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River organisms as indicators of the distribution and sources of persistent organic pollutants in contrasting catchments☆

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ABSTRACT

Persistent organic pollutants (POPs) continue to threaten aquatic organisms, but risk assessments are restricted by poor knowledge of the distribution and quantity of these substances in different biota. Assessments on aquatic invertebrates are particularly scarce. Here, we investigate variation in polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs) and organochlorines (OCs) in sediments, biofilms, macroinvertebrates and fish across rivers in South Wales (UK). Persistent PCB (−118, −153, −180) and PBDE congeners (BDE-47, -99, −100), and OCs (*p,p'*-dichlorodiphenyldichloroethylene [*p,p'*-DDE] and dieldrin [HEOD]) dominated the POPs detected, indicating links to historical emissions. Low concentrations of less persistent PBDEs, PCBs and OCs, however, suggest more contemporary sources. Concentrations of POPs were 2−22 times greater in fish than invertebrates, but their detection frequency (>90%) and concentrations (0−304 ng g^{-1} wet weight) were higher in these organisms than in sediments or biofilms (<10%; 0−12 ng g^{-1} wet weight). Invertebrates and fish also contained several PCB congeners (28, 52, 77 and 105) and *p,p'*-dichlorodiphenyltrichloroethane (*p,p'*-DDT) that were not detected in the environmental samples. Concentrations of PBDEs, PCBs and OCs differed among invertebrate taxa and feeding guilds. After controlling for significant variation among sample types and taxa, PBDEs were found to increase with urban land cover, while increased PCBs were associated with urban land cover and wastewater discharge. These data illustrate how body burdens of POPs across invertebrate and fish taxa provide valuable information on the spatial variation and likely sources of persistent pollutants in freshwater ecosystems. More work is required to resolve differences in POP contamination between taxonomic groups.

1. Introduction

A wide range of xenobiotic or anthropogenic chemicals from both legacy and contemporaneous sources occur in most aquatic environments (Sumpter, 2009; Gavrilescu et al., 2015; Sun et al., 2015). Such pollutants alone or in mixtures can have harmful effects on aquatic organisms (Wasi et al., 2013; Arnold et al., 2014; Malaj et al., 2014), in some cases altering species communities or food webs (Windsor et al., 2018). While recent studies in freshwater systems have focussed more on emerging pollutants, the 'legacy' or persistent organic pollutants (POPs) continue to present an ecological risk to organisms because of their relatively high toxicity and persistence (McKnight et al., 2015; Rasmussen et al., 2015).

Previous modelling studies have linked the distribution and quantity of POPs in river systems to activities and land uses historically associated with pollutant sources (Nizzetto et al., 2010). In reality, however, the distribution of POPs in river catchments is complicated, and includes remobilisation from contaminated soils or sediments (Zoumis et al., 2001) as well as release from landfill or discarded equipment (Diamond et al., 2010; Iqbal et al., 2017). POPs can also be emitted from wastewater treatment works (WwTWs) when historical wastes are discharged inadvertently or illegally via sewers (Jones et al., 2014). Furthermore, long-range transport of POPs too provides a potential route into river systems (Josefsson et al., 2016). In general, however, the distribution of both contemporary and legacy POPs are poorly understood (Lohmann et al., 2007) and there is a need for field-based assessments to validate

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models, appraise sources, and determine more accurately the quantity, composition and potential transfer of POPs in environmental circulation.

Assessments of the dynamics, sources and distribution of POPs have tended to focus on measurements in water or sediment samples but concentrations in these environmental compartments are often low or non-detectable (Schwarzenbach et al., 2006; Loos et al., 2009). In contrast, the hydrophobic nature of many POPS means that they accumulate in organic matter, lipid-rich sediments or biota (Geyer et al., 2000). For this reason, aquatic organisms offer potential advantages for studies investigating the concentration and composition of POPs through time and space (Van der Oost et al., 2003; Schäfer et al., 2015). At one extreme, tissue concentrations of pollutants in organisms with small home ranges or limited dispersal can reveal specific sources of pollution while those with larger territories or those abundant enough to be sampled at multiple locations can integrate pollution signals across whole regions (Ormerod et al., 2000; Van der Oost et al., 2003; Morrissey et al., 2010).

Although sampling POPs in organisms has been widely adopted, particularly in apex predators (see Crosse et al., 2012), some taxonomic groups have been largely overlooked. As an example, although community composition of aquatic invertebrates in freshwaters is used widely to indicate physicochemical conditions or abiotic stressors across ecosystems, the prevalence and concentrations of legacy pollution in these taxa is poorly known (Bonada et al., 2006; Buss et al., 2015). Moreover, invertebrates have a range of contrasting ecological functions, traits and trophic levels in food webs that could reveal different exposure pathways, transformations and cascading effects for xenobiotic substances (Windsor et al., 2018). Improved information on the interactions between biota, xenobiotic contaminants and accumulation of pollutants could provide a more comprehensive understanding of such processes in natural systems, while also augmenting the general indicator of freshwater organisms.

In this paper, we investigate variations among PCBs, PBDEs and a suite of organochlorines (OCs) across compartments of river systems in South Wales by measuring the concentration of POPs in environmental (sediments and biofilms) and biological samples from different invertebrate taxa and a benthic fish species. We compare contrasting sample types, assessing their value for monitoring persistent contaminants in the environment, whilst also assessing the distribution, quantity and potential sources of POPs across a samples of river systems. Specific hypotheses were that:

1. POP composition and concentrations differ between sample types commonly used in monitoring (sediments, invertebrates and fish)
2. Variations in POP concentrations across macroinvertebrate taxa are similar to the variation in other samples (sediments, biofilm and fish)
3. Variations in POP concentrations and composition among different invertebrate taxa are similar across river systems
4. Environmental and biological samples reveal local and regional sources of POP contamination

2. Materials and methods

2.1. Sample sites

The study was carried out across nine river reaches (Fig. 1) distributed across three catchments in South Wales (Taff, Usk and Wye). Land use varied (Table 1) such that the Taff catchment has a large percentage of urban land and a legacy of large-scale industrial activity associated with coal mining, coal gasification and metal smelting (Learner et al., 1971). In comparison, both the Usk and Wye are dominantly agricultural catchments, with arable farming, horticulture, fertilised grassland and rough pasture (HMSO, 1978).

As well as land use, sample sites varied in stream discharge, physicochemical conditions (e.g. conductivity, pH, total dissolved solids) and consented effluent emission from WwTWs (Table 1). The combination of land use and industrial history, with local variations in effluent contributions and other point sources, covers a range of potential point and diffuse POP sources across sites and between catchments (Table 1).

2.2. Environmental covariates and potential source identification

To reveal potential point and diffuse sources of POPs across catchments, land use was determined using ESRI ArcMap (version 10.2). The contributing upstream land cover (urban, agricultural and improved grassland) was determined for each sample site using JNCC phase 1 habitat classification data (JNNC, 2010), in conjunction with the Spatial Tools for the Analysis of River Systems (STARS) and Spatial Stream Network (SSN) tools (Ver Hoef et al., 2014). Additionally, specific information on point sources of pollution, such as WwTW discharges, were collated from Natural Resources Wales (NRW) routine monitoring (© Natural Resources Wales and database right). All rights reserved. At sampling sites downstream of WwTW discharges, we calculated the ratio of wastewater effluent to river discharge (both in m^3/s).

