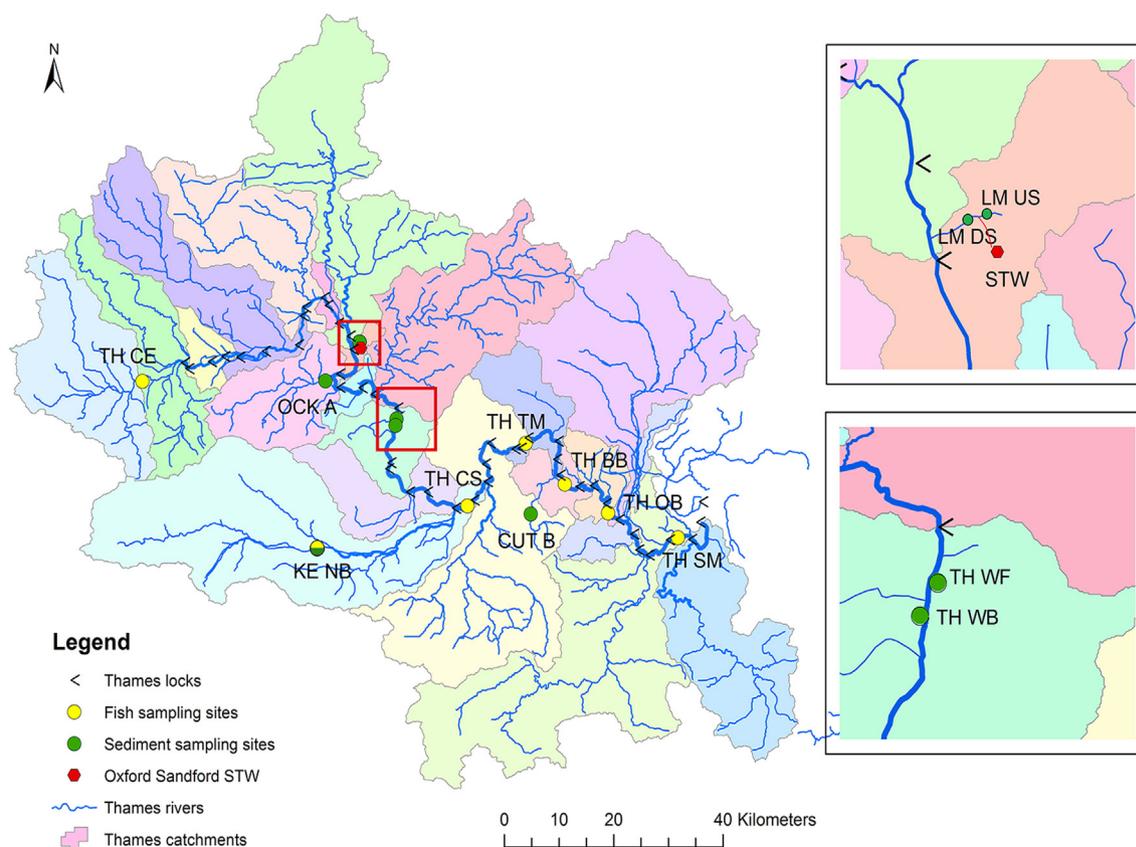


Fig. 1. Fish and sediment sampling sites of the River Thames Catchment (for site names, see Table 1).

been collected and stored frozen for future use, to allow the measurement of chemical contamination levels and their spatial or temporal trends. Normally ten roach (*Rutilus rutilus*, approx. 15 cm long) per site and year are caught by fish monitoring teams of the Environment Agency killed on site with an overdose of 2-phenoxyethanol, and then shipped in a liquid nitrogen cooled dry shipper to a  $-80\text{ }^{\circ}\text{C}$  freezer in CEH. A subset of these fish samples were prepared for analysis by breaking the whole fish into a few pieces without defrosting and grinding them into frozen fish powder with a cryogrinder (SPEX SamplePrep 6850). The powder was then divided into pre-cooled glass vials and kept in a  $-80\text{ }^{\circ}\text{C}$  freezer until further analysis. Around 10% of the collected fish samples have already been analysed and part of the results (HCB, HCBd, PBDEs in fishes from River Glen, Nene, Kennet and Thames, and PCBs, DDTs, Lindane in eels from the lower Thames) have been reported (Jürgens et al., 2013, 2015). Details of the analysed fish can be found in the supporting information, Table SI 2 and the sampling sites are marked in Fig. 1. More detailed fish sampling information is described in Jürgens et al. (2013).

### 2.3. Analytical methods for organic pollutants

#### 2.3.1. Extraction and purification

The analytical methods for determining organic pollutants including PCBs, BDEs and HCB in sediment and biota samples from the River Thames were based on previously established and approved procedures (Jürgens et al., 2013; Ma et al., 2015).

The sediment samples were defrosted overnight and then washed through a 1 mm mesh sieve using Milli-Q water to remove fine particles stuck on the sieve. The resulting samples were centrifuged to reduce water content and sub-samples of 10 g wet sediment were mixed with 10 g anhydrous sodium sulphate to remove water. The prepared sediment samples were then extracted in dichloromethane (DCM) (approximately 150 ml) at  $40\text{ }^{\circ}\text{C}$  for 16 h in a Soxhlet apparatus. The surface

layer from Littlemore Upstream (LM US) was repeated in triplicate to quantify methodological precision. Recovery standards containing  $^{13}\text{C}$ -labeled PCBs: 28, 52, 101, 138, 153, 180 and BDEs: 51, 128, 190 were added to the samples before extraction and 5 g of copper powder was added into the receiving flask to reduce the potential interference of sulphides on the analyses. The resulting extracts were evaporated to about 5 ml on a rotary evaporator and then were further concentrated to about 0.5 ml under a gentle stream of nitrogen. The extracts were purified with an acid silica column followed by a gel permeation column (GPC). The eluent was collected in a vial and then concentrated to about 1 ml under a gentle nitrogen stream. After that, the concentrated eluent was transferred to a GC vial containing a known amount of internal standards: PCB 30,  $^{13}\text{C}$ -PCB141,  $^{13}\text{C}$ -PCB208, BDE69, BDE181 in 25  $\mu\text{l}$  dodecane and blown down under nitrogen to 25  $\mu\text{l}$ .

Frozen fish powder samples (around 5 g of frozen fish powder well mixed with 10 g anhydrous sodium sulphate) were extracted using similar procedures to that used for the sediment samples except that copper addition was not required. Procedural blanks (10 g anhydrous sodium sulphate) were used in each extraction batch. A small portion of the Soxhlet extract was used for gravimetric determination of the lipid content after the solvent had evaporated. The remaining extract was evaporated to a small volume (about 1 ml) and was then taken up for clean-up and further analysis similar to the sediment samples (more details of the fish analysis are in Jürgens et al., 2013, 2015).

#### 2.3.2. GC-MS analysis

The purified sample extracts were analysed on a Thermo Trace GC Ultra gas chromatograph (GC), equipped with a  $50\text{ m} \times 0.25\text{ mm}$ ,  $0.25\text{ }\mu\text{m}$  Agilent CP-Sil 8 CB capillary column, and coupled with a Thermo DSQ mass spectrometer (MS). The instrument was run in EI (electron impact) and SIM (single ion monitoring) mode at a source temperature of  $250\text{ }^{\circ}\text{C}$ . The target compounds were the 7 PCBs, 6 BDEs and HCB. The  $^{13}\text{C}$ -labeled PCB standards and PBDE standards were

purchased from Cambridge Isotope Laboratories, Andover, Massachusetts, while the others were purchased from Wellington Laboratories Inc., Guelph Ontario.

### 2.3.3. Quality assurance/quality control

For quality control, a blank sample of 10 g sodium sulphate was run with every five samples (5 samples + 1 blank per batch). To minimise any inherent experimental bias, samples with a mixture of sites were selected for each batch. Method Detection Limits (MDLs) were derived based on the presence of the analyses in the method blanks. The MDL is defined as  $3 \times$  standard deviation + mean concentration of blanks. The MDLs ranged between 0 and 0.05 ng/g for fish, and 0 and 0.19 ng/g for sediments. For analyte concentrations that are lower than three times of the respective blank value, the MDL was simply the instrumental detection limit (the lowest observable standard on the instrument, equivalent to 1–6.25 µg/µl for the analysed compounds). Recovery standards were used to compensate for any losses during extraction and clean-up. The mean recoveries for the fish samples ranged between 92 and 106% for PCBs and 80–90% for PBDEs, while the mean recoveries for the sediment samples were 59% ( $^{13}\text{C}$ -PCB 209)–93% for PCBs and 65%–110% for PBDEs. The differences in the recoveries between fish and sediment samples may be due to different instrument performance for the different sequences. Usually the instrument changes its performance over the course of the sequence (because it's getting dirtier), and it will become less sensitive (the peaks get smaller). In addition, the differences may be caused by matrix effects and small differences in the clean-up methods for both matrices. However, samples were recovery-corrected to account for these differences.

### 2.4. Sediment organic carbon content

\*additional info. is provided in the Supporting Information (page 75)

The concentrations of organic pollutants in the sediment samples should be normalised to dry weight and their organic carbon content to allow comparison to assessment criteria (e.g. Ecotoxicological Assessment Criteria (EACs) of OSPAR, 2009). Therefore, the moisture content and the organic carbon content of the sediment samples were determined. Around 10–20 g wet sediment samples were oven dried at 105 °C ( $\pm 5$  °C) overnight (24 h), cooled and weighed to determine the moisture content. After that, the dried sediment samples were ground using a Planetary Ball Mill (PM 100, RETSCH). The sediment organic carbon content was determined using an Elemental Vario EL elemental analyser (Elementar Analysensysteme, Hanau, Germany). The instrument is calibrated using a working standard (Acetanilide) with approximate concentrations of 71.1% total C. The standard is analysed

at the beginning of every run, with every 10 samples and again at the end of a run and used to apply a daily correction factor. Two reference soils material are analysed with each batch of samples at intervals of every 20 samples.

## 3. Results and discussion

### 3.1. Contamination levels in sediment

River bed-sediments can be a major sink/source of organic pollutants in river systems (Lu et al., 2015). However, few studies reported the recent contamination levels of organic pollutants in sediment of the Thames. Over the period 1990–1995 a mean value of 34.4 µg/kg was reported for PCB as 249 Aroclor-1248 in salt marsh sediment of Two Tree Island in the Thames estuary (Scrimshaw and Lester, 2001). Twenty-five sediment samples from different sites and core depth were analysed for HCB, ICES 7 PCBs (PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153 and PCB 180), and 6 BDEs (BDE 28, BDE 47, BDE 99, BDE 100, BDE 153, BDE 154) in the current study. ICES 7 PCBs are recommended by the International Council for Exploration of Sea (ICES) for marine environment monitoring. They are also listed in the latest EU Commission Regulation on methods of sampling and analysis for the control of PCBs (European Commission, 2014), without labelling them as ICES 7. The 6 BDEs were chosen as indicators for the contamination of PBDEs in the Thames environment as they are the most commonly found congeners in the environment and are commonly monitored and regulated (e.g. European Union, 2008, 2013).

Comparison of the average results for sediment samples at the seven sites in the River Thames and its tributaries showed a wide range of concentrations (<MDL–0.34 µg/kg dw for HCB, 0.12–27.4 µg/kg dw for  $\Sigma$ ICES 7 PCBs, and <MDL–14.4 µg/kg dw for  $\Sigma$ 6 BDEs) (Table 1). The contamination levels of  $\Sigma$ ICES 7 PCBs were similar to those reported for the Mersey Estuary, UK (11.7–14.4 µg/kg dw) (Vane et al., 2007), but the values for HCB and  $\Sigma$ 6 BDEs were lower than those reported for the Mersey Estuary and the inner Clyde Estuary (Vane et al., 2007; Vane et al., 2010). There are no environmental quality guidelines available for PCBs, BDEs and HCB in fresh water sediment. However, the levels of  $\Sigma$ ICES 7 PCBs were below the current Ecotoxicological Assessment Criteria (EACs) set up for the use in marine sediment (OSPAR, 2009).

The lowest concentrations of HCB,  $\Sigma$ ICES 7 PCBs and  $\Sigma$ 6 BDEs were detected in the sediments from the River Ock, while the highest values were found at the sites in The Cut and Littlemore Brook (Table 1, Fig. 2). The sampling site in the River Ock is in a rural area with little sewage input. The Cut is within an urbanised area and has particularly high

**Table 1**

Concentrations of HCB, PCBs and PBDEs in fish (roach) and sediment samples from the River Thames and its tributaries.

Site ID	Sampling site <sup>a</sup>	HCB		$\Sigma$ ICES 7 PCBs		$\Sigma$ 6 BDEs	
	Fish (min-max, mean [µg/kg fresh weight], upstream to downstream for the Thames)						
TH CE	TH Castle Eaton, 2011 (n = 10)	0.28–1.48, 0.97		7.41–14.23, 11.90		7.50–24.47, 16.48	
TH CS	TH Caversham-Sonning, 2008, 2010, 2012 (n = 8)	0.18–1.45, 0.52		7.47–23.39, 15.36		3.76–11.15, 7.13	
TH TM	TH Temple-Marlow, 2007 (n = 4)	Not measured		9.35–25.66, 15.99		5.01–12.93, 16.84	
TH BB	TH Bray-Boveney, 2012 (n = 2)	0.11–0.16, 0.14		7.18–14.15, 10.67		8.94–20.09, 14.51	
TH OB	TH Old Windsor-Bell, 2007 (n = 5)	0.06–0.57, 0.33		4.67–17.79, 11.82		4.86–8.01, 6.35	
TH SM	TH Sunbury-Molesey, 2012 (n = 4)	0.17–0.46, 0.30		12.32–15.11, 13.76		8.14–11.91, 10.11	
KE NB	KE, Newbury, 2011 (n = 9)	0.16–0.36, 0.24		3.09–6.98, 4.84		2.30–5.62, 3.59	
	Sediment (mean, µg/kg dry weight)	Surface	Second	Surface	Second	Surface	Second
LM US	LM upstream of STW, 2013 (n = 2)	0.19	0.31	2.21	4.38	2.03	3.80
LM DS	LM downstream of STW, 2013 (n = 1)	0.34	0.26	12.3	12.8	3.62	3.69
OCK A	OCK, Abingdon, 2013 (n = 2)	<MDL <sup>b</sup>	0.01	0.12	0.13	<MDL <sup>b</sup>	0.03
TH WF	TH, Wallingford, 2013, 2014 (n = 2)	0.01	0.01	27.4	12.0	0.07	0.04
TH WB	TH, Winterbrook, 2013 (n = 2)	0.02	0.03	0.41	2.08	0.18	0.19
CUT B	CUT, Bracknell, 2013 (n = 2)	0.23	0.21	4.87	5.88	7.22	14.4
KE NB	KE, Newbury, 2013 (n = 2)	0.20	0.06	2.78	0.27	0.81	0.05

<sup>a</sup> Rivers: TH—Thames, KE—Kennet, OCK—Ock, CUT—The Cut, LM—Littlemore Brook.

<sup>b</sup> MDL—Method Detection Limit.

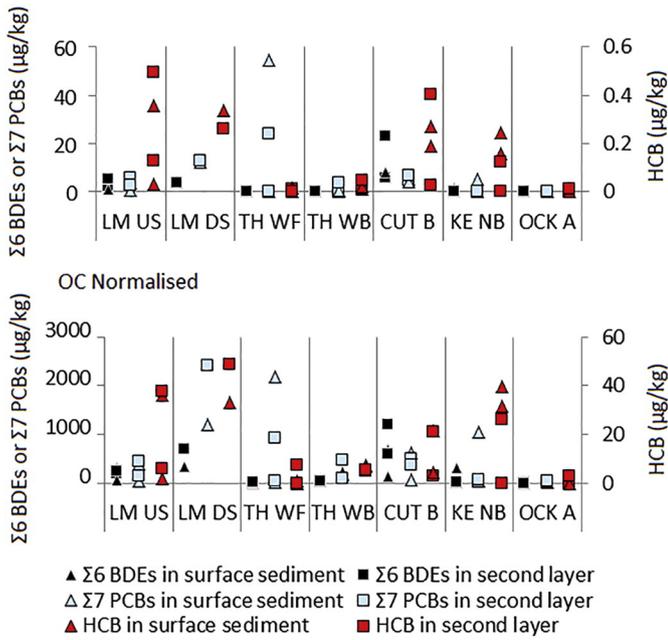


Fig. 2. Concentrations of HCB, ΣICES 7 PCBs and Σ6 BDEs in sediment samples from seven sites in the River Thames and its tributaries.

exposure to human activities (Putro et al., 2016). It receives high sewage effluent input from Bracknell (on average 43.3% of the flow is treated sewage). Littlemore Brook is an urbanised tributary within an industrialised sub-catchment of the River Thames. In Littlemore Brook, samples were taken from two sites close to each other (about 100 m apart), either side of the effluent discharge channel of the Oxford (Sandford) Sewage Treatment Work (STW). In the majority of cases, the concentrations of the studied chemicals were higher in the sediment samples collected from downstream of the STW than in those collected from upstream (Table 1, Fig. 2). The sewage effluent could be an on-going source of the contaminations of the studied chemicals in the sediment. However, overall no significant linear correlations ( $R^2$  ranged

from 0.0677 to 0.2575) were detected between sediment concentrations of HCB, ΣICES 7 PCBs and Σ6 BDEs with the modelled sewage water fraction in the sediment samples from the River Thames and its tributaries (Fig. SI 2). The sewage effluent content at the sediment sampling sites was estimated using the Low Flows 2000 Water Quality eXtension model (LF2000 WQX, Wallingford HydroSolutions). The model calculates in a Monte Carlo framework to account for the variability in river flows and per capita influent load. The model randomly selects river and effluent flows from a defined distribution and does 2000 mass balance calculations using different river and effluent flows for each time. The river flow data used to estimate dilution were taken from the databases within the model (LF2000-WQX). In the modelling, the river flow was defined as log-normally distributed, while the effluent flow was defined as normally distributed. The modelling provides the mean and 90th percentile data for sewage effluent content. Here, the mean percentile effluent content data of the 2000 mass balance calculations was used.

