Science of the Total Environment 576 (2017) 78–84

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

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

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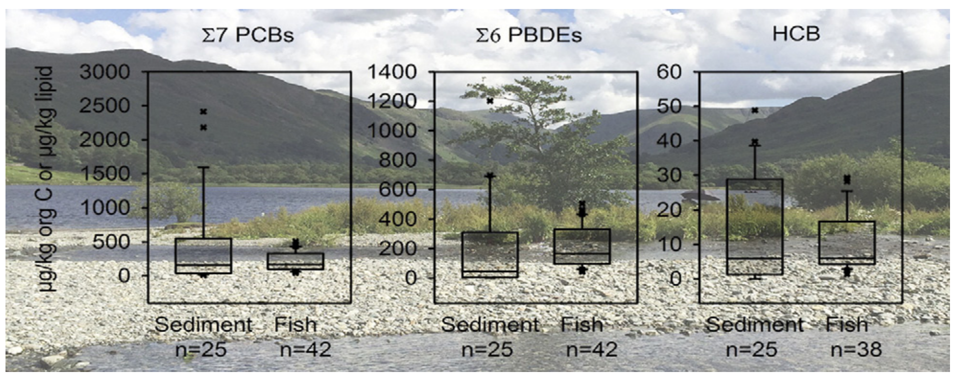
HIGHLIGHTS

- 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



ARTICLE INFO

Article history:
Received 6 July 2016
Received in revised form 8 October 2016
Accepted 9 October 2016
Available online 22 October 2016

Editor: D. Barcelo

Keywords:
POPs
Sediment
Fish
River Thames

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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http://dx.doi.org/10.1016/j.scitotenv.2016.10.067

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[1] 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, *Rutilis rutilis*) 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

[1] 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.