For an additional description of site attributes, we used data available from routine monitoring by Natural Resources Wales (NRW) and the Environment Agency (EA) collected during the period 2010–2015 (Table 1). From these data, we derived two macroinvertebrate indices to assess *in situ* benthic environments: (i) the British Monitoring Working Party (BMWP), a monitoring metric scoring taxa based on their tolerance to pollution (high scores indicate the presence of pollution sensitive taxa); and (ii) Average Score Per Taxon (ASPT), which is the average BMWP score across the taxa sampled and accounts for sampling bias (Armitage et al., 1983; Hawkes, 1998).

2.3. Sample collection

At each of the nine sites, environmental and biological samples were collected for POP analysis along a 20 m river reach downstream of urban areas and point source discharges (e.g. WwTWs). Samples of sediments, biofilms (from the surface of cobbles), invertebrates (Heptageniidae, Baetidae, Rhyacophilidae, Gammaridae, Hydropsychidae, Leuctridae) and European bullhead (*Cottus gobio*; Linnaeus 1758) were collected, under consultation and licencing from NRW, during June–August 2016. Each sample comprised of multiple organisms ($n = 5–200$), or composite samples amalgamated from subsamples across multiple locations ($n = 5$) for sediments and biofilms, hereafter referred to as environmental samples. Samples were kept at −80 °C until analyses.

2.4. Chemical analyses

Environmental and biological samples were analysed at the Centre for Ecology and Hydrology (CEH, Lancaster) for a range of chemical contaminants (OCs: *p,p*'-DDT, *p,p*'-DDE and *p,p*'-DDD [TDE], dieldrin [HEOD], α- and γ-hexachlorocyclohexane [HCH], hexachlorobenzene [HCB]; 36 PCB congeners and 23 PBDE congeners; Appendix S2). Extraction and analysis followed CEH standard operating procedures (also see Morrissey et al., 2013).

Samples (0.5–2 g) were thawed, accurately weighed, ground

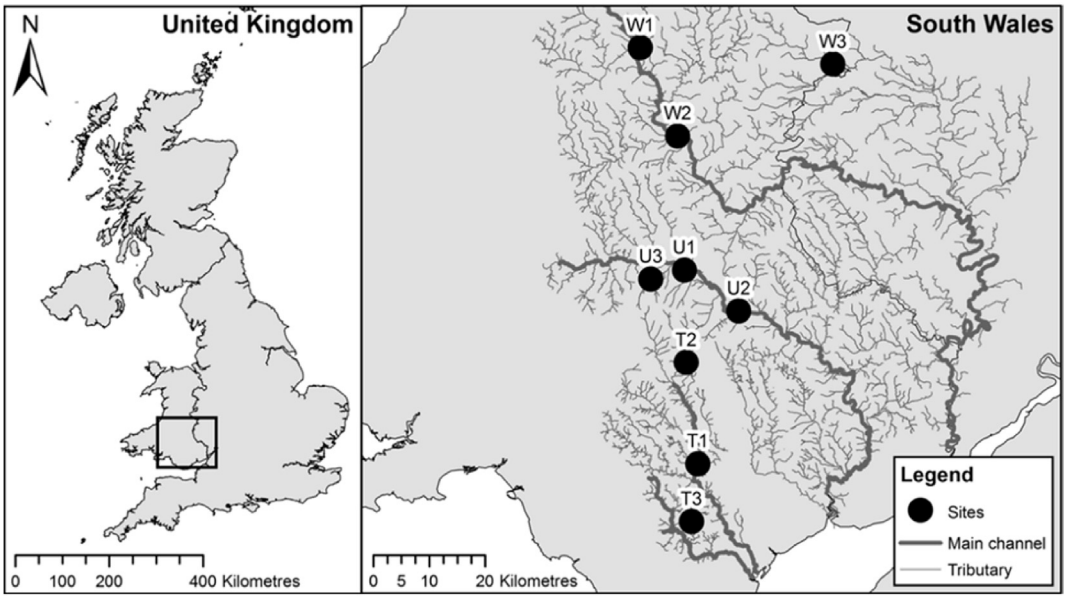

Fig. 1. The location of sample sites in river systems across South Wales. Sample sites were equally distributed across the Taff (T), Usk (U) and Wye (W) catchments in South Wales.

with sand, dried with anhydrous sodium sulphate, spiked with internal recovery standards (^{13}C OCs, ^{13}C PCBs and ^{13}C PBDEs), and Soxhlet-extracted with dichloromethane for 16 h. A small proportion of the extract was subsampled and evaporated to zero volume under N, the lipid content was then determined gravimetrically. The remaining extract was subsequently cleaned using automated size exclusion chromatography followed by filtering through an alumina glass column packed with pre-treated alumina (12 h at 550 °C) that was deactivated using deionised water 5% (w/w). The extract was divided into two: one fraction was spiked with labelled internal standards OCs and PCBs, and the other was spiked with PBDEs.

A 20 μl aliquot of extract was injected into the gas chromatograph – mass spectrometry (Agilent, Wokingham, UK) using a 50 m (OCs and PCBs) or 25 m (PBDEs) HT8 column (0.22 mm internal diameter and 0.25 μm film thickness; SGE, Milton Keynes, UK), and programmable temperature vaporization inlet using different methods for OC/PCBs and PBDEs. The injector temperature was set to 250 °C and helium was used as the gas carrier (2.0 mL min^{-1}). An isothermal temperature regime was programmed at 50 °C for 2 min, then ramped at 45 °C min^{-1} to 200 °C, 1.5 °C min^{-1} to 240 °C, 2 °C min^{-1} to 285 °C, 50 °C min^{-1} to 325 °C and 350 °C for 10 min. The detector temperature was set at 335 °C. Chemicals were detected in electron ionisation mode.

The internal standard method was used to quantify residues as well as calibration curves of commercially available standards for PCBs and OCs (Greyhound Ltd, Birkenhead, UK), and PBDEs (LGC Ltd., Teddington, UK). A series of procedural blanks were concurrently run, and samples were recovery corrected based on values from recovery spikes and concentrations in the procedural blanks. Recovery values were relatively consistent across all sample types and all compounds/congeners (86–104%). Detection limits, defined as the lowest observable calibration standard, averaged 0.04–0.11 ng g^{-1} ww for all congeners and compounds analysed (Appendix S2). Octanol-water partitioning coefficients (log K_{OW}) were collated from a range of sources: PCBs (IARC, 2016), PBDEs and OCs (ChemSpider, 2018).

2.5. Statistical analyses

All statistical analyses were conducted using R Statistical Software (version 3.4.3) (R Core Team, 2015). Individual pollutants and congeners were recorded on a wet weight basis (ww), and lipid concentrations in samples are reported alongside these data (0–4.4% lipid). Values for PCBs, PBDEs and OCs below the detection limits are noted throughout as not detected (ND) and given a value equal to the minimum detection limit (0.04 ng g^{-1} ww) for statistical analysis. Spatial variables and environmental covariates (land cover, catchment area and effluent contribution), were transformed logarithmically (log 10) to normalise variances and aid analyses.

Table 1
Environmental characteristics at sample sites. The calculation and definition of variables are explained in the main text.

Site	Mean river discharge (m^3 s^{-1})	Ratio (E:R)[a]	Urban (km^2)	Arable (km^2)	Total (km^2)	BMWP[b]	ASPT[b]
T1	20.8	0.011	33.5	4.4	304	78.6	5.88
T2	0.78	0.002	0.1	0.1	32.2	72.1	6.36
T3	0.89	0.003	4.3	0.9	20.4	25.6	4.25
U1	18.1	0.004	5.1	8.8	441	65.7	6.06
U2	18.1	0.001	6.3	23.5	582	60.8	5.85
U3	1.03	0.004	0.2	0.1	16.5	70.7	6.26
W1	6.65	0.005	0.8	7.5	170	74.9	6.49
W2	37.2	0.001	7.4	77.1	1120	81.5	6.24
W3	3.93	0.003	2.5	5.4	108	72.7	6.21

[a] Effluent ratio is from NRW and EA data on effluent and river discharge.
[b] ASPT = Average Score Per Taxon; BMWP = British Monitoring Working Party Score.