### 3.2. Variation in sediment concentration with depth

A wide variation in the concentrations of PCBs, BDEs and HCB with depth was observed for the sediment sample from the site at Littlemore Brook Upstream (Fig. SI 3). The concentrations of the chemicals were higher in the second layer of the sediment core than in other layers. The sediment layers were divided according to the visual structure of the sediment core, and have varying amounts of sediment organic carbon (SOC) (top: 0.99%, second: 1.31%, third: 2.04%, fourth: 1.72%, fifth: 1.24%). However, no significant correlation between the sediment concentrations and the sediment organic carbon content was detected (Fig. SI 3). Therefore, the variability cannot be explained by stronger adsorption to SOC only. It could be a reflection of the trend of usage of the organic chemicals in the study area, but, unlike lake sediments, river bed-sediments are subject to disturbance due to flood events, so depth may not always correspond to time. The penta-mix BDEs, which consists mainly of BDE 99 and BDE 47, has been banned in 2004 (European Union, 2003). The concentrations of BDE 99 and BDE 47 remain high in the surface layer of the sediment sample.

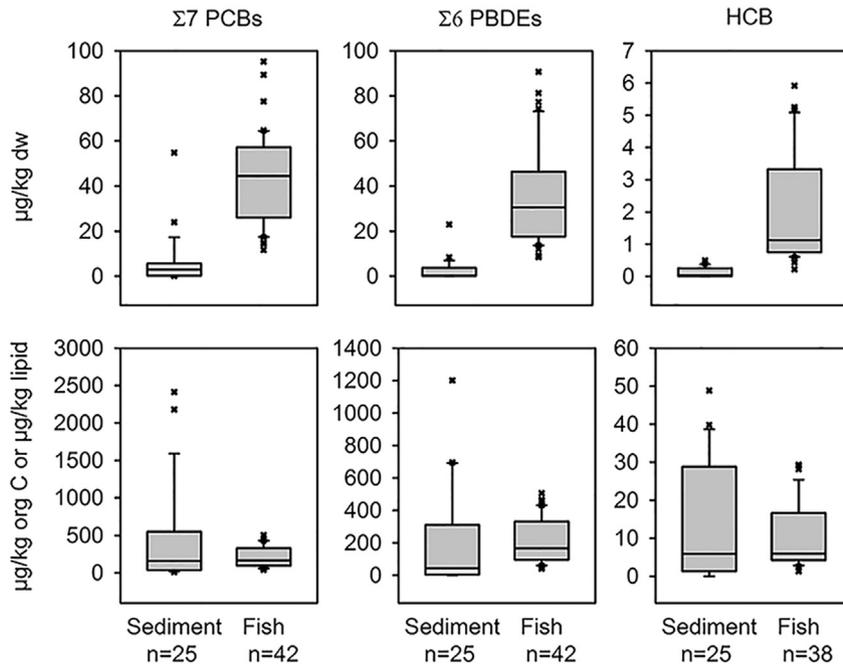


Fig. 3. Comparison between measured chemical concentrations in all River Thames Basin fish and sediments, showing 10, 25, 50, 75, 90%iles as well as outliers.

**Table 2**BSAF ( $\mu\text{g}/\text{kg}$  lipid/ $\mu\text{g}/\text{kg}$  organic carbon) values for PBDEs, PCBs and HCB in the River Kennet.

	PBDE 28	PBDE 47	PBDE 99	PBDE 100	PBDE 153	PBDE 154	PCB 28	PCB 52	PCB 101	PCB 118	PCB 138	PCB 153	PCB 180	HCB
BSAF	18.3 $\pm$ 5.0	13.0 $\pm$ 4.7	0.03 $\pm$ 0.02	5.0 $\pm$ 1.8	0.3 $\pm$ 0.3	4.4 $\pm$ 5.7	0.4 $\pm$ 0.1	1.6 $\pm$ 0.7	1.2 $\pm$ 0.5	5.2 $\pm$ 2.8	1.9 $\pm$ 0.9	1.5 $\pm$ 0.8	0.8 $\pm$ 0.4	0.8 $\pm$ 0.2

### 3.3. Contamination in Thames fish

HCB was detected in all fish samples, but none exceeded the EU EQS (Environmental Quality Standards) of  $10 \mu\text{g}/\text{kg}$  ww (Table 1) (European Union, 2013). The concentrations of HCB in Thames and Kennet fish ( $0.06$ – $1.48 \mu\text{g}/\text{kg}$ ) were similar to those in fish from other UK rivers (River Glen: mean  $0.21 \mu\text{g}/\text{kg}$ ; River Nene: mean  $0.68 \mu\text{g}/\text{kg}$ ) (Jürgens et al., 2013). The sum of the concentrations of the 6 BDEs ( $2.30$ – $24.47 \mu\text{g}/\text{kg}$  with a mean value of  $9.35 \mu\text{g}/\text{kg}$ ) in all of the analysed fish samples from the River Thames were several orders of magnitude higher than the EU EQS of just  $0.0085 \mu\text{g}/\text{kg}$  (European Union, 2013). Nevertheless, the levels of  $\Sigma 6$  BDEs in Thames fish were lower than the levels reported in another recent survey for the River Don ( $10.55$ – $128.40 \mu\text{g}/\text{kg}$ ) (Rose et al., 2015). For PCBs, the concentrations for  $\Sigma$ ICES 7 PCBs in Thames fish (ranged from  $3.09$ – $25.66 \mu\text{g}/\text{kg}$  with a mean value of  $11.65 \mu\text{g}/\text{kg}$ ) exceeded the US EPA unrestricted consumption threshold of  $5.9 \mu\text{g}/\text{kg}$  for  $\Sigma$ PCBs (Lu et al., 2015). The levels of  $\Sigma$ ICES 7 PCBs were higher than those previously reported in fish from the upper Thames ( $<0.77$ – $3.32 \mu\text{g}/\text{kg}$ ) and the River Glen ( $2.22$ – $3.84 \mu\text{g}/\text{kg}$ ), and were comparable to the levels in fish from the River Nene ( $3.57$ – $16.39 \mu\text{g}/\text{kg}$ ) (Yamaguchi et al., 2003; Jürgens, 2015). As only a limited number of fish have been analysed, it is difficult to demonstrate either temporal or spatial trends of the contaminants in Thames fish, but the fish contamination was much lower in the River Kennet tributary than those detected in the sites of the main river. The catchment of the River Kennet is mainly rural in character and the average sewage content at the sampling site is only 3% by volume (Jürgens, 2015).

### 3.4. Comparison of fish concentrations with sediment values

It should be noted that the fish and sediment sampling sites were not in identical locations within the Thames Basin, nor was sampling carried out at the same time. So it might have been assumed that contamination levels in the fish and sediment would bear no relation to one another. Indeed, when comparing the fish and sediment concentrations on a weight for weight basis it is clear that there is higher contamination in the fish (Fig. 3). The median values in fish samples from the River Thames and its tributaries were 30.5, 44.4, and  $1.12 \mu\text{g}/\text{kg}$  dw respectively for  $\Sigma 6$  BDEs,  $\Sigma$ ICES 7 PCBs, and HCB, which were higher than those in the sediment samples<sup>2</sup> ( $0.30$ ,  $2.90$ , and  $0.03 \mu\text{g}/\text{kg}$  dw) (Fig. 3). Therefore, at first it might seem that there is no relationship between fish and sediments with respect to POPs in the Thames Basin. However, when the data is normalised to either lipid (for the fish) or organic carbon (for the sediment) then a similar level of contamination to these matrices can be seen (Fig. 3). There is one site on the River Kennet where the fish samples and sediment samples were from the identical location. The dry weight values in fish were about 2–10 times higher than that in the sediment (Fig. SI 4). Applying the normalisation for OC and lipid content however didn't influence the described relationship significantly.

In this study, the BSAFs (biota-sediment accumulation factors) (Burkhard et al., 2005) were calculated for the POPs in the roach from the River Kennet to evaluate the relationship between the fish and sediment contamination (Table 2). It is assumed that POPs in water, fish and sediment are at equilibrium and the BSAFs do not substantially change with varying environmental factors. For the 6 BDEs and the

ICES 7 PCBs, the BSAF factors were a bit lower than those reported for the same fish species from the Orge River (France) (Teil et al., 2012). The BSAF factors for BDE 28 and BDE 47 were much higher than those for other congeners, which is consistent with the findings of Teil et al. (2012) and Sellström et al. (1998). To our knowledge, there is no BSAF data available for HCB in roach in the literature. However, the BSAF values were comparable to those reported for caged carp in Dutch freshwater sites field studies ( $0.17$ – $1.42 \mu\text{g}/\text{g}$  lipid/ $\mu\text{g}/\text{g}$  OC) (Verweij et al., 2004).

## 4. Conclusion

There is a continuing need to find the best approach to assess levels of POPs contamination in aquatic environments, which correctly reflect the state of the pollution problem. It is clear that water measurements alone are inefficient and misleading. Passive samplers, whilst a better option, also have their problems since they are not linked to the food web. Bed-sediments and biota with a measurable lipid content are sinks for POPs and thus are good options, but at first sight their results may appear quite variable. This study suggests that OC/lipid normalised results in sediment and fish are at a similar level of contamination, which suggests that the two are connected and can provide reassuring corroboration. Thus, even pelagic fish that don't spend all their time in the sediments appear to reflect their level of contamination, presumably through food web connections. The higher concentrations found in fish compared to sediments or water make them suitable markers of POPs contamination in aquatic environments.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2016.10.067>.

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<sup>2</sup> Sediment samples include all surface and second layer sediments, with a total number of 25 samples.

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## Supporting Information to:

### Persistent organic pollutants in sediment and fish in the River Thames Catchment (UK)

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## 1. Sediment Sampling

Figure SI 1 shows the sediment sampling method. Dry ice was filled into the pipes so that sediment would freeze to the core. Around 30-40 cm long sediment cores were pulled out, labelled and packaged in plastic bags, and shipped back to the lab with dry ice. After careful defrosting the sediment cores were sliced into layers according to their appearance. Detailed site and layer information of the analysed sediment samples in this study is given in Table SI 1.

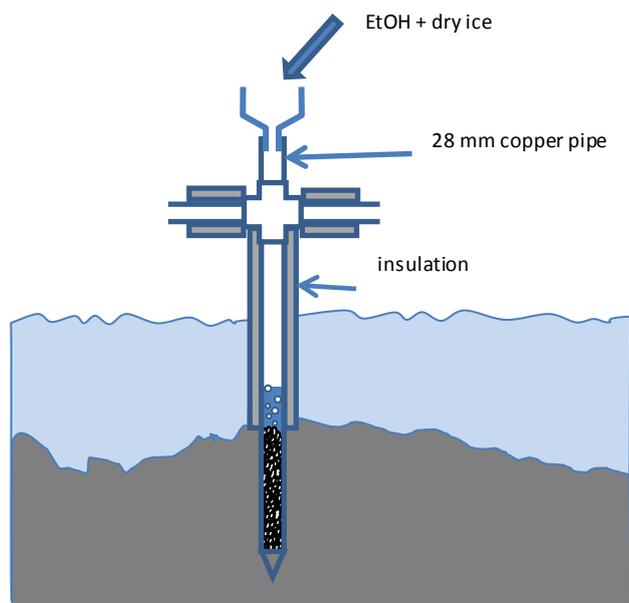


Figure SI 1. Schematic of the freeze-coring sampling system (Jürgens *et al.*, 2014)

Table SI 1. Site and layer information of the analysed sediment samples from the River Thames

Sampling site	Sampling Date	Sediment sample ID	Layers
Thames at Wallingford Bridge	05/10/2013	Wallingford A	0-4 cm
		Wallingford B	4-8 cm
Thames at Winterbrook	18/09/2013	Winterbrook A	0-2 cm
		Winterbrook D	2-5 cm
Thames at Winterbrook	18/09/2013	Winterbrook A	0-8 cm
		Winterbrook D	8-15 cm
Kennet at Newbury	28/11/2013	Kennet C	0-8 cm
		Kennet E	8-15 cm
The Cut at Bracknell	03/12/2013	Kennet C	0-9 cm
		Kennet E	9-16 cm
The Cut at Bracknell	03/12/2013	Bracknell B	0-7 cm
		Bracknell C	7-12 cm
Littlemore Brook upstream of STW	09/10/2013	Littlemore Upstream A	0-6 cm
			6-12 cm
		Littlemore Upstream B	0-12 cm
			12-18 cm
Littlemore Brook downstream of STW	09/10/2013	Littlemore Upstream A	0-4.5 cm (was repeated in triplicate)
		Littlemore Upstream B	4.5-11.5 cm
Littlemore Brook downstream of STW	09/10/2013	Littlemore Downstream A	11.5-22 cm
		Ock. B	22-35 cm
Ock at Caldecott	22/11/2013	Ock. B	35-end (42) cm

## 2. Fish Sampling

In Table SI 2 detailed information of the analysed fish samples (Roach) from the River Thames is presented.

Table SI 2. Sampling information of the analysed fish (Roach) from the River Thames and its tributary River Kennet

Sampling Site	Sampling date	Length (mm)	Weight (g)	Dry matter	Lipid content
Thames, Castle Eaton (n=10)	13/10/2011	212	160	31%	4.9%
	13/10/2011	205	169	27%	4.8%
	13/10/2011	165	76	27%	5.7%
	13/10/2011	115	22	25%	3.6%
	13/10/2011	122	27	25%	3.7%
	13/10/2011	123	29	25%	3.8%
	13/10/2011	114	24	25%	5.3%
	13/10/2011	118	25	26%	4.5%
	13/10/2011	119	23	24%	3.9%
Thames, Caversham- Sonning (n=8)	13/10/2011	127	28	28%	4.9%
	23/07/2008	145	58	28%	6.4%
	23/07/2008	130	38	26%	7.3%
	21/07/2010	132	41		6.9%
	30/07/2012	142	43		7.9%
	30/07/2012	200	146		5.1%
	30/07/2012	199	141		4.7%
	30/07/2012	160	67		5.6%
Thames, Temple- Marlow (n=4)	30/07/2012	169	75		4.6%
	03/09/2007	195	124	27%	4.6%
	03/09/2007	170	78	26%	2.4%
	03/09/2007	159	67	26%	2.1%
Thames, Bray-Boveney (n=2)	03/09/2007	150	56	28%	3.2%
	04/09/2012	132	37		4.4%
Old Windsor-Bell (n=5)	04/09/2012	168	76		2.8%
	07/09/2007	184	93	28%	3.8%
	07/09/2007	165	68	27%	4.6%
	07/09/2007	145	46	29%	4.9%
	07/09/2007	129	31	27%	5.2%
Thames, Sunbury- Molesey (n=4)	07/09/2007	180	82	29%	
	11/09/2012	134	37		5.3%
	11/09/2012	155	59		7.0%
	11/09/2012	155	65		2.9%
Kennet, Newbury (n=9)	11/09/2012	144	48		7.9%
	04/11/2011	200	135	27%	5.5%
	04/11/2011	180	99	26%	5.4%
	04/11/2011	170	76	27%	5.0%
	04/11/2011	175	86	24%	3.7%
	04/11/2011	140	43	27%	7.2%
	04/11/2011	170	79	26%	4.4%
	04/11/2011	160	62	27%	5.5%
	04/11/2011	160	65	25%	3.8%
04/11/2011	140	43	27%	5.6%	

### 3. Correlation between sediment concentration and estimated fraction of the flow consisting of treated sewage

Figure SI 2 shows the relationship between the sediment concentrations of HCB,  $\Sigma$  ICES 7 PCBs and  $\Sigma$  6 BDEs and the fraction of that treated sewage contributes to the river flow at the sampling sites.