To address the first hypothesis, Multivariate Generalised Linear Models (M-GLMs) were fitted using the 'mvabund' package (Wang et al., 2012) and used to analyse variations in the composition of POP compounds and congeners among sample types, as well in relation to land use, sites and catchments with environmental variables treated as covariates. All models were fitted with a negative binomial structure to account for the distribution of data. To further interrogate multivariate relationships in POP composition across samples and sites, we used non-metric multidimensional scaling (NMDS) (Kenkel and Orloci, 1986), calculated using Jaccard similarity indices with a double-Wisconsin square root standardisation. Differences in the concentration of POPs across sample types were assessed using a series of Generalised Linear Models (GLMs). Regression analyses were used to assess how POP concentrations covaried across sample types (sediments, biofilms, invertebrates and fish).

To test the second hypothesis, POP composition and concentration measured in different invertebrate taxa were analysed separately. GLMs were used to investigate differences in POP concentrations between different invertebrate taxa and feeding guilds (filterers, grazers, shredders and predators; Cummins, 1973), with sample site included as an independent variable to account for variation in POP concentration across river systems.

The third hypothesis was tested using Generalised Linear Mixed Models (GLMMs) (Bolker et al., 2009), implemented using the 'lme4' package (Bates et al., 2015). These models were used to assess relationships between POP concentrations and environmental variables. Concentrations of POPs were summed for groups (e.g. ∑PCBs, ∑PBDEs and ∑OCs) due to the low detection frequency of congeners and chemicals, while the sample type (sediments, microbial biofilms, invertebrates and fishes) was included as a random effect. Linear regression with log transformed POP concentrations were used to assess covariation in the levels of frequently detected PBDEs, PCBs and OCs to appraise whether patterns in sources and dynamics were similar.

The validity and accuracy of statistical tests and models was assessed following Zuur et al. (2007) and Thomas et al. (2015). Briefly, residual normality was assessed using QQ plots, homogeneity of variance was determined by plotting residuals against fitted values and influential observations were investigated by calculating Cook's leverage distances. Only valid and accurate models are reported in the subsequent sections.

3. Results

3.1. POP contamination in environmental and biological samples

Most samples contained PBDEs, PCBs and OCs (86.6%, 61.1% and 98.5%, respectively), but their concentrations and composition varied across sample types, sites and river catchments (Table 2; Fig. 2A). Samples were dominated by several congeners for PBDEs (47, 99 and 100) and PCBs (81, 118, 153, 138, 169, 170 and 180), whereas the composition of OCs was relatively uniform and neither γ-HCH nor α-HCH was detected. Some of the more scarce PBDEs, PCBs and OCs were detected, but only in a small proportion of environmental and biological samples ($n \leq 25\%$) or infrequently across sample sites (Appendix S3).

Multivariate analysis of POP composition indicated relatively similar distribution and concentration of PCBs, PBDEs and OCs across sites, but significant variation among sample types (Fig. 2; Table 2). In general, variation between sites explained a greater amount of variation in the concentration of PBDEs, PCBs and OCs than catchments, but in neither case were effects statistically significant (Sites: $F_{8,56} = 21.9$, $p = 0.80$; Catchments: $F_{2,64} = 7.66$, $p = 0.61$). Differences between sites were likely confounded by large variation between sample types ($F_{11,48} = 196.0$, $p < 0.001$) and differences in detection frequencies of POP compounds across sites.

The concentrations of PCBs, PBDEs and OCs were an order of magnitude lower in environmental samples (sediments and biofilms) than invertebrate or fish samples ($R^2 = 0.26$, $F_{1,65} = 23.1$, $p < 0.001$; $R^2 = 0.28$, $F_{1,65} = 25.4$, $p < 0.001$; $R^2 = 0.38$, $F_{1,65} = 40.1$, $p < 0.001$; for PBDEs, PCBs and OCs respectively), while POP concentrations in biological and environmental samples from the same sites were not correlated ($R^2 = 0.01$, $F_{1,47} = 0.31$, $p = 0.58$). There were also differences in the detection frequency of POPs, with at least one PCB, PBDE congener or OC chemical detected in 63.8% of biological samples, but only 27.5% of environmental samples. Furthermore, PBDEs, PCBs and OCs not found in sediments were detected in biological samples: PBDEs (119, 85), PCBs (28, 52, 77, 81, 101, 114, 118, 149, 153, 209, 214) and OCs (TDE, *p,p*'-DDT). One PBDE congener, 66, was detected in sediment and not in other samples (biofilms, invertebrates and fish).

3.2. Variation in POP contamination across different taxonomic groups

There were large differences in the composition, concentrations and spatial variation of POPs across different taxonomic groups (Figs. 2 and 3). The concentrations of PBDEs, PCBs and OCs in the tissues of invertebrates were not significantly related to the concentrations measured in the benthic fish *Cottus gobio* ($F_{1,7} = 0.28$, $p = 0.79$; $F_{1,7} = 0.19$, $p = 0.85$; $F_{1,7} = 0.51$, $p = 0.63$; for PBDEs, PCBs and OCs respectively). Furthermore, the concentrations of POPs in sediments, biofilms, invertebrates and fish were generally not significantly related to one another and were dissimilar even among organisms in the same broad taxonomic groups (Appendix S4).

3.3. Comparisons of POP contamination between invertebrate taxa

There was marked variation in the concentrations of PBDEs PCBs and OCs among invertebrates across sites (Fig. 4). For PBDEs, concentrations varied across sites as well as invertebrate taxa ($R^2 = 0.75$, $F_{13,26} = 9.95$, $p < 0.001$); when inter-site variation was controlled for mayflies had the lowest concentrations (*Baetis* and *Ecdyonurus*), with intermediate concentrations in *Gammarus* (crustacean) and *Leuctra* (stonefly), and the highest concentrations in caddisflies (*Rhyacophila* and *Hydropsyche*). OCs also varied significantly between different invertebrate taxa ($R^2 = 0.39$, $F_{5,33} = 1.20$, $p = 0.34$). Conversely, concentrations of PCBs varied less among invertebrates, with the majority of taxa containing statistically similar concentrations ($R^2 = 0.39$, $F_{5,34} = 4.66$, $p = 0.01$). The exceptions to this were lower concentrations of PCBs in *Leuctra* and lower concentrations of OCs in *Hydropsyche* ($F_{13,26} = 1.34$, $p = 0.25$; $F_{13,26} = 2.88$, $p = 0.01$; for PCBs and OCs, respectively). PCBs and OCs also varied less across sites ($F_{8,26} = 1.77$, $p = 0.13$; $F_{8,26} = 1.29$, $p = 0.29$; for PCBs and OCs, respectively), with large intra-site variation masking potential patterns (Fig. 3).

Concentrations of POPs in some taxa were consistently higher or lower irrespective of the sites sampled (Fig. 4). For example, the mayfly genus *Ecdyonurus* had consistently lower POP concentrations than the majority of other invertebrate taxa, while *Baetis* spp. had significantly higher concentrations of PCBs in the Usk and Wye catchments (Table S4.1). In general, however, there was large variability in the concentrations of POPs for different taxonomic groups at the same sites (Fig. 3). Only taxa with similar feeding behaviours had concentrations of POPs that varied in similar ways across multiple sites, for example the grazing mayfly genera *Baetis* and *Ecdyonurus* (Table S4.1).