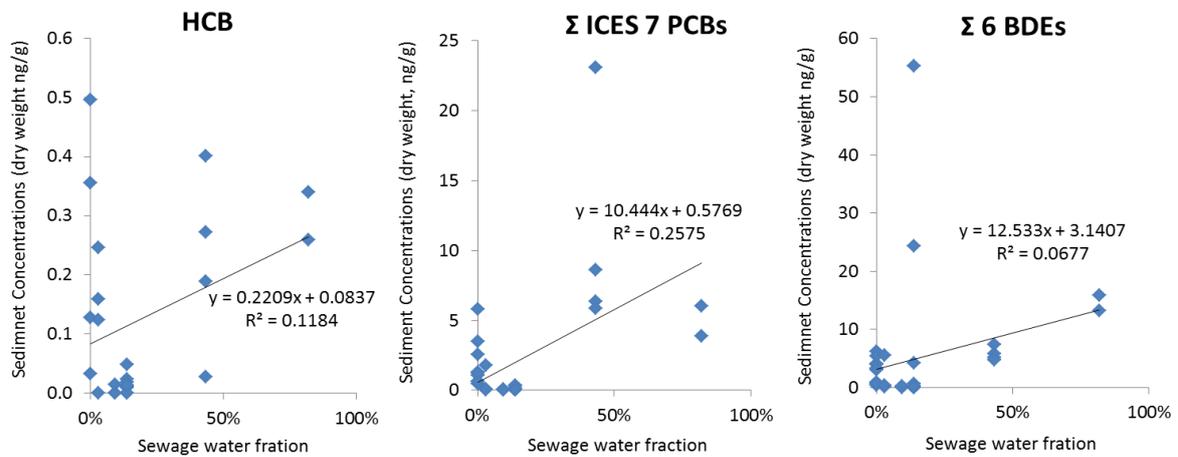


Figure SI 2. Comparison of sediment contaminations of HCB,  $\Sigma$  ICES 7 PCBs and  $\Sigma$  6 BDEs with sewage water fraction

### 4. Variation in sediment pollutant concentration with depth

The sediment organic carbon (SOC) values and the concentrations of BDEs, PCBs and HCB at different depths of the sediment sample collected at Littlemore Brook Upstream site are shown in Figure SI 3.

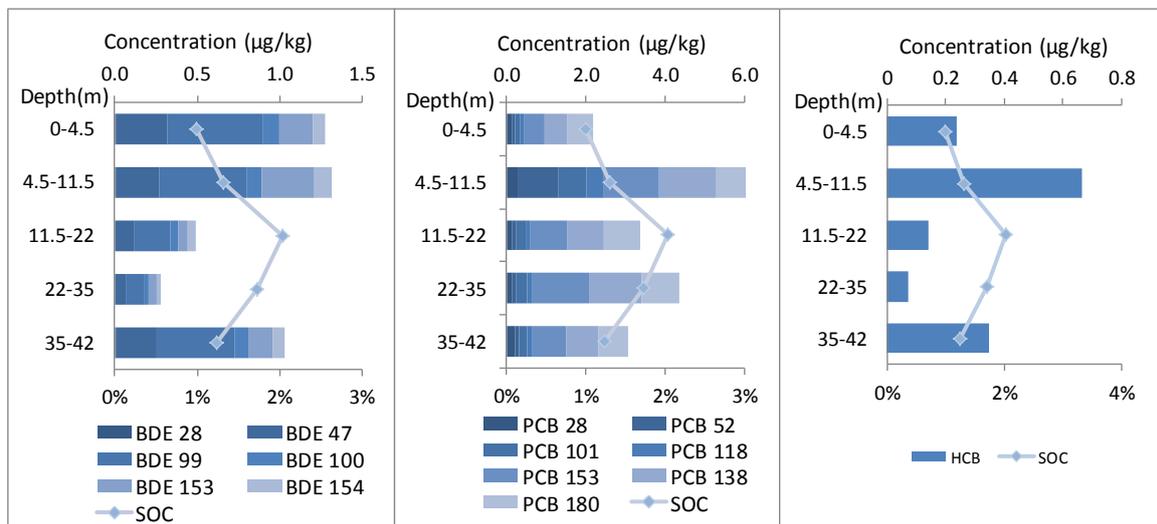


Figure SI 3. The sediment concentrations of BDEs, PCBs and HCB with depth at Littlemore Brook Upstream of the Sewage Treatment Work (but downstream of an industrial area)

## 5. Comparison of Fish Concentrations against Sediment Values

Figure SI 4 presents the contamination values of BDEs, PCBs, and HCB in sediment and fish samples collected at the same site in the River Kennet at Newbury.

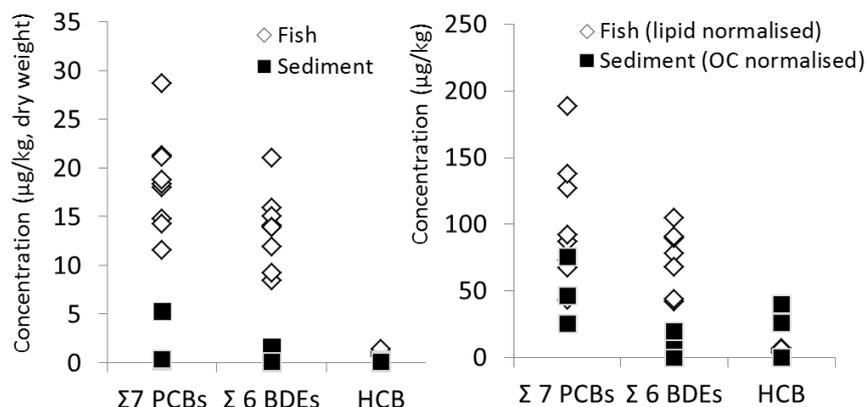


Figure SI 4. The concentrations of BDEs, PCBs and HCB in fish and sediment samples collected from the site in the River Kennet

## 6. Reference

Jürgens M.D., *et al.* Assessment of the current exposure of the British natural environment to silver (CB0464) - Silver in sewage sludge, soil and river bed-sediments, 2014, [http://randd.defra.gov.uk/Document.aspx?Document=12427\\_CB0464\\_FinalReport\\_Silverinsewagesludgesoilandriverbedsediments.pdf](http://randd.defra.gov.uk/Document.aspx?Document=12427_CB0464_FinalReport_Silverinsewagesludgesoilandriverbedsediments.pdf).

\*The OSPAR Environmental Assessment Criteria (EACs):

The OSPAR EACs are developed for the use in the assessment of contaminant concentrations in marine sediment and biota corresponds to the achievement, or failure to achieve, statutory targets or policy objectives for contaminants in these matrices. The EACs represent the contaminant concentration in the environment below which no chronic effects are expected to occur in marine species, including the most sensitive species. EACs are recommended for use for PCBs in marine sediment. The EACs for PCBs in sediment are expressed for sediment of 2.5% organic carbon. The EACs used for PCBs in biota (mussels and oysters and fish) were derived from the sediment EACs on the basis of the biota sediment accumulation factor (BSAF) (OSPAR, 2009).

Some studies indicated that marine biota could be more sensitive to organic pollutants than freshwater organisms (Suter and Rosen, 1988; Mancini *et al.*, 2002). Therefore, the marine criteria values could be lower than equivalent freshwater criteria. Information given in the review, however, is very restricted. The tested species were not given. The database available is too limited to make a general conclusion about the difference between marine and freshwater biota.

Reference:

Mancini E., *et al.* MTBE ambient water quality criteria development: a public/private partnership. ACS Publications, 2002.

Suter G.W., Rosen A.E. Comparative toxicology for risk assessment of marine fishes and crustaceans. *Environmental science & technology* 1988; 22: 548-556.

# **Chapter 5. Fate and transport of polychlorinated biphenyls (PCBs) in the River Thames catchment – Insights from a coupled multimedia fate and hydrobiogeochemical transport model**



## 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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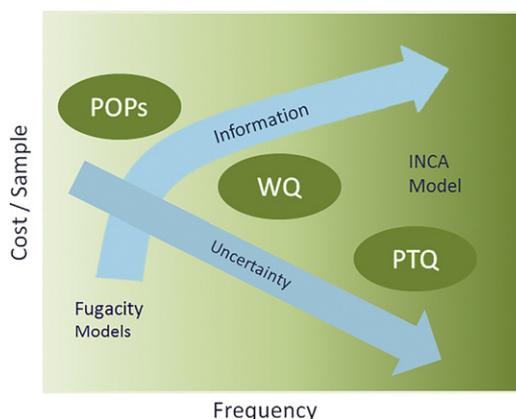
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### HIGHLIGHTS

- A INCA-Contaminants model is applied to provide additional insights into PCBs fate.
- The model performs well in simulating the PCB dynamics in the Thames system.
- The model predicts high bulk water concentrations in summer low flow periods.
- Sharp increases in upper sediment PCBs after extreme flooding period were predicted.

### GRAPHICAL ABSTRACT



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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 (MMFMs) 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 POP 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 POP 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

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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.

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## Acronyms

POPs	persistent organic pollutants
PCBs	polychlorinated biphenyls
DOC	dissolved organic carbon
WQ	water quality
PTQ	Precipitation, Temperature, Flow
INCA	Integrated Catchment model
INCA-C	Integrated Catchment Carbon model
INCA-Sed	Integrated Catchment Sediment model
SOC	solid organic carbon
SOC <sub>ea</sub>	solid organic carbon easily accessible fraction
SOC <sub>pa</sub>	solid organic carbon potentially accessible fraction
H	Henry's law constant
TPD	truly dissolved phase
SUS <sub>i</sub>	arbitrary number <i>i</i> of suspended solid classes ranked by their size
PERSIST	Precipitation, Evapotranspiration and Runoff Simulator for Solute Transport model
K <sub>ow</sub>	the octanol – water partition coefficient
HER	hydrologically effective rainfall
SMD	soil moisture deficit
CEH	Centre for Ecology and Hydrology
SS	suspended sediments
GPC	gel permeation chromatography
GC–MS	Gas Chromatography–Mass Spectrometry
MCMC	Markov chain–Monte Carlo tool

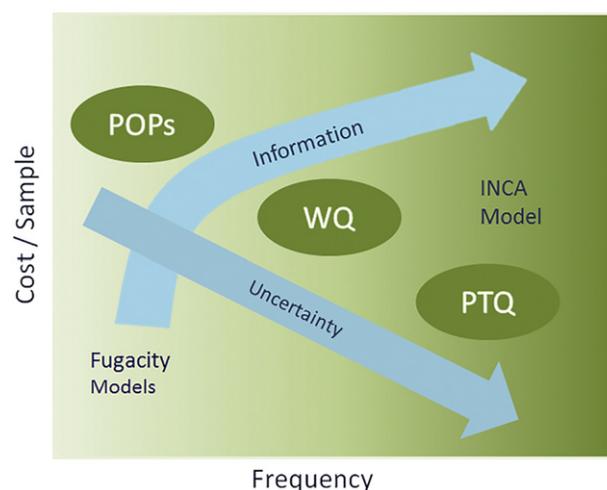
## 1. Introduction

Persistent organic pollutants (POPs) include a wide range of organic compounds characterised 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 mobilisation 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, POP measurements are characterised by their relative infrequency, analytic complexity and high cost. Typically, POP 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 (Fig. 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 POP 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 POP fate and transport (Fig. 1). The cost per sample for POP analysis (Fig. 1; vertical axis) is much higher than costs for water quality (WQ) or hydrometeorological measurements



**Fig. 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.

of precipitation, temperature or flow (PTQ). The big difference in sample costs is one reason that POP measurements are much less frequent than routine water quality (WQ) measurements 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 POP 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 POP samples, water quality measurements and hydrometeorological observations to deliver an integrated and intrinsically consistent representation of the system dynamics. Using such complementary environmental data can increase the available information while simultaneously reducing uncertainty in POP fate and transport estimates.

Here, the River Thames catchment (Southern England) has been used as the study area. The legacy of industrial activities and urbanisation has resulted in high levels of contamination in the catchment. For example, PCBs remain at levels which may be of environmental and health concern in the catchment soils (Vane et al., 2014), sediment and resident fish (Jürgens et al., 2015; Lu et al., 2015). A level III fugacity model was previously used to estimate contaminant concentrations in fish and sediment, which predicted the concentrations of PCBs in Thames fish to exceed the U.S. EPA unrestricted consumption advisory thresholds for  $\Sigma$ PCBs (5.9  $\mu\text{g}/\text{kg}$ ) and the sediment concentrations to exceed the Environmental Assessment Criteria for ICES7 PCBs in marine sediment (Lu et al., 2015). However, concentrations of PCBs in sediment were greatly overestimated by the fugacity model when compared to recent 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 118, and 1.70  $\mu\text{g}/\text{kg}$  for PCB 153 on average (Lu et al., in preparation - see Supporting information). Catchment soils could be the most important current source of PCBs in the catchment while riverine sediments could be an important reservoir and secondary source in the river system (Hope, 2008; Lu et al., 2015). With their greatly simplified representations of climate, hydrology and biogeochemical processes, level III fugacity models can only predict general conditions across a region and have limited ability to represent environmental variability. Unsteady state fugacity level IV models have also been developed and applied to explore the seasonal response and dynamic chemical concentrations in the environment (Dalla Valle et al., 2005; Sweetman et al., 2002). However, level IV fugacity models are only suitable to estimate the average contaminant mass and concentrations over a region large enough so that the wind dispersion would not be a dominant chemical removal processes in the catchment.

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

## 2. Materials and methods

### 2.1. The River Thames catchment

With a length of 346 km (255 km are non-tidal), the River Thames is the longest river in England and the second longest river in the UK. It officially rises at Thames Head near Cirencester, passes first through relatively rural areas and then through the most urbanised area in the UK including Greater London, which is in the tidal area, and flows into the

North Sea. Average flows range from about 1.5  $\text{m}^3/\text{s}$  at Cricklade in the upper reaches, to around 29.8  $\text{m}^3/\text{s}$  near the middle of the non-tidal length at Days Weir and 65.8  $\text{m}^3/\text{s}$  at its tidal limit at Teddington (see Fig. 2). The River Thames and its tributaries drain a catchment area of approximately 10,000  $\text{km}^2$  (non-tidal part) in Southern England, with both permeable and impermeable geologies (Crooks and Davies, 2001; Whitehead et al., 1998) (Fig. 2). The land cover of the catchment is characterised by arable agriculture and pasture throughout the catchment, while the urban areas are mainly located lower in the catchment. Forests are found mainly in the lower part of the catchment (Table 1).

### 2.2. The INCA-Contaminations model

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

The INCA-Contaminants model used here is the newest member of the INCA family (Nizzetto et al., 2016) and was developed based on two extensively tested INCA models: the carbon model INCA-C (Futter et al., 2007) and the sediment model INCA-Sed (Lazar et al., 2010). INCA-C produces daily estimates of organic matter mass balance in multi-branched catchment, while the INCA-Sed simulates sediment production and delivery from land to the in-stream system and subsequent transport, deposition and remobilisation in the stream. All processes are forced by daily input time series of precipitation, hydrologically effective rainfall (the part of total precipitation that contributes to runoff), soil moisture deficit and air temperature. In the INCA-Contaminants model, a daily time step dynamic multimedia box model has been integrated in the INCA-C/INCA-Sed coupled structure (Nizzetto et al., 2016). All land phase equations are solved for a 1  $\text{km}^2$  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 (Fig. SI 1); 2) the in-stream model describing the contaminations fate and transformation in the aquatic system (Fig. 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 (Fig. SI 1). The SOC within each box is divided into easily accessible (SOC<sub>ea</sub>) and potentially accessible (SOC<sub>pa</sub>) 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

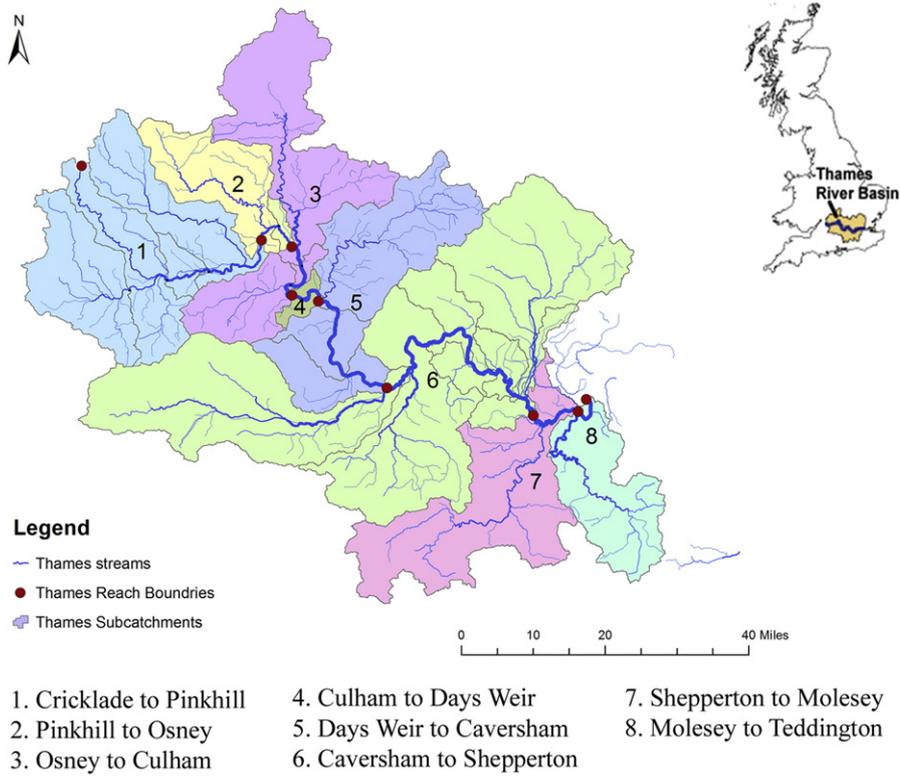


Fig. 2. Map of the River Thames Catchment showing the points where flow, water chemistry and sediment PCB concentrations were simulated.

dynamically based on soil moisture. The model also allows fixed or time varying contaminant inputs including wet and dry atmospheric deposition, litterfall associated pollutant inputs and accidental spills. All relevant model parameters can vary on a sub-catchment basis and according to soil and land use type. This degree of flexibility in the model allows the process rates, hydrological pathways and the mass of contaminants in soil to vary spatially across a catchment or region. Although the fugacity notation was not used in the mathematical formalism of INCA-Contaminants, the diffusive exchange that controls the distribution of contaminants between different phases and soil layers was predicted using the thermodynamic equations derived from the fugacity models (Eq. SI 1–SI 15, Supporting Information). Contaminant concentrations in each phase of the soil layers were calculated based on the thermodynamic equilibrium partitioning coefficients including Henry's law constant (H), enthalpy of phase transfer between air and water, octanol-water equilibrium partitioning coefficients, enthalpy of phase transfer between water and octanol, and the scaling from octanol-water to SOC-water and DOC-water equilibrium partitioning coefficients.