POPs varied in different ways among invertebrate feeding guilds

Table 2
Concentrations of POPs in different samples across sites. Data reported as mean (min-max) and in ng g^{-1} ww.

Location	Site	Sample	N[a]	% lipid	∑PCBs	∑PBDEs	∑DDTs	HEOD	HCB
Taff	T1	Sediment	1	ND	2.7	ND	0.1	7.4	ND
		Biofilm	1	ND	ND	1.6	0.6	2.8	ND
		Invertebrates	6	0.8 (0.1–4.4)	2.9 (1.3–5.8)	2.2 (0.05–7.6)	3.9 (1.6–7.3)	9.9 (1.5–22.0)	0.3 (0.2–0.5)
		Fish	1	1.6	44.1	12.7	22.6	147.0	2.7
	T2	Sediment	1	ND	ND	ND	0.6	ND	0.2
		Biofilm	1	ND	ND	0.08	0.4	2.3	ND
		Invertebrates	6	0.11 (0.04–0.2)	1.3 (ND-2.9)	0.5 (0.1–0.8)	3.2 (1.6–5.9)	6.1 (3–14.3)	0.2 (0.1–0.3)
	T3	Sediment	1	ND	ND	0.2	1.6	ND	0.2
		Biofilm	1	ND	ND	1.9	0.2	ND	0.2
		Invertebrates		ND	2.9	3.6	1.9	12.6	ND
Usk	U1	Sediment	1	ND	ND	ND	1.5	ND	0.2
		Biofilm	1	0.1	ND	ND	ND	ND	ND
		Invertebrates		0.1 (0.1–0.3)	0.7 (ND-2.9)	0.4 (0.2–0.9)	10.0 (5.8–17.4)	9.8 (6.2–14.4)	0.3 (0.2–0.4)
		Fish	1	0.6	1.2	6.3	31.3	47.2	0.2
	U2	Sediment	1	ND	ND	ND	0.7	ND	0.2
		Biofilm	1	0.05	ND	ND	1.3	1.4	ND
		Invertebrates	5	0.1 (0.06–0.2)	8.1 (ND-36.3)	0.7 (0.2–1.2)	6.7 (ND-17.0)	10.4 (2.7–24.6)	0.2 (0.16–0.3)
		Fish	1	1.6	3.3	9.3	101.0	145.0	2.4
	U3	Sediment	1	ND	ND	ND	2.0	ND	0.3
		Biofilm	1	ND	ND	ND	3.2	9.0	ND
		Invertebrates	6	0.1 (0.1–1.3)	4.9 (0.5–15.9)	0.5 (0.1–1.6)	1.6 (0.7–3.2)	6.7 (0.1–11.9)	0.2 (0.15–1.9)
		Fish	1	1.8	7.8	4.6	5.0	125.0	1.4
Wye	W1	Sediment	1	ND	ND	ND	ND	5.2	ND
		Biofilm	1	0.07	ND	2.6	0.2	0.6	ND
		Invertebrates	4	0.1 (0.06–0.2)	2.5 (ND-8.5)	2.8 (1.6–3.9)	2.3 (1.1–4.2)	3.2 (0.9–7.0)	0.2 (0.15–0.3)
		Fish	1	0.9	1.9	11.7	10.3	108.0	1.9
	W2	Sediment	1	ND	ND	ND	0.9	0.8	0.2
		Biofilm	1	0.1	5.7	0.1	0.2	ND	ND
		Invertebrates	5	0.4 (0.1–1.6)	1.6 (ND-6.7)	1.4 (0.5–2.7)	4.1 (1.8–8.2)	11.9 (1.5–38.7)	0.2 (0.2–0.3)
		Fish	1	0.9	4.2	9.7	17.7	106.0	1.3
	W3	Sediment	1	ND	ND	ND	1.3	1.8	0.2
		Biofilm	1	0.05	ND	0.1	2.6	ND	ND
		Invertebrates	4	0.3 (0.05–0.8)	0.3 (ND-0.8)	1.2 (0.5–2.3)	6.4 (1.3–11.0)	7.1 (0.4–13.9)	0.3 (0.2–0.5)
		Fish	1	0.9	4.4	3.6	26.4	278.0	ND

*ND = Not detected, i.e. below the limits of detection.
[a] Where N = 1, composite samples were amalgamated from 5 regions of the stream or >5 individual fish (see *Sample collection*).

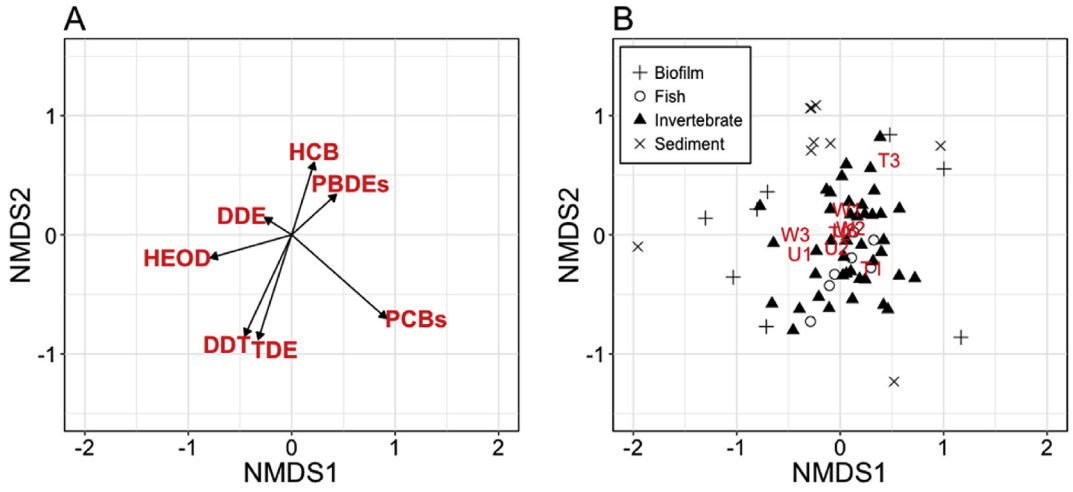

Fig. 2. Concentration and composition of POPs across sites and sample types (sediments, biofilms, invertebrates and fish). (A) NMDS of POP congeners and chemicals across sites (n = 9) and catchments (n = 3). (B) Variation in POP composition between sample types.

and were also complicated by significant inter-site variation (Fig. 5). In combination, however, site and feeding guild explained a significant proportion of the variation in PBDEs ($R^2 = 0.76$, $F_{11,28} = 12.3$, $p < 0.001$) and OCs ($R^2 = 0.55$, $F_{11,28} = 3.15$, $p = 0.01$) but not PCBs ($R^2 = 0.28$, $F_{11,28} = 0.99$, $p = 0.47$). After controlling for variation among sample sites, PBDEs differed among feeding guilds in the order Filterer = Predator > Shredder > Grazer ($F_{3,36} = 14.8$, $p < 0.001$) while OCs varied in the order Shredder > Predator = Grazer > Filterer ($F_{3,36} = 6.93$, $p = 0.01$); in the latter case (OCs) there was less variation among sites in comparison to other POP compounds ($F_{8,28} = 1.74$, $p = 0.13$).