The in-stream sub-model consists of a series of reaches (or stream segments). Each reach is comprised of a water column and underlying sediments. Within the water column, contaminants can be present in

a truly dissolved phase (TPD), associated with DOC, and with an arbitrary number *i* of suspended solid classes ranked by their size (SUS<sub>*i*</sub>). The underlying sediment consists of two vertically stacked layers. Only the upper layer undergoes material exchange with the overlying water column. The depth of the upper sediment layer is dynamically calculated depending on the deposition and erosion of sediment. The sediment exchange processes in the stream system could be dominant affecting the fate of contaminants in the sediment layers. When deposition becomes the dominant dynamic processes, the contaminants associated with SUS<sub>*i*</sub> in the water column would accumulate into the upper sediment layer. In contrast, the contaminants in the lower bed sediment would re-integrate into the upper sediment layer and become available for dynamically enhanced exchange with the water column if erosion of sediment dominates the processes.

Within each sediment compartment, contaminants are present in TDP, DOC-associated and SOC-associated sub-phases (Fig. 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 SUS<sub>*i*</sub> in the water column includes upstream inputs, entrainment associated

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

No.	Reach name	Length (km)	Area (km <sup>2</sup> )	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

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 (Fig. 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, silt 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 characterise 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 (Table 3, Table SI 1).

**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	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 et al. (2014) in the PERSiST application	Delineated based on the location of flow measuring stations (Futter et al., 2014)
Residence time	Measurements for groundwater residence time for each sub-catchment	Calculated from hydrological response curves (Crossman 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 et al. (2015)
$\Delta U_{AW}$ (kJ/mol) $\Delta U_{OW}$ (kJ/mol)	Enthalpy of phase transfer between air and water, enthalpy of phase transfer between water and octanol	Taken from Schenker 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	
	Scaling factor (a4)	0.7	10	kg/m <sup>2</sup>	
	Non-linear coefficient (a6)	0.7	0.9	—	
Reach	Scaling factor (a7)	8E–05	1	—	
	Scaling factor (a8)	2E–07	1E–04	s <sup>2</sup> /kg	
	Scaling factor (a9)	3.0E–10	1.0E–7	kg/m <sup>2</sup> /m <sup>3</sup>	
	Non-linear coefficient (a10)	0.01	1.2	—	
Contaminations	PCB 52	Henry's law constant	13.6	54.4	Pa · m <sup>3</sup> /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 <sup>2</sup>
	PCB 118	Atmospheric wet deposition	2.0E + 05	2.0E + 07	ng/day/km <sup>2</sup>
		Henry's law constant	5.4	21.6	Pa · m <sup>3</sup> /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 <sup>2</sup>	
	Atmospheric wet deposition	2.0E + 05	2.0E + 07	ng/day/km <sup>2</sup>	
	Henry's law constant	9.2	36.8	Pa · m <sup>3</sup> /mol	
	Koc	3.6E + 06	1.4E + 07	—	
	Degradation half-life (water column)	2395	9584	days	
	Degradation half-life (sediment)	3292	13,166	days	
	Atmospheric dry particle deposition	2.0E + 05	2.0E + 07	ng/day/km <sup>2</sup>	
	Atmospheric wet deposition	2.0E + 05	2.0E + 07	ng/day/km <sup>2</sup>	

2.4. 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 Fig. 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) (Fig. 3). For the modelling period, the river flows were at low levels in the summer periods (June to September)

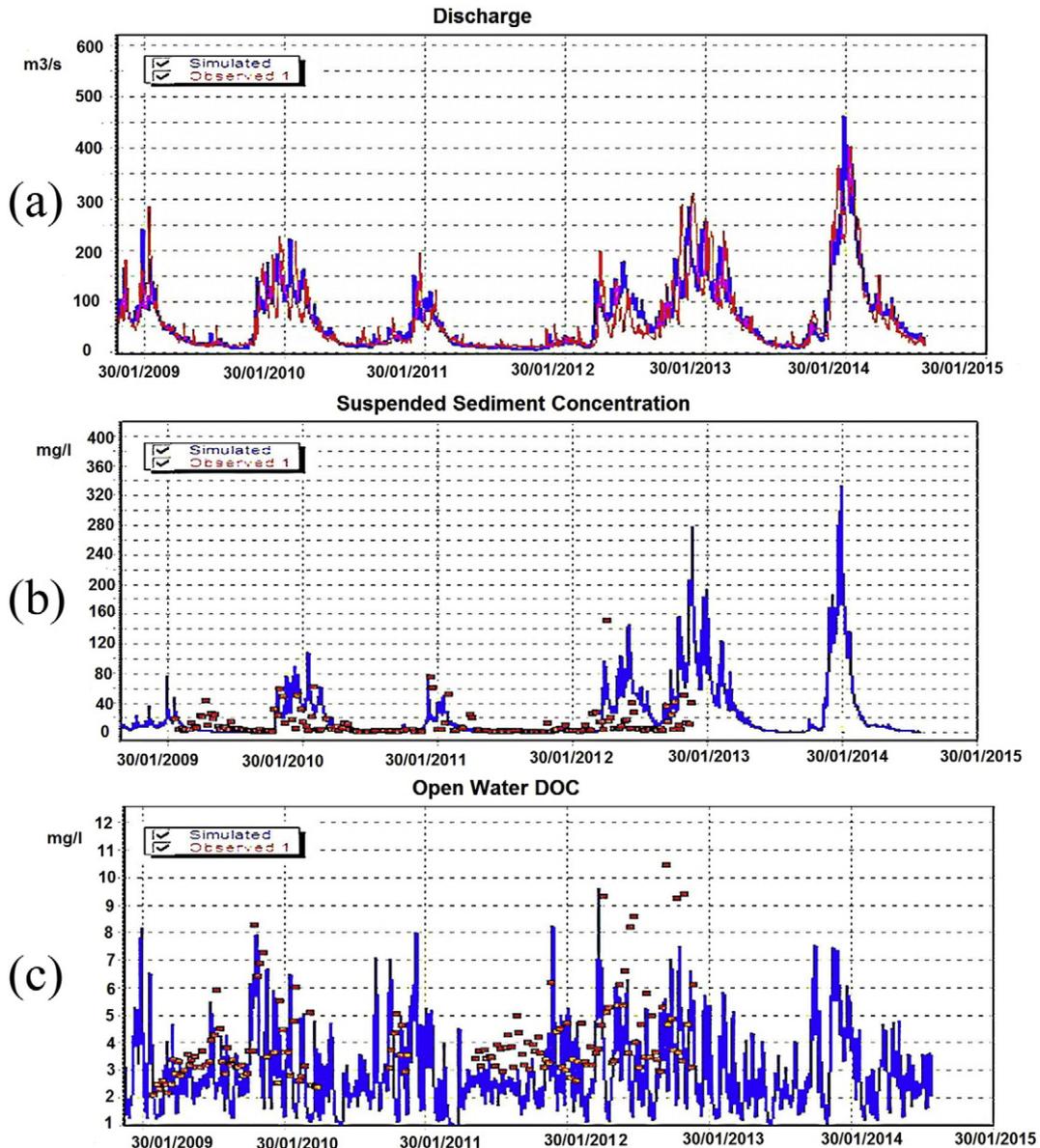


Fig. 3. (a) Observed and simulated flow for reach 6 (Caversham - Shepperton); (b) Observed and simulated suspended sediment data for reach 6; (c) Observed and simulated DOC data for reach 2 (Pinkhill–Osney).

**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

and then higher throughout the winter (October to February). The flood at the beginning of 2014 was successfully simulated in the INCA modelling (Fig. 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 (Fig. 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.

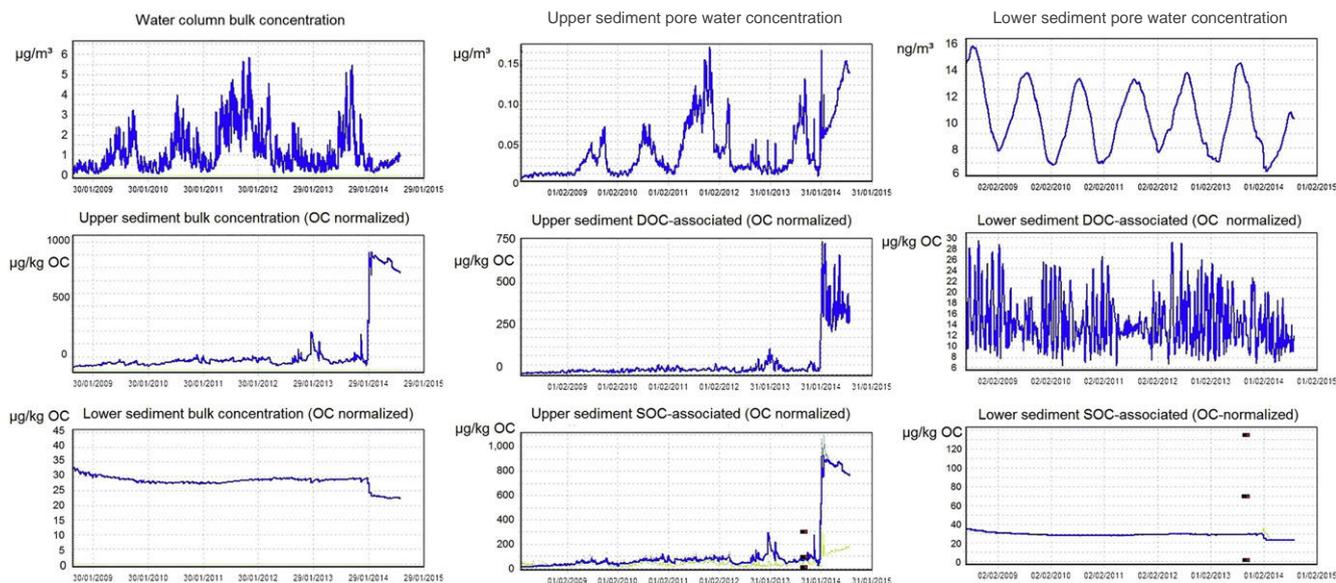
To assess the model performance for the predictions of PCBs in the Thames system, the simulated upper and lower sediment SOC associated contaminants concentrations, obtained using the best set of hydrological and biogeochemical parameters from the sensitivity analysis, were compared to the observed values. Measured PCB 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 (Fig. SI 3, Fig. SI 4, Fig. 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 (Fig. SI 3), PCB 118 (Fig. SI 4), and PCB 153 (Fig. 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/m<sup>3</sup> (<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 (Fig. 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.

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

**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

While this increase is much higher than that obtained in our simulations, it does lend credence to the simulated temporal dynamics or 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 (Fig. 4, SI 3 and SI 4). However, this could not be verified with measured data due to lack of observed data concerning the PCB 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 mobilised 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 (Fig. 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 POP 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 POP 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.

#### 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 contaminant 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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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2016.03.029>.

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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;

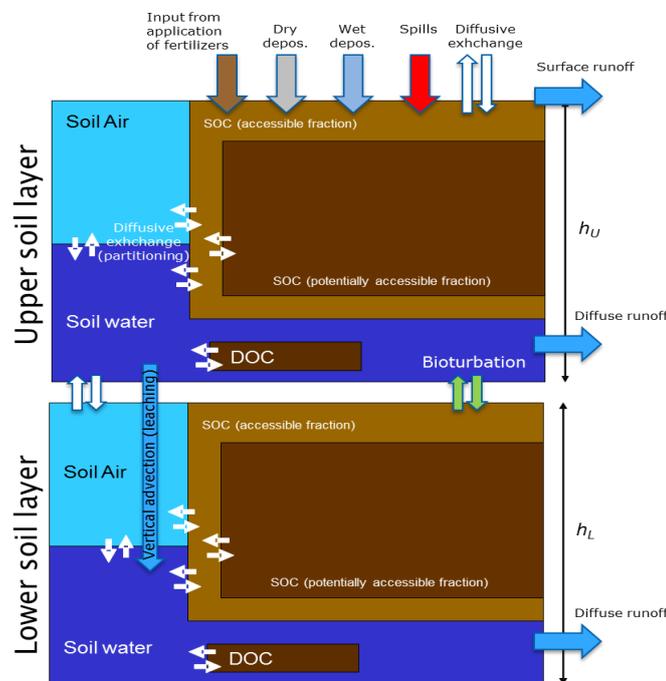


Figure. SI 1 Structure of the soil compartment, adapted from Nizzetto et al. (2016)

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**

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

**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**

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

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

### 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;  $\Delta U_{AW}$  - 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;  $\Delta U_{OA}$  - 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;  $\rho_{OC}$  - 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<sub>ea</sub>, 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.

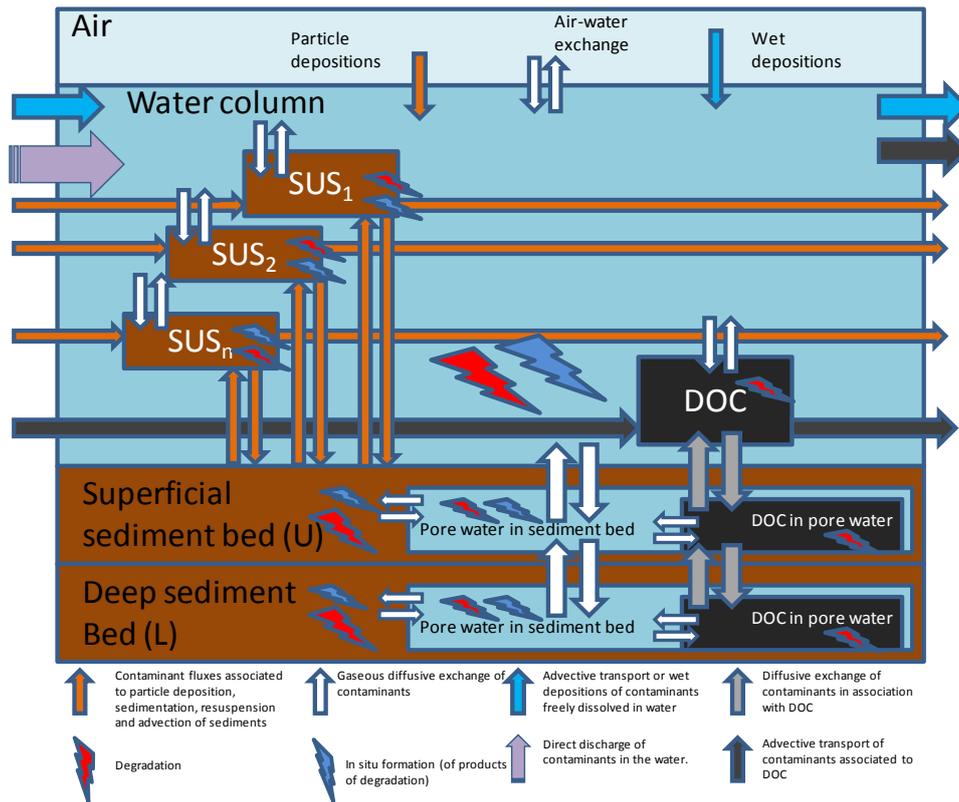


Figure. SI 2 Structure of the in-stream compartment, adapted from Nizzetto et al. (2016)

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):

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

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

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

$$D_{H2O} = 10^{-3} \cdot \frac{\left( T_w^{1.75} \left[ \left( \frac{1}{28,97} \right) + \left( \frac{1}{18} \right) \right]^{\frac{1}{2}} \right)}{1 \cdot [20 \cdot 1^{1/3} + 18^{1/3}]^2} \cdot 10^{-4} \quad m^2 s^{-1} \quad \text{SI 19}$$

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

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  $\mu$ 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.