3.4. Spatial distribution of POPs in relation to environmental covariates

After controlling for the large variation in POP concentrations

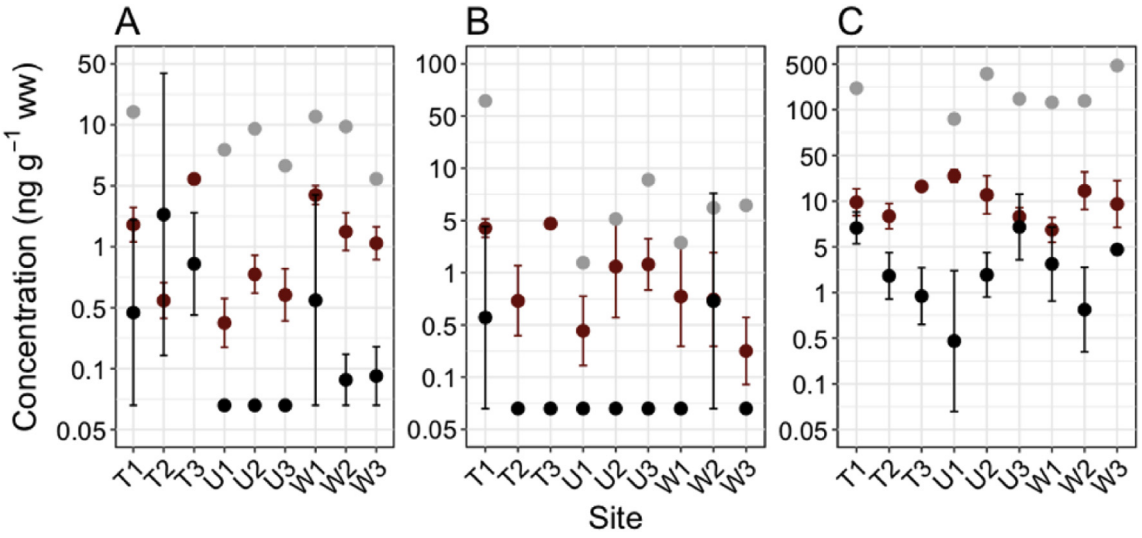

Fig. 3. Concentrations of POPs in environmental (sediment and biofilm), invertebrate and fish samples across river systems. (A) PBDEs. (B) PCBs. (C) OCs. Black symbols are mean values for environmental samples, grey symbols are *Cottus gobio* samples and red samples are mean values for invertebrate taxa. Error bars for invertebrate and environmental samples indicate ±1 standard error. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

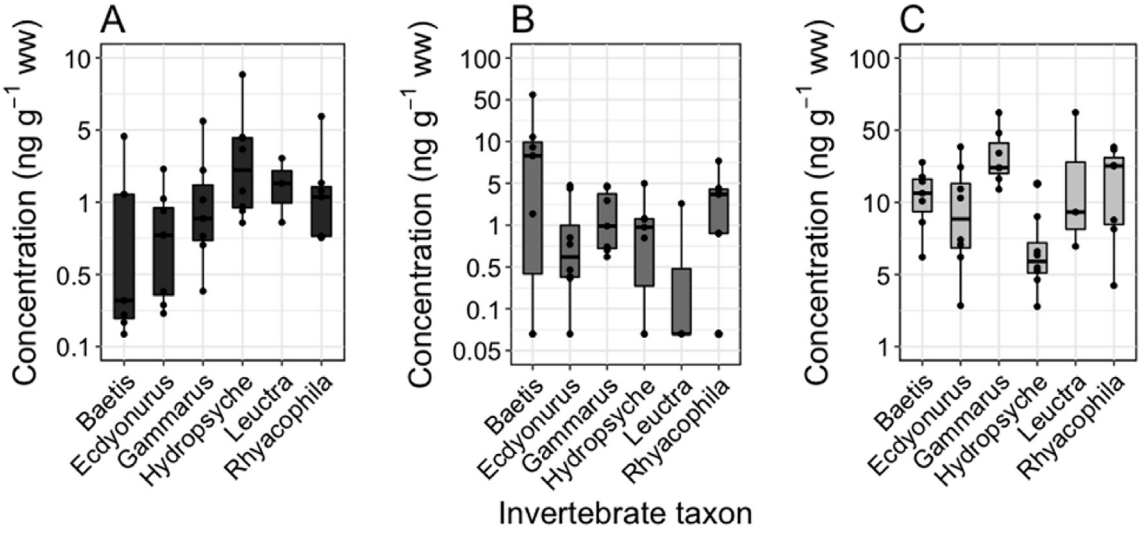

Fig. 4. Concentrations of POPs in the tissues of invertebrate taxa across sample sites. (A) PBDEs. (B) PCBs. (C) OCs. The results of statistical analyses are reported in the main text.

among sample types using random effects, total concentrations of PCB, PBDE and OCs were related to land-use and other environmental factors. PBDEs were increased with higher urban land-cover ($R^2c = 0.53$, $F_{7,54} = 9.21$, $p = 0.03$) whereas urban land cover and low wastewater dilution were most strongly associated with high PCB concentrations ($R^2c = 0.55$, $F_{1,53} = 5.19$, $p = 0.03$). OC concentrations were highest in the Usk and Wye (Table 2), but none of urban land use, agricultural activity, or point-sources, explained significant variation.

The PBDE and PCB congeners occurred at similar concentrations in samples (Fig. 6) and were significantly intercorrelated across the sites (Appendix S5). The concentrations of different OCs were also related to one another, although less clearly (Fig. 6; Table S5.1). There was some evidence that structural properties affected POP occurrence as the concentrations between congeners or chemicals with structural similarities were significantly correlated (Table S5.1). However, water-lipid solubility had no detectable effect: the log K_{OW} of compounds was not significantly related to the observed concentrations of individual PCBs, PBDEs or OCs across sites ($R^2 = 0.06$, $F_{1,41} = 2.47$, $p = 0.12$). Instead, concentrations were highest in a number of compounds with relatively low (~5 log K_{OW}) and intermediate values (~7 log K_{OW}) for example HEOD, *p,p*'-DDE, BDE-47, BDE-99 and PCB-153.

4. Discussion

Persistent organic pollutants were detected in both environmental and biological samples from rivers in South Wales, but their concentration and composition differed among sample types: several PBDEs, PCBs and OCs were below detectable concentrations in sediments and biofilms, but present in high concentrations in invertebrates and fish. While no single taxonomic group indicated POP concentrations in the environment or in other aquatic organisms consistently, variations in POP composition and concentration across invertebrate taxa with different feeding behaviours and habitat preferences provides valuable insight into the distribution

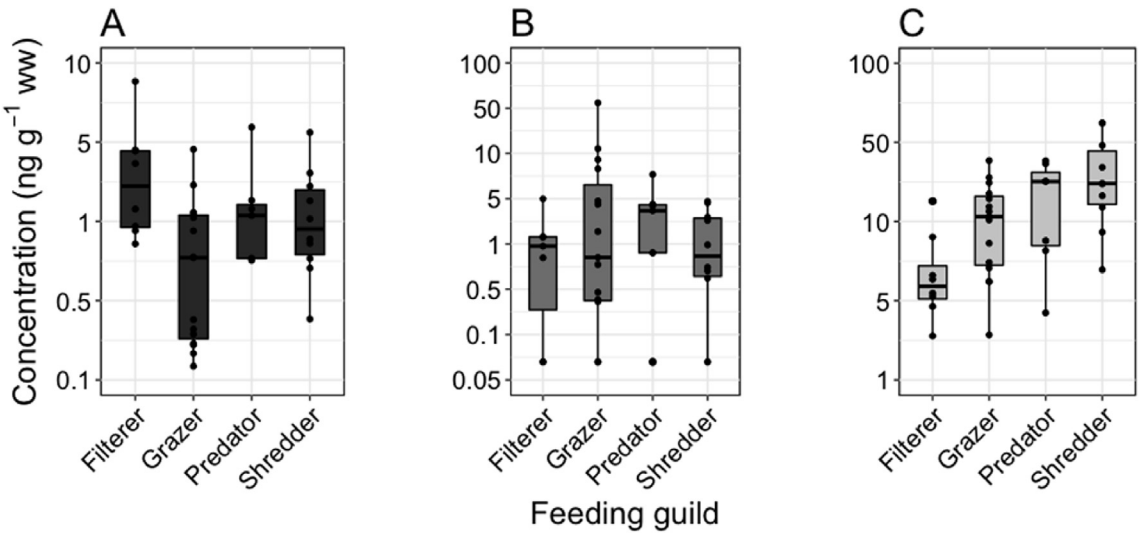

Fig. 5. Differences in PBDE, PCB and OC concentrations between invertebrate feeding guilds. (A) PBDEs. (B) PCBs. (C) OCs. Not all taxa or feeding guilds were represented across all sample sites.