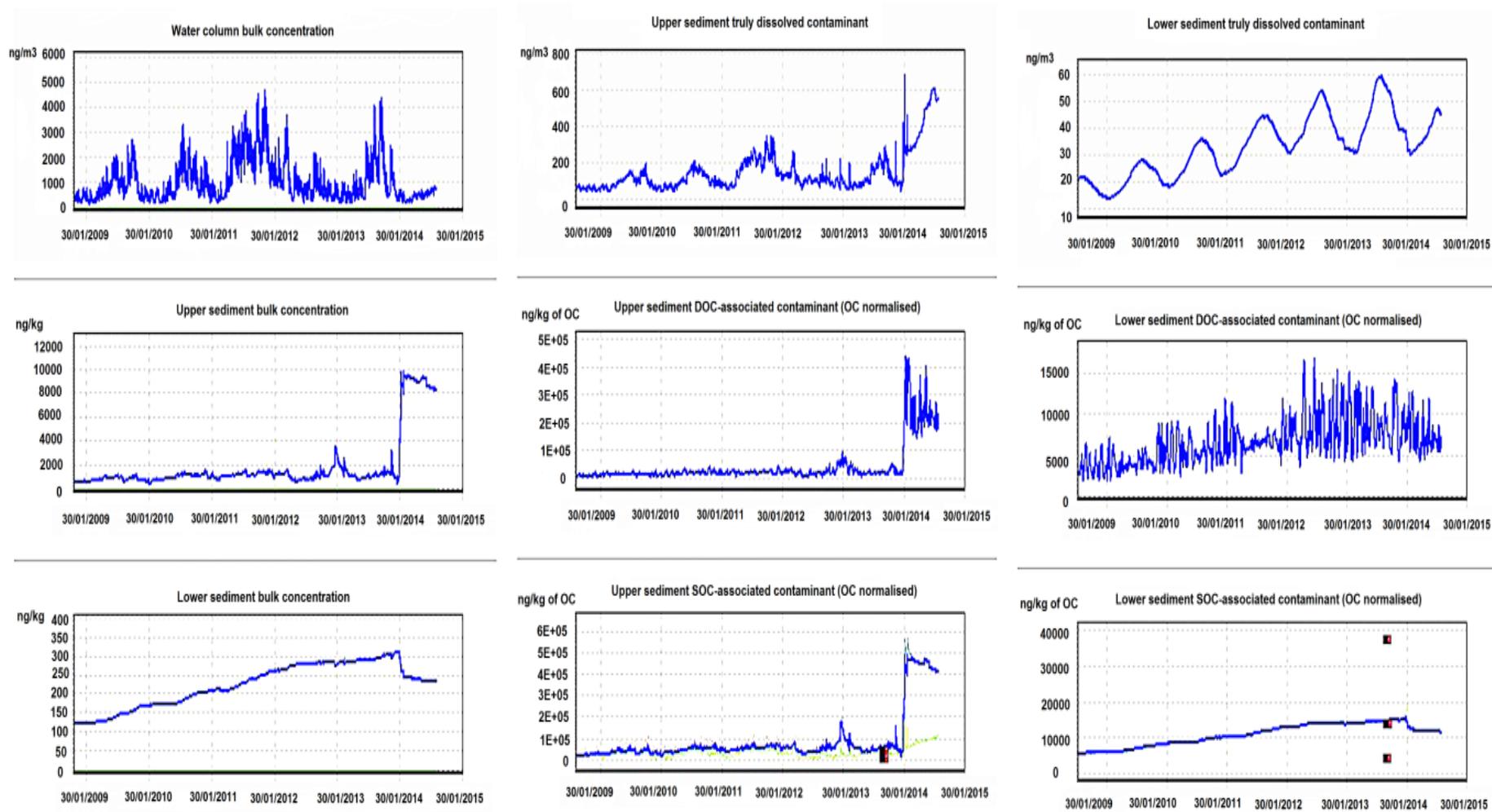


Figure SI 3. The simulated dynamics of PCB 52 in water column, upper sediment and lower sediment layers for Reach 6

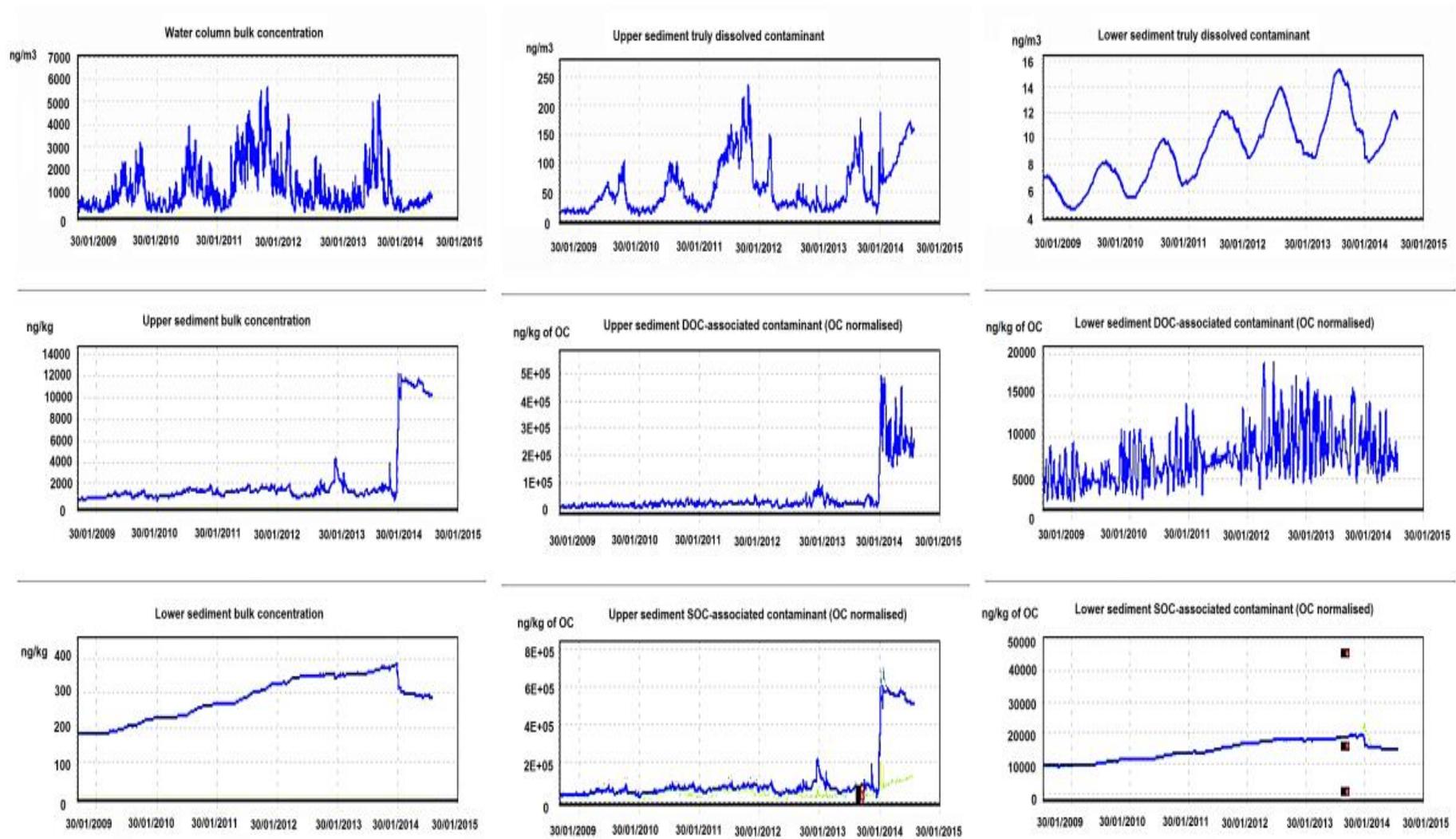


Figure SI 4. The simulated dynamics of PCB 118 in water column, upper sediment and lower sediment layers for Reach 6

#### **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.

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# **Chapter 6. Modelling Metaldehyde in Catchments: A River Thames Case-Study**



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## Modelling metaldehyde in catchments: a River Thames case-study†

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The application of metaldehyde to agricultural catchment areas to control slugs and snails has caused severe problems for drinking water supply in recent years. In the River Thames catchment, metaldehyde has been detected at levels well above the EU and UK drinking water standards of 0.1  $\mu\text{g l}^{-1}$  at many sites across the catchment between 2008 and 2015. Metaldehyde is applied in autumn and winter, leading to its increased concentrations in surface waters. It is shown that a process-based hydro-biogeochemical transport model (INCA-contaminants) can be used to simulate metaldehyde transport in catchments from areas of application to the aquatic environment. Simulations indicate that high concentrations in the river system are a direct consequence of excessive application rates. A simple application control strategy for metaldehyde in the Thames catchment based on model results is presented.

### Environmental impact

The River Thames is the longest river in England and it supplies drinking water to around 14 million people in the surrounding areas. In recent years, there is a great concern on the presence of metaldehyde at levels exceeding drinking water standards in the Thames water. Metaldehyde breaks slowly in water and is very difficult to remove by current technology in drinking water treatment plants, thus posing a challenge for water companies to comply with the drinking water standards and a potential threat for human health. To reduce the potential risk, it is important to understand the behaviour of metaldehyde in the catchment. But so far, there's very little focus on the analysis of the fate and transport of metaldehyde in river basins. Here, we present the first modelling study describing the metaldehyde dynamics in the River Thames catchment. A simple application strategy for metaldehyde control was developed based on the modelling results.

## 1. Introduction

The presence of pesticides in rivers and groundwater has been recognised as a problem in the UK since the 1970s.<sup>1–3</sup> Excessive pesticide levels pose a considerable threat to aquatic life and human health. The most harmful pesticides are gradually being withdrawn from agricultural use due to their adverse effects on water supply and potential impacts on freshwater ecology (*e.g.* DDT in 1991; Lindane in 2002; Atrazine in 2004).<sup>4,5</sup> With improvements in analytical methods, a number of pesticides which were not previously detected have been regularly observed at trace levels in surface and groundwater.<sup>6</sup> For example, metaldehyde,<sup>7</sup> the active ingredient in snail and slug control pellets, has been widely detected at levels exceeding drinking water standards in rivers in Southern England. The

damage to crops (principally oilseed rape, winter wheat and vegetables) caused by snail and slug attack is a growing problem in many countries, including the UK<sup>8</sup> and has been compounded by a wetter and milder climate. The problem is exacerbated by changing agricultural regulations and practices, including a ban on straw burning in 1993 (ref. 9 and 10) and increased rotations with non-cropped areas. In order to protect crops and control slugs, metaldehyde is generally applied in autumn and, if required, during winter. It is estimated that metaldehyde has been applied to more than 8% of the UK arable crop area,<sup>8</sup> and has been applied extensively to vegetable and horticultural crops. Household use of metaldehyde by members of the public to kill pests in their gardens and allotments may also be significant, but little information is available on the application rates or extent.<sup>8</sup>

Metaldehyde first came to the attention of the UK water sector in 2007/8. In recent years, it has been widely detected in many UK rivers at concentrations above the 0.1  $\mu\text{g l}^{-1}$  European and UK standards for pesticides in drinking water<sup>11</sup> following heavy and sustained periods of rainfall.<sup>12,13</sup> Although the levels of metaldehyde detected in surface water do not necessarily represent a direct risk to human health, they do present a risk to drinking water quality compliance<sup>14</sup> when surface water is used as the drinking water source. With an organic carbon sorption coefficient ( $K_{oc}$ ) value ranging between 34 and 240  $\text{l kg}^{-1}$  and

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additional info. on the techniques for treatment of metaldehyde is provided in the supporting Information (Page 110)

a half-life in soil value ranging between 3.17 and 223 days, metaldehyde has the potential to be persistent and mobile in the environment.<sup>13,15</sup> Due to its physico-chemical properties and relatively simple chemical structure, metaldehyde breaks down very slowly in water (Table 2) and is very difficult to effectively remove by current drinking water treatment options (including advanced treatment processes).<sup>8</sup> To reduce the potential risk of metaldehyde, it is important to control metaldehyde at its source. Water companies have undertaken legal programmes to control the agricultural use of metaldehyde in river basins. The Metaldehyde Stewardship Group (MSG) (Get Pelletwise: <http://www.getpelletwise.co.uk/msg-guidelines/>) has developed application guidelines for the protection of waters. Farmers are allowed to apply a maximum total dose of 700 g active substance per ha per year, plus the maximum single dose should not exceed 210 g active substance per ha. Between 1st August and 31st December farmers are advised to use a maximum total dose of 210 g active substance per ha. Autumn is when metaldehyde has the highest likelihood of getting into freshwaters as soils wet up and increased rainfall drives surface and soil waters into streams. Farmers are advised to leave a 6 m “no spread zone” adjacent to water courses.<sup>12,14</sup> However, implementing the application guidelines is challenging, as it is difficult to control the quantity of pellets actually used and limited information on the exact application rates is available. In addition, the relationship between application rates and water concentrations is complex and varies considerably over time and space. It is influenced by many factors, such as rainfall patterns, land slopes, soil characteristics, land and stream management and crop choice.<sup>16</sup> Despite the large amount of measurement data of metaldehyde in rivers, limited assessment on the transport of metaldehyde from the land phase to rivers is available. In order to mitigate the metaldehyde problem, a better understanding of its behaviour in river basins is needed.

Modelling is often used to provide additional information on the fate and transport of contaminants in catchments to support decision making. There has been one previously published modelling study of metaldehyde dynamics in UK river systems (Anglian Water, retrieved Feb 2017).<sup>17</sup> However, a number of pesticide fate models have been used to predict watershed-scale pesticide fluxes to surface waters, such as DRIPS (Drainage Runoff Input of Pesticide in Surface Water),<sup>18</sup> SEPTWA (System for the Evaluation of Pesticide Transport to Waters),<sup>19</sup> SWAT (Soil and Water Assessment Tool), and CatchIS (Catchment Information System).<sup>20,21</sup> DRIPS is a regional-scale model that estimates the pesticide loads to surface waters on a yearly basis, while SEPTWA is a catchment-scale model which predicts the average pesticide concentration in water over the catchment. However, average concentrations are of little help for water utilities, as peak concentrations may occur in a period with high application rates or extreme weather conditions. The SWAT model is a conceptual semi-distributed model which can be used to predict water concentration dynamics in river basins, accounting for the spatial distribution of land use, soil type and orography.<sup>22</sup> It has been successfully applied to many catchments to simulate the fate of pesticides.<sup>16,22–24</sup> However, SWAT is a complex model with high data requirements and a large number of parameters that need to

be estimated.<sup>20,25</sup> The CatchIS model is widely used in the water industry to predict the leaching and surface run-off of applied pesticides.<sup>21</sup> But, the application of CatchIS to predict pesticides in a drinking water supply catchment was not successful due to problems with historic pesticide data and the temporal and spatial variability in pesticide usage in CatchIS.<sup>26</sup> In addition to the models mentioned above, Nizzetto *et al.*<sup>27</sup> have developed a new integrated hydro-biogeochemical-multimedia fate model which simulates the fate of organic pollutants in catchments. This is the Integrated Catchment Contaminants model (INCA-contaminants). The transport of pesticides in the catchment is associated with suspended sediment (SS) and dissolved organic carbon (DOC). Integrating the simulations of river flow, DOC, SS and contaminant dynamics, the INCA-contaminants model provides the possibility of improved predictions of contaminant fluxes and their fate. The temporal and spatial variability in the application rates of contaminants could be addressed in the modelling. The INCA-contaminants model has been proved to be a useful tool for simulating the fate and transport of a range of substances including PCBs in the River Thames catchment (UK)<sup>28</sup> and in a boreal catchment in Norway,<sup>27</sup> Perfluoroalkyl substances in the Ganges river<sup>29</sup> and DDT in the Morava river catchment in Czech Republic.<sup>30</sup>

In this study, the River Thames catchment has been investigated and the INCA-contaminants model has been used as a quantitative tool to assess the fate of metaldehyde in the catchment. A key current issue in the Thames is the transport of pulses of metaldehyde down the river system towards public water abstraction locations during high flow conditions with farming controls based on voluntary stewardship organised by the Metaldehyde Stewardship Group.<sup>31</sup> The major aim of this study has been to: (1) use the INCA-contaminants model to simulate the metaldehyde dynamics in the catchment; (2) investigate the impact of application rates on metaldehyde concentrations in river systems using the INCA approach.