of these pollutants among river basal resources and mesohabitats. Additionally, after accounting for variation between sample types, PBDEs were increased with higher urban land cover, while PCBs were elevated with increased urban land cover and wastewater discharge, though the relationships were weak. Overall, the data reveal that POPs still occur locally and regionally in selected Welsh rivers, sometimes at relatively high concentrations, indicating both their persistence and potential for continued low-level releases. The data also illustrate the value of biological samples in understanding the distribution, quantity and potential ecological risk of POPs in river systems.

Differences in the composition and concentration of PBDEs, PCBs and OCs between environmental and biological samples indicate the value of body burden data in monitoring POPs in aquatic systems (Van der Oost et al., 2003). In general, the low detection frequencies of these compounds across environmental samples restricted spatial analysis, thus limiting understanding of potential sources of pollution across the landscape. For biota this was not the case, with lower chlorinated PCB congeners and a range of other less stable PBDEs and OCs, as well as higher detection frequencies enabling the identification of POP sources across the river systems. Differences between environmental and biological samples also have implications for understanding exposure and potential ecological risk in natural systems – with the use of POP composition data from different sample types potentially misrepresenting the toxicity of POP mixtures (e.g. sediments not representing the non dioxin-like PCBs observed in invertebrates and fish). Our data demonstrate that monitoring that includes both environmental and biological samples will more likely provide better accuracy in determining the risks posed by a range of chemicals, that can translocate in the environment multiple exposure pathways.

Among existing biomonitoring schemes that analyse the body burden of pollutants in biota, the vast majority have used fishes and mammals (Van der Oost et al., 2003; Bettinetti et al., 2011; Pountney et al., 2015), with invertebrates used infrequently (Ravera, 2001). This contrasts with their more widespread incorporation into metrics to appraise, and sometimes diagnose, the effects of acidification, gross pollution, sediments, pesticides and other water quality alterations in freshwater ecosystems (Armitage et al., 1983; Davy-Bowker et al., 2005; Liess and Von Der Ohe, 2005). In our data, the composition and concentration of POPs in invertebrates varied among taxa and feeding guilds in ways that differed among compounds. The explanation for these patterns is uncertain, but might include: (i) differential metabolisation of POPs between organisms; (ii) the variable distribution of POPs in river mesohabitats (e.g. riffles, pools, margins); or (iii) the differential distribution of POPs in the basal resources used differentially across invertebrate taxa (e.g. sediments, detritus, biofilms, leaf litter). More detailed investigations on a wider array of invertebrate taxa are needed to fully understand the factors responsible for the observed variation.

With an appreciation of the above variation, data here provided information on both local (meso-habitat) and regional distribution of pollutants across our study area, while also revealing contrasting patterns in the accumulation of different pollutants in organisms at the lower trophic levels of food webs. This suggests an optimum sampling strategy for POPs in which different taxa are sampled in ways that allow data from different taxa to be combined to provide an overall indication of pollutant distribution but also specific details on food-web transfers and contrasting sources. We advocate further studies in other freshwater systems to evaluate these possibilities as well as assessments of more extensive relationships between POP concentrations in invertebrates and more conventional bioassessment metrics.

With differences between sample types and taxonomic groups accounted for, spatial variation among POPs became clearer – at least for PCBs and PBDEs. The concentrations of these two groups of compounds was increased in urbanised regions or where wastewater effluents contributed most to river discharge. As well as the persistence and local remobilisation of these compounds from secondary sources (e.g. temporary sediment stores; Weber et al., 2008; Kallenborn et al., 2012), the extremely persistent, non-dioxin like PCB congeners (66, 153 and 180), and less stable, dioxin-like PCBs (81, 105 and 118) appear to remain in the urban river environments across South Wales. Similarly, stable PBDE congeners (47, 99 and 100) were dominant in urban regions. This is consistent with the detection of elevated concentrations of PCBs and, particularly, PBDEs in the eggs of a river bird, the Eurasian dipper (*Cinclus cinclus*; Linnaeus 1758) along the urban rivers of South Wales (Morrissey et al. 2013). Although the precise sources are uncertain, links to the widespread and intense industrial

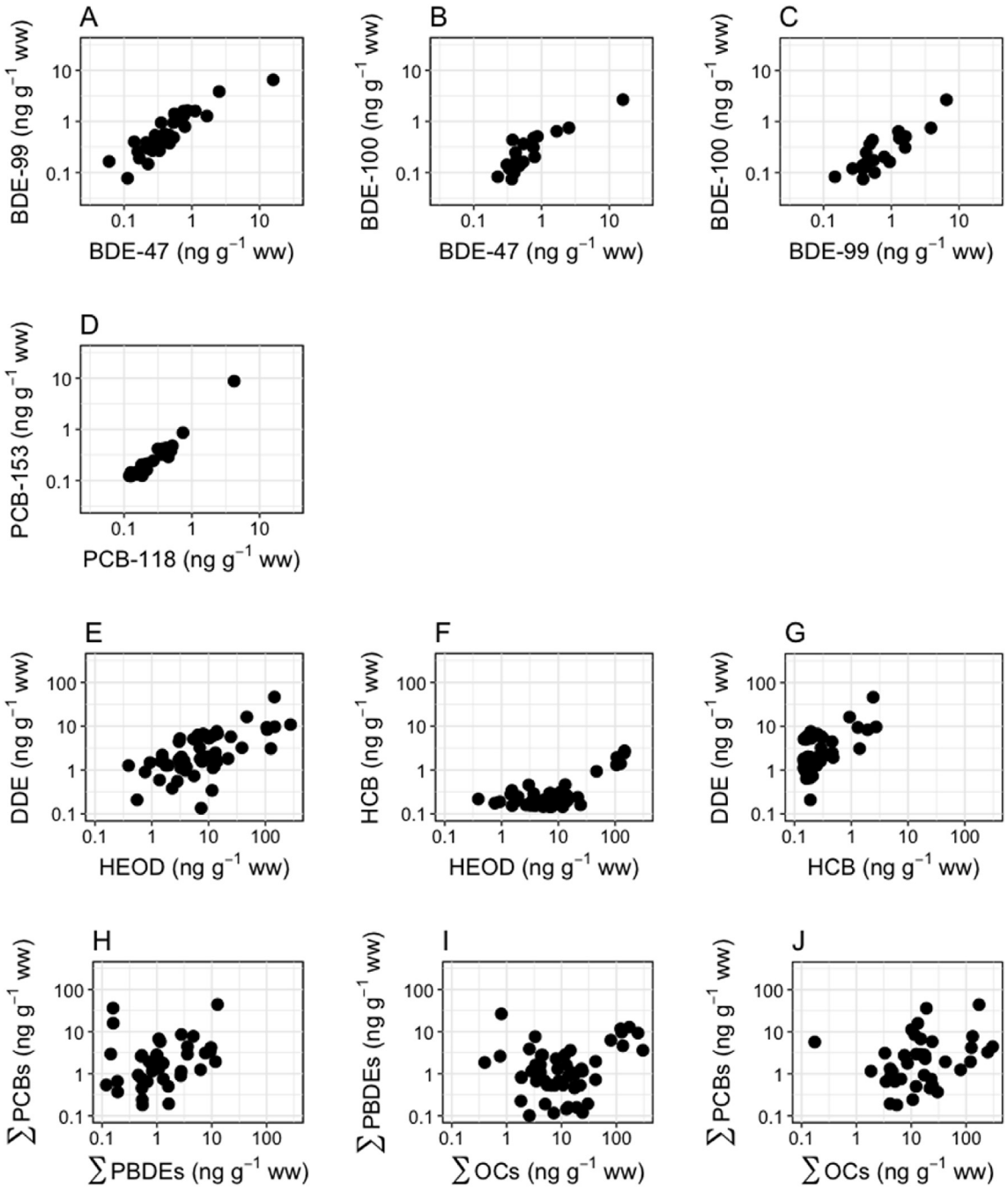

Fig. 6. Relationships between the concentrations of frequently detected (≥30% of samples) PBDE and PCB congeners, as well as OC compounds. (A–C) Pairwise comparisons of PBDE congeners (n = 3). **(D)** Pairwise comparisons of PCB congeners (n = 2). (E–G) Pairwise comparisons of OCs (n = 3). (H–J) Pairwise comparisons of ΣPBDEs, ΣPCBs and ΣOCs. Results of statistical analyses are provided in Appendix S5.

activity in this region are likely to be implicated, and less stable dioxin-like PCB congeners (e.g. PCB 81) indicate the potential for continued mobilisation across catchments. At its industrial peak, South Wales had supported around 600 collieries, together with associated coking, gasification, smelting and manufacturing industries, with smaller hundreds of more mechanised mines still operating up to their progressive closure from the late 1970s and early 1980s onwards (see Bateson et al., 2015).

In contrast, OCs appeared to be highest concentration in the more rural Usk and Wye catchments, although statistically significant patterns were not detected. Although OCs were widely used in agricultural, domestic and industrial activities across the landscape (Barber et al., 2005), the concentrations of several compounds (dieldrin, DDE, HCB) in our samples exceeded levels typically associated with persistence and remobilisation. The concentrations we observed were comensurate with concentrations detected in freshwater organisms from other regions, for example Europe, North America and Asia (Table 3). Elevated concentrations of these chemicals were detected in the eggs of Eurasian dippers during the 1980s along tributaries of the Usk and Wye where previous agricultural uses, such as sheep dipping using dieldrin (HEOD), had once been more widespread (Ormerod and Tyler, 1990,

Table 3
Concentrations of persistent organic pollutants in the tissues of organisms from freshwater environments.

Location	Taxonomic group	Pollutant	Concentration (ng g^{-1} ww)	Reference
River Po (Italy)	Fish	PCBs	40–372	Viganò et al. (2009)
		PBDEs	17–51	
		DDT	21–519	Viganò et al. (2015)
River Thames (UK)	Fish	PCBs	7–232	Jürgens et al. (2015)
		DDT	1–38	
		HCB	0.05–6	
		Lindane	0.05–3	
Frodolfo stream (Italy)	Invertebrate	PCBs	10–308	Bizzotto et al. (2009)
		DDT	8–621	
		HCB	0.4–9	
Sara River (Croatia)	Fish	DDT	2–25	Bosnir et al. (2007)
		Lindane	0.3–15	
Lake Baiyangdian (China)	Fish	DDT	0.3–8	Hu et al. (2010)
		DDE	0.5–14	
	Invertebrate	DDT	0.4–2	
		DDE	0.8–12	
	Algae	DDT	8–22	
		DDE	0.6–51	
Columbia River (USA)	Fish	PCBs	7–52	Nilsen et al. (2014)
		PBDEs	4–78	
		HCB	0.3–4	
		Dieldrin	1.5–3	
Scheldt River (Belgium)	Fish	PCBs	132–225	Bonnineau et al. (2016)
		DDE	6–18	
		DDT	0.2–5	

1993; Morrissey et al., 2013), yet, some of the high OC concentrations we detected could be more recent. For example, HCB was relatively absent in the eggs of the river bird *Cinclus cinclus* the 1980s (Ormerod and Tyler, 1990), yet detected at significant concentrations over 2008–2010 (Morrissey et al., 2013), as well as in biota within this study. Though now banned for direct use, recent sources include fungicidal use in agriculture and emission from metal production, while lower level emissions might arise from the domestic waste combustion (Barber et al., 2005; NAEI, 2016).

5. Conclusions

Overall, using environmental and biological samples, our data illustrate how significant concentrations of POPs continue to pervade river systems across South Wales (UK). Although we identified discrepancies in the composition and concentration of pollutants across different taxonomic groups, our study indicates that a combination of samples from different sample types and different organisms is needed to optimise the detection of different legacy pollutants in river systems. By accounting for variation in this way, the contaminant profiles for POPs were shown to relate to potential sources including the remobilisation or circulation of legacy contaminants, as well as the continued or recent emission of some POP compounds. The widespread contamination of river ecosystems by persistent, legacy contaminants highlights a need to consider these pollutants, alongside current-use and emerging compounds, in contemporary risk assessments.

Declaration of interest

The authors declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2019.113144.

References

Armitage, P., Moss, D., Wright, J., Furse, M., 1983. The performance of a new biological water quality score system based on macroinvertebrates over a wide range of unpolluted running-water sites. Water Res. 17, 333–347.
Arnold, K.E., Brown, A.R., Ankley, G.T., Sumpter, J.P., 2014. Medicating the environment: assessing risks of pharmaceuticals to wildlife and ecosystems. Philos. Trans. R. Soc. Lond. Ser. B Biol. Sci. 369, 1–11.
Barber, J., Sweetman, A., Jones, K., 2005. Hexachlorobenzene - Sources, Environmental Fate and Risk Characterisation (Brussels, Belgium).
Bates, D., Maechler, M., Bolker, B., Walker, S., 2015. Fitting linear mixed-effects models using lme4. J. Stat. Softw. 67, 1–48.
Bateson, L., Cigna, F., Boon, D., Sowter, A., 2015. The application of the intermittent SBAS (ISBAS) InSAR method to the South Wales Coalfield, UK. Int. J. Appl. Earth Obs. Geoinf. 34, 249–257.
Bizzotto, E.C., Villa, S., Vighi, M., 2009. POP bioaccumulation in macroinvertebrates of alpine freshwater systems. Env. Poll. 157, 3192–3198.
Bettinetti, R., Galassi, S., Quadroni, S., Volta, P., Capoccioni, F., Ciccotti, E., De Leo, G.A., 2011. Use of Anguilla anguilla for biomonitoring persistent organic pollutants (POPs) in brackish and riverine waters in central and southern Italy. Water, Air, Soil Pollut. 217, 321–331.
Bolker, B.M., Brooks, M.E., Clark, C.J., Geange, S.W., Poulsen, J.R., Stevens, M.H.H., White, J.-S.S., 2009. Generalized linear mixed models: a practical guide for ecology and evolution. Trends Ecol. Evol. 24, 127–135.
Bonada, N., Prat, N., Resh, V.H., Statzner, B., 2006. Developments in aquatic insect biomonitoring: a comparative analysis of recent approaches. Annu. Rev. Entomol. 51, 495–523.
Bonnineau, C., Scaion, D., Lemaire, B., Belpaire, C., Thomé, J.-P., Thonon, M.,