## 2. Materials and methods

### 2.1 River Thames Catchment

The River Thames is the longest river in England with a length of 255 km from the headwaters to the tidal limit. The catchment upstream of the tidal limit at Teddington, SW of London, covers an area of approximately 10 000 square kilometres in Southern England.<sup>32</sup> The average flows of the River Thames range from about 1.5 m<sup>3</sup> s<sup>-1</sup> at Cricklade, in the upper reaches, to 29.8 m<sup>3</sup> s<sup>-1</sup> at Days Weir and 65.8 m<sup>3</sup> s<sup>-1</sup> at Teddington.<sup>28</sup> The River Thames flows through many urban areas such as London, Oxford, Reading and Windsor, and it supplies drinking water for about 14 million people in the surrounding areas.<sup>33</sup> The precipitation in the catchment ranges from 600 to 900 mm per year. The main land use type is arable agriculture, which covers about 57% of the whole catchment. Agricultural lands used for potatoes and other vegetables, which are thought to be particularly vulnerable to slugs and snails, only take up a small fraction of the catchment (Table 1). The urban areas are mainly located in the lower reaches, although there are substantial cities upstream including Swindon and Oxford.

Table 1 Sub-catchment and Land Use Information for the Thames river system

No.	Reach name	Reach length (km)	Sub-catchment area (km <sup>2</sup> )	Land use %					
				Other arable	Total vegetable	Potato	Pasture	Forest	Urban
1	Cricklade to Pinkhill (Farmoor)	54.1	1609	74.18	0.14	0.07	16.5	2.8	6.3
2	Pinkhill to Osney	12.4	526	59.56	0.44	0.20	16.3	5.0	18.5
3	Osney to Culham	19.0	1288	72.11	0.16	0.22	15.3	2.2	10.0
4	Culham to Days Weir	9.30	58	78.43	0.34	0.13	0.0	2.8	18.3
5	Days Weir to Caversham	35.2	1154	72.74	0.06	0.10	10.3	8.2	8.6
6	Caversham to Shepperton (Datchet)	70.4	3632	43.71	0.21	0.10	12.2	15.1	28.7
7	Shepperton to Molesey	9.54	1102	38.32	0.35	0.23	13.1	25.3	22.7
8	Molesey to Teddington (Walton)	7.74	589	30.43	0.17	0.003	15.4	17.7	36.3

The safeguard of water quality of the River Thames is a pressing concern for the society and Thames Water, with several modelling approaches utilised in the last few years for different aspects of water pollution (e.g., nitrogen,<sup>34</sup> phosphorus,<sup>35</sup> pathogens,<sup>36</sup> phytoplankton,<sup>37</sup> and microplastics<sup>38</sup>).

Despite its importance, no catchment-scale study of metaldehyde in Thames river water has been conducted before to address the causes behind the routine detection of metaldehyde at concentrations exceeding regulatory standards during recent years. The average water concentrations of

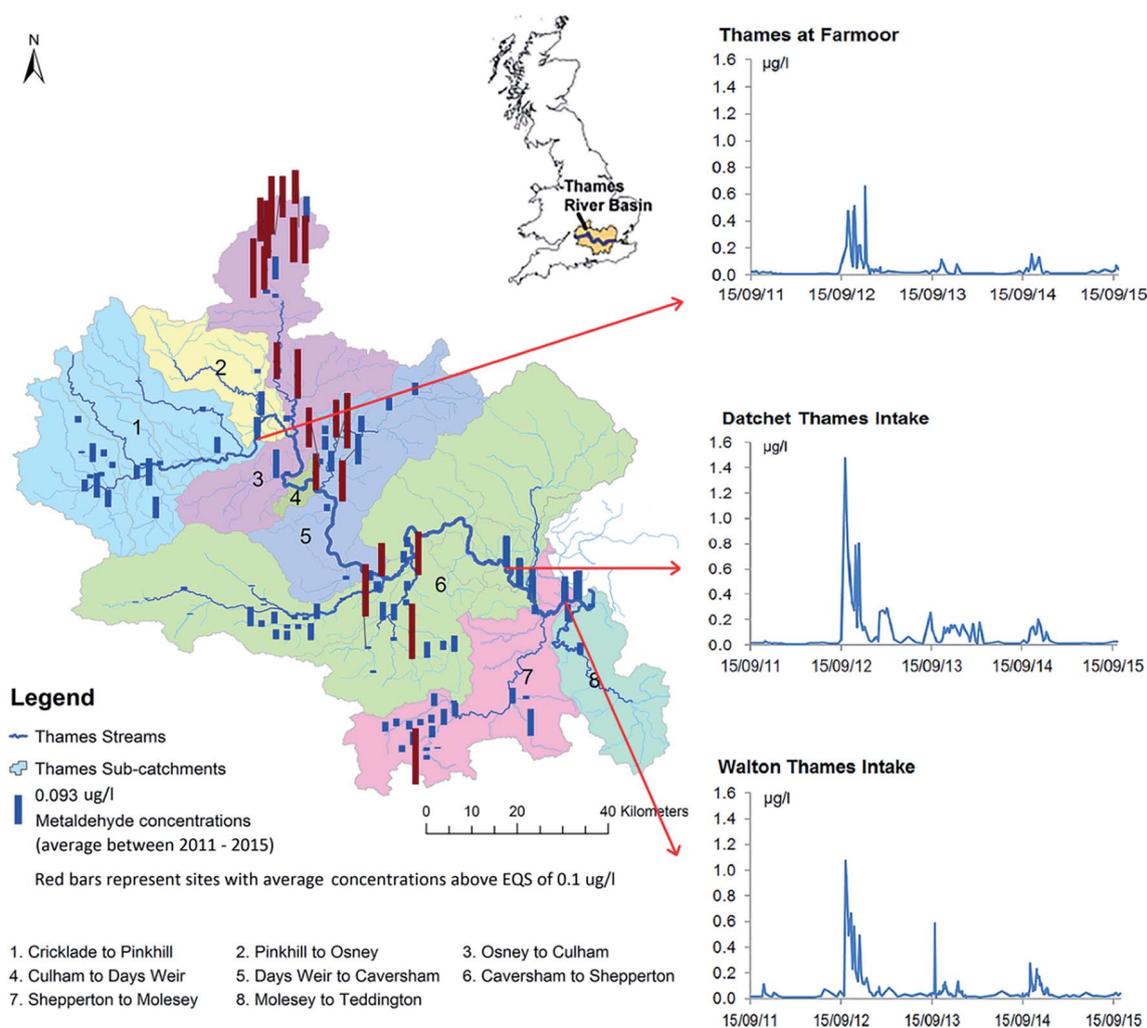


Fig. 1 Average concentrations of metaldehyde in the River Thames catchment (2011–2015) and the observed concentrations of metaldehyde between 2011 and 2015 in the Thames at Farmoor, Datchet and Walton.

metaldehyde between 2011 and 2015 were above the drinking water quality standard of  $0.1 \mu\text{g l}^{-1}$  in 31 out of 140 sites across the Thames catchment (Fig. 1). At many sites the levels of metaldehyde increased in autumn and winter periods of 2012, 2013 and 2014 due to wetter weather. In autumn 2012, following heavy rainfall, the peak concentrations of metaldehyde at all 12 abstraction points (Grimsbury, Girling Lee, Datchet, Hythe End, Hampton, Kennet Fobney, Laleham, New Gauge Lee, Hornsey, Walton, Lockwood, and Sor Brook) used by Thames Water (the River Thames catchment water utility) were many times higher than the UK and EU Environmental Quality Standard (EQS) for drinking water. The observed values for metaldehyde at the Thames freshwater abstraction points of Farmoor, Datchet and Walton (reaches 1, 6 and 7 respectively in Fig. 1) are shown in Fig. 1. The average concentrations of metaldehyde in the sampling sites (2011–2015) are in the range of  $0.002\text{--}0.40 \mu\text{g l}^{-1}$ , with peaks ranging between  $0.5$  and  $4.0 \mu\text{g l}^{-1}$  at the abstraction points, whereas the EU limit in waters for public supply is  $0.1 \mu\text{g l}^{-1}$ , so the observations are well above the EU limit.

## 2.2 INCA-contaminants

The INCA-contaminants model developed by Nizzetto *et al.*<sup>27</sup> is a member of the INCA family. The INCA models, including INCA-N, INCA-P, INCA-sediment, INCA-carbon, INCA-chloride, INCA-mercury and INCA-metals, have been developed since 1998 to simulate hydrology flow pathways in fresh water systems, and to track contaminant fluxes on a daily time step in both terrestrial and aquatic phases of basins.<sup>35,39–42</sup> They are process-based and semi-distributed models that can account for the spatial variability of the catchment. Thus, they can be used for simulating water quality in large complex river basins with varying land use, soil types, and hydrological conditions. The INCA models have been successfully applied to more than 100 catchments across the world.<sup>34,39,42,43</sup>

The INCA-contaminants model is based on two extensively tested models: the INCA-carbon model<sup>42</sup> and the INCA-sediment model.<sup>39</sup> It couples simulations of river flow, dissolved organic carbon (DOC), suspended sediment (SS) and organic pollutants, and can be used to gain a detailed understanding of the fate and fluxes of metaldehyde in the River Thames system.<sup>28</sup> The underlying hydrological model simulates the daily surface and diffusive runoff from land to surface waters as well as in-stream flow conditions.<sup>38</sup> Utilizing the runoff fluxes and flow rates generated from the hydrological model, the INCA-sediment model calculates sediment production and delivery from land to river, plus transport, deposition and remobilisation of sediment within the in-stream system. The INCA-sediment model simulates the detachment of soil particles by splash and flow erosion, through the use of physically based equations, which depends on catchment characteristics such as erosivity and slope, and proportionally to the direct runoff generated by the hydrological sub-model. The direct runoff is also used to compute the slope transport capacity, which is used to route the detached material (or part of it, if the maximum transport capacity is lower than the material

available) from the hillslope to the channel network. The Bagnold stream power formula<sup>44</sup> is used to compute the stream network suspended transport capacity and route the eroded material downstream. Several texture classes can be defined within INCA, thus computing the sediment load for each class. An application of the INCA-sediment model to the Thames catchment can be found in a paper by Bussi *et al.*<sup>45</sup>

The INCA-carbon model produces daily estimates of the distribution of solid and dissolved organic carbon in soils and waters across the catchment. Contaminants are delivered from soils to surface waters through surface runoff delivering solid organic carbon (SOC) associated contaminants and both truly dissolved and DOC associated contaminants and diffuse runoff from upper and lower layers of the soil compartment. The model allows for fixed or time varying inputs of contaminants from atmospheric deposition, fertiliser application, litterfall, accidental spills or direct applications (as in the case of pesticides).<sup>27,28</sup> Like all versions of the model, the INCA-contaminants model is driven by an input of daily time series of precipitation, temperature, hydrologically effective rainfall (HER), soil moisture deficit (SMD), and wind speed.

The INCA contaminants model consists of two main components:<sup>28</sup>

(1) a land phase model simulating the multimedia distribution, transport, storage and transformation of contaminants in the land phase (Fig. SI1†);

(2) an in-stream model simulating the fate and transformation of organic pollutants in the aquatic system (Fig. SI2†).

A brief description of the land phase model and the in-stream model is presented in the ESI.† The contaminant fluxes in the modelling are computed by multiplying their concentrations by the velocity components of the water and organic matter exchange. Contaminant concentrations in different phases of the catchment are calculated using thermodynamic equations derived from fugacity models.<sup>28</sup> The concentrations and transport of contaminants in different phases of the catchment are determined based on temperature dependent thermodynamic equilibrium partitioning coefficients (eqn (1)–(5)):

### 2.2.1 Air–water partitioning coefficient.

$$\log H_T = \log H_{25^\circ} - \frac{(10^3 \times \Delta U_{AW} + R \times 298.15)}{\ln(10) \times R} \times \left( \frac{1}{T} - \frac{1}{298.15} \right) \quad (1)$$

$$K_{AW} = \frac{H_T}{R \times T} \quad (2)$$

where  $H_T$  is the Henry's law constant;  $\Delta U_{AW}$  is the enthalpy of phase transfer between air and water;  $R$  is the ideal gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ),  $T$  is the water temperature (K); and  $K_{AW}$  is the air–water equilibrium partitioning coefficient.

### 2.2.2 Water–SOC partitioning coefficient.

$$\log K_{OW_T} = \log K_{OW_{25^\circ}} - \frac{(10^3 \times \Delta U_{AO})}{\ln(10) \times R} \times \left( \frac{1}{T} - \frac{1}{298.15} \right) \quad (3)$$

$$K_{W-SOC} = K_{OC} = K_{OW_T} \times r_{OC} \times \frac{1}{\rho_{OC}} \quad (4)$$

where  $K_{OW}$  is the octanol–water equilibrium partitioning coefficient;  $\Delta U_{OA}$  is the enthalpy of phase transfer between octanol and air;  $K_{OA}$  is the octanol–air equilibrium partitioning coefficient;  $K_{W-SOC}$  is the temperature corrected SOC–water equilibrium partitioning coefficient;  $K_{OC}$  is the water–organic carbon partitioning coefficient;  $r_{OC}$  represents the empirical coefficient; and  $\rho_{OC}$  is the density of solid organic carbon;

### 2.2.3 Water–DOC partitioning coefficient.

$$K_{W-DOC} = \frac{10^{(0.93 \log K_{OW_T} - 0.45)}}{\rho_{DOC}} \quad (5)$$

where  $K_{W-DOC}$  is the temperature corrected DOC–water equilibrium partition coefficient.

More detailed information on the INCA-contaminants model can be found in the work done by Nizzetto *et al.* (2016).<sup>27</sup> Here, we limit ourselves to a short overview of the main components of the model, although more information is available in the ESI.†

## 2.3 Model set up

The INCA-contaminants model has been applied to simulate metaldehyde behaviour for the period of 1st Jan 2008–30th Sep 2014 in the River Thames system. The model has been successfully applied to the River Thames in a previous paper<sup>28</sup> considering other organic contaminants (PCBs). Coupling river

flow, suspended sediment and organic carbon simulations, the INCA-contaminants model has led to a better representation of PCB contamination in the river system compared to more simplistic approaches based on the traditional fugacity modelling approach. In this study, we adopted the calibrated and validated parameters relating to sediments and hydrology from the earlier PCB study in the simulation for metaldehyde dynamics. Further details of this earlier study are given elsewhere by Lu *et al.* (2016).<sup>28</sup>

In the modelling, the catchment was divided into 8 reaches and sub-catchments (Table 1). The set-up has been previously used in many applications of INCA models to simulate the transport of contaminants in the Thames.<sup>28,33,38</sup> Five sediment size classes were used, including clay, silt, and fine, medium and coarse sand. Six land use types were used representing arable, total vegetable, potato, pasture, forest and urban (Table 1). Land use classifications were based on the Land Cover Map 2000 (LCM2000) land coverage map and the crop area maps (Table 3). Pesticide application to autumn sown arable crops such as winter wheat and oilseed rape plus other potato crops and general vegetables was considered to be the major input of metaldehyde to the catchment. But limited information on the usage pattern of metaldehyde (application rates, time and method) in the catchment is available. Due to the lack of data, roughly estimated application rates based on the current Metaldehyde Stewardship Group (MSG) application guidelines and measured metaldehyde concentrations in water were used in the modelling. Although it could not guarantee a high quality predictive performance, the current method is, nonetheless, the only practicable option for metaldehyde modelling at present. In the modelling, equal values of metaldehyde application rates were used for land use including arable, total vegetable, and potato. But, we separate the crop areas for total vegetable and potato from arable to show that the variability in the application rates of metaldehyde for different crop types could be addressed in the modelling when there are data available. More information on the application rates of metaldehyde is described in the following section.

Table 2 Physical properties of metaldehyde<sup>15</sup>

Molar mass (g mol <sup>-1</sup> )	176.2
Molar volume (cm <sup>3</sup> mol <sup>-1</sup> )	186
Henry's law constant (25°) (Pa m <sup>3</sup> mol <sup>-1</sup> )	3.8
$K_{OW}$	1.318
Half-life in water (days)	200
Half-life in soil (days)	30
Half-life in sediment (days)	1000

Table 3 Data sources for the metaldehyde modelling in the River Thames catchment

Data	Sources
Land cover for the Thames basin	LCM2000 land coverage map (Centre for Ecology and Hydrology (CEH)) <a href="http://www.ceh.ac.uk/services/land-cover-map-2000">http://www.ceh.ac.uk/services/land-cover-map-2000</a>
Crop growth data	Crop area map (DEFRA), <a href="http://www.gov.uk/government/uploads/system/uploads/attachment_data/file/183108/defra-stats-foodfarm-landuselivestock-june-detailedresults-cropmaps111125.pdf">http://www.gov.uk/government/uploads/system/uploads/attachment_data/file/183108/defra-stats-foodfarm-landuselivestock-june-detailedresults-cropmaps111125.pdf</a>
Meteorological data	Precipitation and temperature: Met Office (UK), <a href="http://www.metoffice.gov.uk/services/industry/data/commercial/rainfall">http://www.metoffice.gov.uk/services/industry/data/commercial/rainfall</a> , wind speed: Meteorological Station at CEH Wallingford, SMD and HER: PERSiST model derived
Fertilizer input data	Thames Water; local farmers and chemical suppliers; Get Pelletwise, <a href="http://www.getpelletwise.co.uk/msg-guidelines/">http://www.getpelletwise.co.uk/msg-guidelines/</a>
Water quality data	DOC and suspended sediment: CEH the River Thames Initiative, <a href="http://www.ceh.ac.uk/our-science/projects/river-thames-initiative">http://www.ceh.ac.uk/our-science/projects/river-thames-initiative</a> , metaldehyde concentrations in water: Thames Water
Flow data	CEH National River Flow Archive, <a href="http://nrfa.ceh.ac.uk">http://nrfa.ceh.ac.uk</a>

The relevant physical–chemical properties of metaldehyde were taken from the European Food Safety Authority (EFSA) report<sup>15</sup> and are shown in Table 2. In the INCA-contaminants model, a daily time series of precipitation, air temperature, hydrologically effective rainfall (HER), soil moisture deficit (SMD) and wind speed were loaded as driving data. The daily time series inputs were adopted from the earlier PCB study of the River Thames.<sup>28</sup> The daily time series of precipitation and temperature used in the modelling were the spatially weighted average of the data provided by the UK Met Office for all the meteorological stations within the catchment. Daily wind speeds were obtained from the Meteorological Station at CEH Wallingford. The HER and SMD data were generated using the PERSiST (Precipitation, Evapotranspiration and Runoff Simulator for Solute Transport) model. The PERSiST model is a conceptual and semi-distributed model that simulates the water stores and pathways across the catchment.<sup>33</sup> It was developed primarily for providing input data series to the INCA family of models.

### 3. Results and discussion

#### 3.1 Flow simulation

In order to successfully model contaminants in river systems, it is necessary to ensure that the flow is correctly modelled. The daily flow simulations for the eight reaches of the River Thames were compared with observed flow data, available from the UK CEH National River Flow Archive. A good correspondence between modelled and observed flows was obtained for all eight reaches with simulations at Shepperton (Nash-Sutcliffe statistic of 0.67 and an  $R^2$  of 0.69, Table 4) shown in Fig. 2.

#### 3.2 Metaldehyde simulation and application rates

A key requirement in the model analysis is the metaldehyde application rates. As described above, the application rates vary throughout the year and depend on the farmers' perception of the problem so that they apply higher rates if large slug/snail populations are observed. The model is driven by a daily time series of metaldehyde application rates (based on an appropriate application rate chosen depending on the season and the periods of agricultural use).<sup>12</sup> Observations show that the levels of metaldehyde generally reach a maximum in autumn and winter (Fig. 1). In the model set-up, it is assumed that

metaldehyde is only applied each year from 1st August to 31st December. Application rates were estimated based on information provided by Thames Water, chemical suppliers and local farmers, and have been calibrated based on the observed concentration values. Metaldehyde has a very low  $K_{ow}$  and long environmental half-lives (Table 2) and its interaction with soil and stream/sediment organic matter is limited. Soil hydraulic properties, precipitation and application rates are the main parameters controlling stream concentrations. Thames Water has provided the observed metaldehyde concentration from a wide range of monitoring points along the River Thames and in its tributaries (Fig. 1, Table 3). We found that by introducing application rates matching metaldehyde usage guidelines, the measured baseline concentration could be predicted.

Monitoring data from 2012 show very high concentrations with peaks of  $1.5 \mu\text{g l}^{-1}$  (15 times the drinking water threshold) in September. This extremely high concentration occurs after the very warm 2011/12 winter and following a wet summer in 2012. The damage to crops was severe that year and metaldehyde was used extensively to control the slug population. In order to simulate the 2012 dataset we were forced to assume quantities of applied metaldehyde significantly exceeding doses from application guidelines. Fig. 2 shows metaldehyde simulations at 6 sites along the river assuming an application rate for 2012 of 700 g per ha per year, which is high but consistent with observed data. A good fit to the observations is obtained at all 6 sites down the river system. It is not surprising that farmers would apply different rates from year to year depending on weather conditions and slug populations. Furthermore, in 2012 an invasive species of slug ("Spanish" slug) was first found in the UK, probably representing an additional driver for intense use of metaldehyde by farmers (SlugWatch: <http://www.slugwatch.co.uk/>). Another contributing factor to the extreme peaks was the very wet conditions in summer and autumn 2012 which created saturated soils and, hence, applied metaldehyde would have been flushed rapidly into surface waters.

#### 3.3 Control options

Using the calibrated INCA-contaminants model, a set of synthetic application scenarios were run to evaluate possible control strategies. Fig. 3 and Table 5 show the peak concentration profiles down the river at the 8 simulated reaches, for 2012, with each profile based on differing application rates. The highest application rate of 290 g per ha per year, as shown in Fig. 3, generates a peak concentration of  $0.9 \mu\text{g l}^{-1}$ , at Farmoor (Reach 1), approximately half the observed 2012 peak values. The results suggest that in 2012 it would have been impossible to meet the intake water standard of  $0.1 \mu\text{g l}^{-1}$  at Farmoor (Reach 1) and Datchet (Reach 6) even at the recommended lower rates of application (*e.g.* 160 g per ha per year). In fact, only when the application rate is reduced to 33 g per ha per year can the intake water standard be reached, as shown in Fig. 3.

Although a management strategy needs to be devised in collaboration with the farmers, a total ban on metaldehyde use is a possibility. This would be the ultimate measure but would lead to an unacceptable loss of crops. An alternative control

Table 4 The Nash-Sutcliffe efficiency criterion and regression analysis for the flow simulations

No.	Reach name	Nash-Sutcliffe	$R^2$
1	Cricklade to Pinkhill (Farmoor)	0.61	0.67
2	Pinkhill to Osney	0.66	0.69
3	Osney to Culham	0.62	0.65
4	Culham to Days Weir	0.60	0.64
5	Days Weir to Caversham	0.63	0.64
6	Caversham to Shepperton (Datchet)	0.67	0.69
7	Shepperton to Molesey	0.66	0.69
8	Molesey to Teddington (Walton)	0.65	0.67

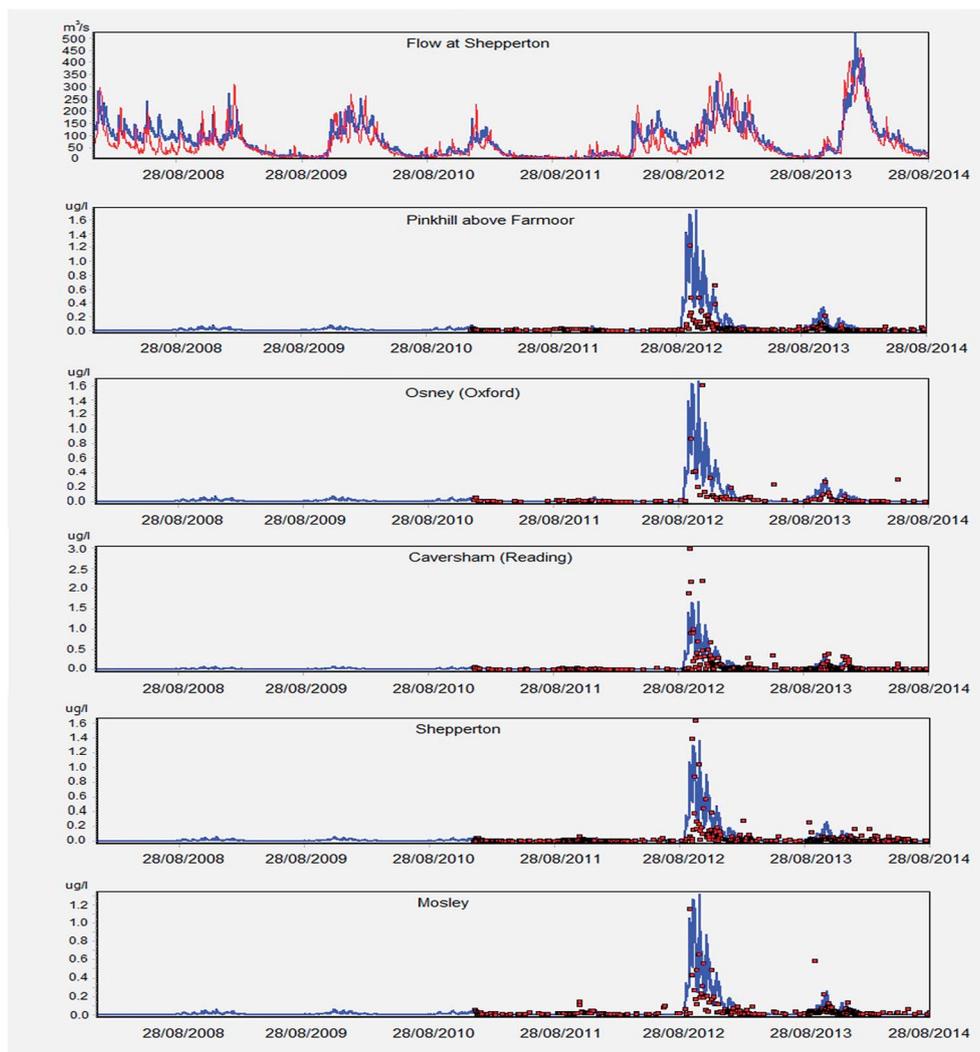


Fig. 2 Simulated and observed flow and metaldehyde concentrations at several sites along the Thames, 2008–2014.

measure is the use of ferric phosphate as a substitute for metaldehyde. This is nontoxic and completely removes the need for metaldehyde use, but it is a more expensive option. Therefore

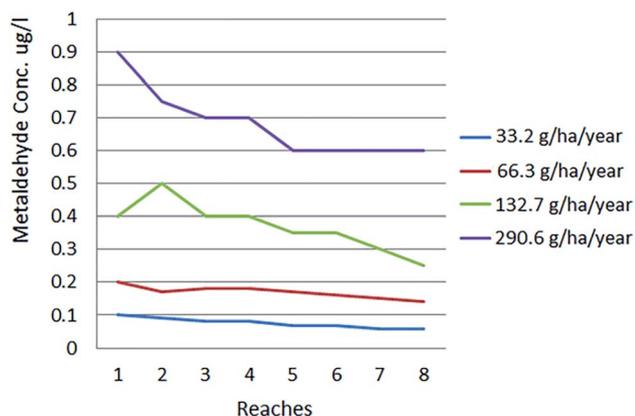


Fig. 3 Metaldehyde concentrations along the Thames reaches over a 2012 type hydrological year for different application rates ranging from 33 g per ha per year up to 290 g per ha per year.

we have considered a control strategy whereby ferric phosphate is used on a selected area of the catchment. We can use the INCA Thames model to determine this area and from this the reduced metaldehyde application rates needed to meet the water quality standards at the abstraction points at Farmoor and Datchet are calculated. Firstly, an analysis of the peak concentrations at Farmoor against different application rates shows a linear relationship with the following predictive equation:

Table 5 Simulated metaldehyde peak concentrations at the 8 reaches along the Thames against application rates (note – Reach 1 is Farmoor and Reach 6 is Datchet)

Application rate (g per ha per year)	1	2	3	4	5	6	7	8
33.2	0.10	0.09	0.08	0.08	0.07	0.07	0.06	0.06
66.4	0.20	0.17	0.18	0.18	0.17	0.16	0.15	0.14
132.7	0.40	0.50	0.40	0.40	0.35	0.35	0.30	0.25
290.7	0.90	0.75	0.70	0.70	0.60	0.60	0.60	0.60

Table 6 Reach areas, and A and B parameters for the loading equation

No.	Reach name	Cumulative upstream arable winter crop area (ha)	a	b
1	Cricklade to Pinkhill (Farmoor)	65 646	0.0031	47.2
2	Pinkhill to Osney	82 876	0.0028	33.8
3	Osney to Culham	133 959	0.0025	18.7
4	Culham to Days Weir	136 461	0.0025	18.3
5	Days Weir to Caversham	182 629	0.0022	12.0
6	Caversham to Shepperton (Datchet)	269 944	0.0022	8.1
7	Shepperton to Molesey	293 170	0.0021	7.2
8	Molesey to Teddington (Walton)	303 028	0.0020	6.6

$$C_{\text{peak}} (\mu\text{g l}^{-1}) = a \times \text{application rate (g per ha per year)} \quad (6)$$

where  $a = 0.0031$  is obtained from regression analysis ( $R^2$  of 0.99). Repeating this analysis for all reaches gives a set of regression parameters as shown in Table 6.

If the area of application is considered as well, then this loading equation becomes

$$C_{\text{peak}} (\mu\text{g l}^{-1}) = b \times \text{application rate} \times \text{area (ha)} / 10^9 \quad (7)$$

where reach areas and the associated parameter  $b$  are listed in Table 6.

Given the area of winter sown arable crops is 65 646 ha in the upper reaches of the Thames to Farmoor and assuming an application rate of  $300 \text{ g ha}^{-1}$ , eqn (7) yields

$$C_{\text{peak Farmoor}} = 47.2 \times 300 \times 65646 / 10^9 \mu\text{g l}^{-1} = 0.92 \mu\text{g l}^{-1} \quad (8)$$

In order to obtain peaking concentrations below the standard ( $0.1 \mu\text{g l}^{-1}$ ), either the application rate has to drop to  $30 \text{ g ha}^{-1}$  or the area treated has to fall to 6500 ha.

At Datchet, where the cumulative upstream area of treated crop is very large (269 944 ha), the concentration peak assuming an application rate of  $160 \text{ g ha}^{-1}$  would be

$$C_{\text{peak Datchet}} = 8.1 \times 160 \times 269944 / 10^9 \mu\text{g l}^{-1} = 0.35 \mu\text{g l}^{-1} \quad (9)$$

In this case either the application rate would have to be reduced to  $50 \text{ g ha}^{-1}$  or the area of crops treated would have to be reduced by a third. This could be achieved by reducing the crop area treated in the Cherwell and the Thames catchments (sub-catchment 3) as these are severely impacted catchments. Using the simple loading equation and the area and  $b$  parameters of Table 6, it is possible to calculate the approximate metaldehyde concentration peaks for wet years at different locations along the Thames based on 2012 type conditions. This simple tool could be used to inform management plans for balancing applications of metaldehyde and ferric phosphate in the critical areas in the high part of the catchment in order to ensure fulfillment of water quality standards at the abstraction points.

## 4. Conclusions

Metaldehyde application for pest control creates serious issues for water supply in the Thames, especially during years where a warm winter is followed by a wet summer and autumn. In this situation, farmers tend to apply metaldehyde at the maximum allowable rate to control slugs. These high application rates result in excessive runoff of metaldehyde in wet conditions. In order to manage and control metaldehyde pollution, an integrated approach relying on coordination between farmers, Thames Water and the Environment Agency is needed, along with a deeper understanding of the behaviour and transport of metaldehyde in the catchment.

In this study, the INCA-contaminants model has been applied to simulate the metaldehyde dynamics in the River Thames catchment. This is the first time a dynamic modelling approach has been used to predict the behaviour of metaldehyde in river basins. It is proposed that application rates are the key driver of concentrations in rivers. But, little information on the slug population in the River Thames catchment is available and hence it is difficult to create a control system based on slug population numbers. In this study we used a scenario strategy to derive a simple decision support tool based on variable application rates and application areas. This decision support tool is now being used by Thames Water to help control peak concentrations of metaldehyde at key water supply locations. This is an excellent demonstration of where complex models can help to both explore land to river pollutant transfer and help devise decision support tools to address complex management options.

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## Supporting Information to:

### Modelling Metaldehyde in Catchments: A River Thames Case-Study

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## 1. The INCA-Contaminants Model

Figure S11 illustrated the structure of the INCA-contaminants land phase model. In the land phase model, the soil has been divided into two layers which are conceptualized as a superficial organic layer and an underlying mineral layer. Each layer contains soil air and soil water (which includes the fraction of dissolved organic carbon, DOC, and soil organic carbon, SOC). The relative volumes of soil air and soil water are dynamically determined by the inputs of SMD. In addition, the SOC is divided into two pools representing easily and potentially accessible fractions to allow a better simulation for contaminants interaction with the solid organic phase and to allow for different breakdown rates in soils in relationship to the contaminant pool availability to degrading microorganisms. Within the soil, the main transport processes represented in the model include: partitioning among sub-phases of the soil layers; gaseous diffusion across the atmosphere and the upper soil layer, diffusion across the upper and lower soil layer in the soil water and soil air; bioturbation; and vertical advection (leaching) from upper to lower soil layer. The outputs of contaminants from the soil layers include surface and diffuse runoff from the upper layer and diffuse runoff from the lower layer and the degradation of contaminants.<sup>1</sup>

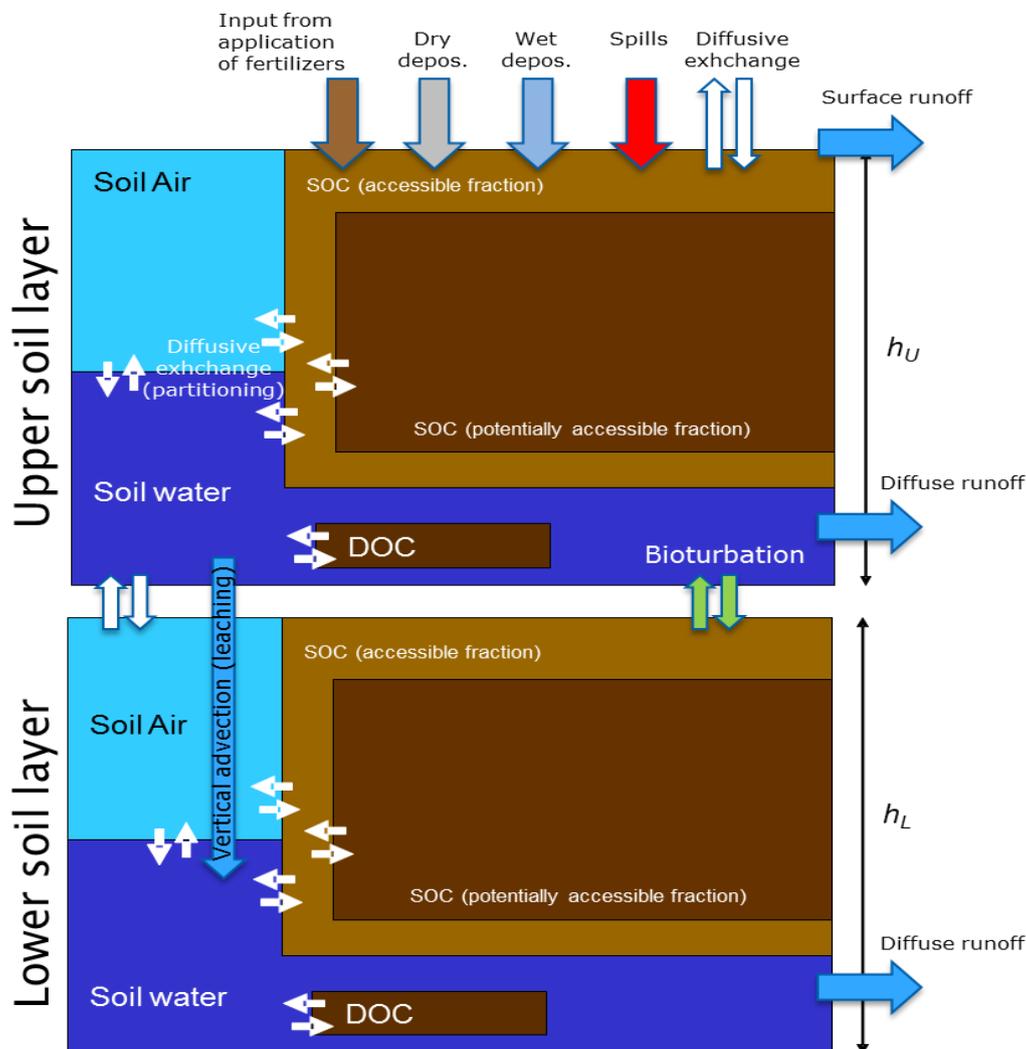


Figure S11. Structure of the soil compartment, adapted from Nizzetto et al. (2016)<sup>1,2</sup>. The degradation process (not depicted in the figure) occurs in any of the soil sub-compartments with independent user-definable rates.

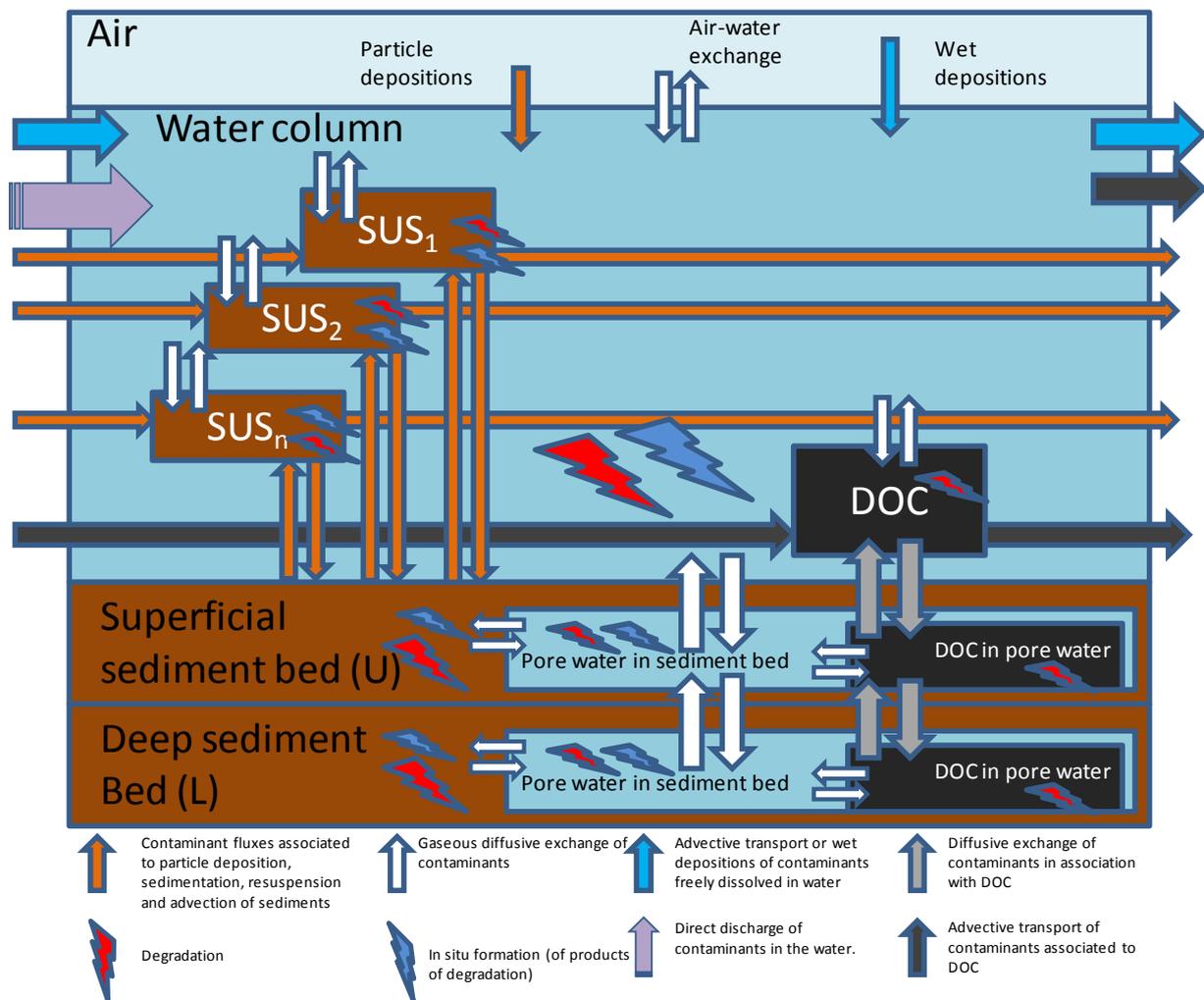


Figure SI2. Structure of the in-stream compartment, adapted from Nizzetto *et al.* (2016)<sup>1,2</sup>

The structure of the INCA-contaminants in-stream model was illustrated in Figure SI2. The INCA-contaminants model takes into account information on river network structure, catchment topography, soil properties and land use. In the model, the in-stream phase is simulated as a group of several stream segments (reaches). In each reach the water column and the bed sediment are simulated as two different but interconnected compartments. The bed sediments are divided into superficial and deep layers. The depth of the superficial sediment bed is dependent on the in-stream suspended sediment transport dynamics (sediment deposition and mobilisation rates). Multiple sediment grain size classes can be simulated. For each grain size class, a mass balance is maintained based on the following processes: inputs from upstream reaches, entrainment with soil, flow erosion, sediment erosion, downstream advection and deposition of suspended sediment.<sup>1</sup> Mass balance calculations are based on those in the INCA-sediment model.<sup>3</sup>

The suite of possible inputs of contaminants to the in-stream system includes: wet and dry atmospheric deposition, diffusive air-water exchange, advection from upstream, possible point sources, and inputs from surface and diffuse runoff from the soil detailed at an arbitrary sub-catchment scale. The diffusive air-water exchange is dynamically calculated based on the inputs of wind speed and stream turbulence. After entering the water, the contaminants can be

in a truly dissolved phase (TDP), associated with DOC, or associated with suspended matter in the streams.<sup>4</sup> The partitioning of contaminants to suspended material in the water column is calculated separately for each grain size class, therefore the mass budget of contaminant bounded to solids is calculated individually per each class of sediment. Losses of contaminants from the in-stream system include: degradation of contaminants, formation of degradation products, and downstream advection.

## 2. References

1. Q. Lu, M. Futter, L. Nizzetto, G. Bussi, M. Jürgens and P. Whitehead, Fate and transport of polychlorinated biphenyls (PCBs) in the River Thames catchment—Insights from a coupled multimedia fate and hydrobiogeochemical transport model, *Science of the Total Environment*, 2016.
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Techniques for treatment of metaldehyde:

Due to the characteristics of metaldehyde, it is very difficult to effectively remove using existing water treatment processes. Its simple chemical structure means it cannot be broken down by water treatment processes using chlorine or ozone. It is also not effectively removed by Granular Activated Carbon (GAC), which is an advanced system used to remove pesticides and organic compounds. Metaldehyde adsorption onto GAC are driven by hydrophobic interactions and hydrogen bonding. But leaching tendencies were high since no degradation of metaldehyde are occurred.

Recent work has shown that metaldehyde can be possibly treated by new techniques, such as:

- (1) carbon based system using the bespoke sorbent Nyex™ (Nabeerasool et al., 2015),
- (2) aqueous solution using GAC, a non-functionalised hyper-cross-linked polymer Macronet (MN200), and an ion-exchange resin (S957) (Tao and Fletcher, 2013),
- (3) and advanced oxidation processes (AOPs) using UV/H<sub>2</sub>O<sub>2</sub> and UV/TiO<sub>2</sub> (Sanches et al., 2010).

In response to rising metaldehyde concentrations the River Trent, Anglian Water has installed the TrojanUVTorrent™ ECT UV-oxidation system as part of a multi-barrier approach to ensure it produced a potable water supply that matched the EU standards. The new UV-oxidation system is expect to treat various pesticides, including metaldehyde.

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## Chapter 7. Conclusions

In the United Kingdom (UK), the production and use of POPs has been eliminated or reduced since the 1970s (Environment Agency, 2007; Lu *et al.*, 2015), but due to their great persistence and lipophilicity, they can remain in the environment for a long period of time. They are likely to accumulate to the organic matters in soil and sediment, and bio-accumulate in the food chain (Jones and De Voogt, 1999; Darko *et al.*, 2008). On the catchment scale, the residual POPs in soil and sediment could be secondary and diffuse sources and pose potential risks to ecosystems and human health (Lu *et al.*, 2015). Managing these risks at catchment level is challenging, as very little information on their distribution and fate in river basins—or in different compartments of catchments—is currently available. The monitoring of POPs is characterised by great complexity and high cost.

In order to address the potential risks of POPs, a modelling approach has been applied to simulate their behaviour and transport within a catchment. For this thesis, the River Thames catchment was chosen as the study area. The major aim of this research was to predict the distribution of POPs in the catchment, including exploring potential secondary sources of POPs, and to understand how the fate of POPs could be driven by future changes in climate and extreme weather conditions. This thesis is intended to provide guidelines to support decision-making in the risk management of POPs.

In Chapter 3, a multimedia fate model (the fugacity level III model) was used to predict the distribution of POPs throughout the Thames catchment: PCB 52, PCB 118 and PCB 153 were selected as the study chemicals. Fugacity modelling was also used to estimate the extent to which climate change might alter the fate of the PCBs in the catchment and so affect

environmental and human exposure. The modelling results indicated that sediments and fish represent environmental compartments with the highest PCB concentrations; however, only a limited number of recent observed sediment and fish data are available to test the modelling results. To inform decision-making, additional measurement of the chemicals in sediment and fish from the River Thames is needed. In order to overcome the limitation in observed data, chemical analysis of sediment and fish samples collected from the Thames were carried out in collaboration with the Lancaster University Environment Centre. Chapter 4 presents the analysis methods and the current contamination levels of POPs including PCBs, PBDEs and HCB in Thames sediment and fish. The correlation between POP concentrations in bed sediment and fish was also examined in Chapter 4.

With their greatly simplified representations of climate, hydrology and biogeochemical processes, the level III fugacity models can only predict general conditions across a region and have limited ability to represent environmental variability; however, the fate of organic pollutants could be greatly influence by many factors, such as weather conditions, hydrology and the fluxes of sediments and organic carbon. Chapter 5 applied the INCA-Contaminants model to simulate PCB dynamics in the Thames catchment. The INCA set-up was based on the parameters used in the previous fugacity modelling. The modelling has reproduced observed sediment PCB concentrations for a range of congeners at multiple locations in the River Thames. It also successfully simulated the consequences of the severe flooding on the contaminations of PCB in the Thames sediment.

In addition to POPs, a number of pesticides which were not previously detected have caused severe problems for drinking water supply in recent years (Skinner *et al.*, 1997; Environment Agency, 2009). For example, metaldehyde, which is the active ingredient in snail and slug control pellets, has been regularly observed at levels exceeding drinking water standards in

rivers in the UK (Environment Agency, 2009). Despite the large amount of measurement data of metaldehyde in rivers, limited assessment on the transport of metaldehyde from land phase to river are available. Chapter 6 shows that the INCA-Contaminants model can be used to simulate metaldehyde transport in the Thames catchment. The relationship between application rates, application area and metaldehyde concentrations in the river system was assessed.

The major findings of this thesis can be summarised as follows:

- The fugacity level III model offers a helpful approach to predicting the distribution and long-term fate of PCBs in the Thames catchment. The majority of PCBs were predicted to reside in the soil, whilst their highest concentrations were estimated to lie in sediment.
- Few recent measured data were available to validate the modelling predictions for PCB concentrations in sediment.
- Over the next 80 years, a significant overall drop in PCB concentrations is expected in all compartments. Soil would become a significant ongoing secondary source of the PCBs, and the river sediment compartment could serve as the primary reservoir for PCBs in the catchment.
- The predicted climate change (forecast in UKCP09) was predicted to have only a modest influence on the fate of PCBs in the catchment over the next 80 years.
- Fish and sediment sampling and analysis were carried out to address the limitation in the measured concentration data of POPs in Thames fish and sediment. The highest sediment concentrations of POPs were detected in an urbanised tributary of the Thames.
- The measured concentrations of POPs in fish and river sediment samples appear quite variable. No significant correlation between sediment concentration and local sewage effluent discharge was detected.

- But when normalised to OC/lipid, a similar contamination level in fish and sediment can be seen. This indicated that both river sediment and wild fish can be considered suitable for representing the contamination level of POPs in the river system, given sufficient sample numbers.
- It was shown that the INCA contaminants model can lead to a better representation of PCB dynamics in the River Thames catchment.
- Accurate sediment and organic carbon simulation is important for the successful prediction of riverine PCB transport.
- According to the modelling results, the PCB contamination in Thames sediment was greatly disturbed after the severe flooding in early 2014.
- The INCA-Contaminants model successfully simulated metaldehyde transport in the River Thames Catchment. Simulations indicated that high concentrations in the river system are a direct consequence of excessive application rates.
- Based on the modelling results, a simple decision-support tool was developed to inform management plans for balancing applications of metaldehyde and ferric phosphate in the critical areas, in order to ensure fulfilment of water quality standards.

The work presented in this thesis provided a comprehensive assessment of the current contaminations of POPs and pesticides in catchment. The fugacity modelling predicted the general distribution of contaminants between different compartments. The INCA-Contaminants model provided more detailed information and simulated the contaminant dynamics and fluxes in the catchment; however, there was a large degree of uncertainty over the modelling due to the lack of emission and observed data on the contaminants. Further work is, therefore, required to gain a better estimation of the contaminant emission and pesticide use in the catchment through, for example, more extensive farm surveys and

monitoring practice. Targeting limited resources monitoring would be very beneficial to corroborate the findings of the simulations and to improve our understanding of the problem of POPs and pesticides in the catchment. The fugacity model provided a preliminary exploration of the influence of climate change on the yearly average concentrations of POPs in compartments, but the potential extreme weather conditions caused by climate change were not addressed in the modelling. Further work is recommended, to forecast the effects of climate change using the daily time-step INCA-Contaminants model. It is also possible to expand the modelling to evaluate the influence of land use change and catchment management practices and to test the effects of mitigation strategies. This thesis suggests that the INCA-Contaminants model is an effective tool in modelling the behaviour of metaldehyde in the catchment. The decision-support tool, derived from the modelling results, is now being used by Thames Water for metaldehyde management in catchment. The method used in this thesis could be used to develop management strategies for other commonly used pesticides that cause problems with drinking water supply, such as simazine, isoproturon, 2,4-dichlorophenoxyacetic acid, 4-chloro-2-methylphenoxyacetic acid (MCPA), mecoprop and chlorotoluron.

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