Leermaker, M., Gao, Y., Debier, C., Silvestre, F., Kestemont, P., Rees, J.-F., 2016. Accumulation of neurotoxic organochlorines and trace elements in brain of female European eel (Anguilla anguilla). Environ. Toxicol. Pharmacol. 45, 346–355.
Bosnir, J., Puntarić, D., Smit, Z., Klarić, M., Grgić, M., Kosanović, L.M., 2007. Organochlorine pesticides in freshwater fish from the Zagreb area. Arh. Hig. Rad. Toksikol. 58, 187–193.
Buss, D.F., Carlisle, D.M., Chon, T.-S., Culp, J., Harding, J.S., Keizer-Vlek, H.E., Robinson, W.A., Strachan, S., Thirion, C., Hughes, R.M., 2015. Stream biomonitoring using macroinvertebrates around the globe: a comparison of large-scale programs. Environ. Monit. Assess. 187, 4132.
ChemSpider, 2018. ChemSpider Database. Royal Society of Chemistry.
Crosse, J.D., Shore, R.F., Wadsworth, R.A., Jones, K.C., Pereira, M.G., 2012. Long-Term trends in PBDEs in sparrowhawk (Accipiter nisus) eggs indicate sustained contamination of UK terrestrial ecosystems. Environ. Sci. Technol. 46, 13504–13511.
Cummins, K.W., 1973. Trophic relations of aquatic insects. Annu. Rev. Entomol. 18, 183–206.
Davy-Bowker, J., Murphy, J.F., Rutt, G.P., Steel, J.E.C., Furse, M.T., 2005. The development and testing of a macroinvertebrate biotic index for detecting the impact of acidity on streams. Arch. Hydrobiol. 163, 383–403.
Diamond, M.L., Melymuk, L., Csiszar, S.A., Robson, M., 2010. Estimation of PCB stocks, emissions, and urban fate: will our policies reduce concentrations and exposure? Environ. Sci. Technol. 44, 2777–2783.
Gavrilescu, M., Demnerová, K., Aamand, J., Agathos, S., Fava, F., 2015. Emerging pollutants in the environment: present and future challenges in biomonitoring, ecological risks and bioremediation. N. Biotech. 32, 147–156.
Geyer, H.J., Rimkus, G.G., Scheunert, I., Kaune, A., Schramm, K.-W., Kettrup, A., Zeeman, M., Muir, D.C.G., Hansen, L.G., Mackay, D., 2000. Bioaccumulation and occurrence of endocrine-disrupting chemicals (EDCs), persistent organic pollutants (POPs), and other organic compounds in fish and other organisms including humans. In: Beek, B. (Ed.), The Handbook of Environmental Chemistry. Springer-Verlag, Berlin/Heidelberg, pp. 1–166.
H.M.S.O, 1978. River Pollution Survey of England and Wales (London, UK).
Hawkes, H.A., 1998. Origin and development of the biological monitoring working party score system. Water Res. 32, 964–968.
Hu, G., Dai, J., Mai, B., Luo, X., Cao, H., Wang, J., Li, F., Xu, M., 2010. Concentrations and accumulation features of organochlorine pesticides in the Baiyangdian Lake freshwater food web of North China. Arch. Environ. Contam. Toxicol. 58, 700–710.
IARC, 2016. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, vol. 107. Polychlorinated and Polybrominated Biphenyls. Lyon.
Iqbal, M., Syed, J.H., Katsoyiannis, A., Malik, R.N., Farooqi, A., Butt, A., Li, J., Zhang, G., Cincinelli, A., Jones, K.C., 2017. Legacy and emerging flame retardants (FRs) in the freshwater ecosystem: a review. Environ. Res. 152, 26–42.
JNNC, 2010. Handbook for Phase 1 Habitat Survey - a Technique for Environmental Audit. JNNC, Peterborough, UK.
Jones, V., Gardner, M., Ellor, B., 2014. Concentrations of trace substances in sewage sludge from 28 wastewater treatment works in the UK. Chemosphere 111, 478–484.
Josefsson, S., Bergknut, M., Futter, M.N., Jansson, S., Laudon, H., Lundin, L., Wiberg, K., 2016. Persistent organic pollutants in streamwater: influence of hydrological conditions and landscape type. Environ. Sci. Technol. 50, 7416–7424.
Jürgens, M.D., Chaemfa, C., Hughes, D., Johnson, A.C., Jones, K.C., 2015. PCB and organochlorine pesticide burden in eels in the lower Thames River (UK). Chemosphere Pergamon 118, 103–111.
Kallenborn, R., Halsall, C., Dellong, M., Carlsson, P., 2012. The influence of climate change on the global distribution and fate processes of anthropogenic persistent organic pollutants. J. Environ. Monit. 14, 2854–2869.
Kenkel, N.C., Orloci, L., 1986. Applying metric and nonmetric multidimensional scaling to ecological studies: some new results. Ecology 67, 919–928.
Learner, M.A., Williams, R., Harcup, M., Hughes, B.D., 1971. A survey of the macrofauna of the river Cynon, a polluted tributary of the river Taff (South Wales). Freshw. Biol. 1, 339–367.
Liess, M., Von Der Ohe, P.C., 2005. Analyzing the effects of pesticides on invertebrate communities in streams. Environ. Toxicol. Chem. 24, 954.
Lohmann, R., Breivik, K., Dachs, J., Muir, D., 2007. Global fate of POPs: current and future research directions. Environ. Pollut. 150, 150–165.
Loos, R., Gawlik, B.M., Locoro, G., Rimaviciute, E., Contini, S., Bidoglio, G., 2009. EU-wide survey of polar organic persistent pollutants in European river waters. Environ. Pollut. 157, 561–568.
Malaj, E., von der Ohe, P.C., Grote, M., Kühne, R., Mondy, C.P., Usseglio-Polatera, P., Brack, W., Schäfer, R.B., 2014. Organic chemicals jeopardize the health of freshwater ecosystems on the continental scale. Proc. Natl. Acad. Sci. 111, 9549–9554.
McKnight, U.S., Rasmussen, J.J., Kronvang, B., Binning, P.J., Berg, P.L., 2015. Sources, occurrence and predicted aquatic impact of legacy and contemporary pesticides in streams. Environ. Pollut. 200, 64–76.
Morrissey, C.A., Elliott, J.E., Ormerod, S.J., 2010. Local to continental influences on nutrient and contaminant sources to river birds. Environ. Sci. Technol. 44, 1860–1867. https://doi.org/10.1021/es903084m.
Morrissey, D. W. G. Stanton, Pereira, M.G., Newton, J., Durance, I., Tyler, C.R., Ormerod, S.J., 2013. Eurasian dipper eggs indicate elevated organohalogenated contaminants in urban rivers. Environ. Sci. Technol. 47, 8931–8939.
NAEI, 2016. Pollutant information: hexachlorobenzene. National atmospheric emissions inventory. http://naei.beis.gov.uk/overview/pollutants?pollutant_id=49.
Nilsen, E., Zaugg, S., Alvarez, D., Morace, J., Waite, I., Counihan, T., Hardiman, J., Torres, L., Patiño, R., Mesa, M., Grove, R., 2014. Contaminants of legacy and emerging concern in largescale suckers (Catostomus macrocheilus) and the foodweb in the lower Columbia River, Oregon and Washington, USA. Sci. Total Environ. 484, 344–352. http://www.sciencedirect.com/science/article/pii/S0048969713004336.
Nizzetto, L., Macleod, M., Borgå, K., Cabrerizo, A., Dachs, J., Di Guardo, A., Ghirardello, D., Hansen, K.M., Jarvis, A., Lindroth, A., Ludwig, B., Monteith, D., Perlinger, J.A., Scheringer, M., Schwendenmann, L., Semple, K.T., Wick, L.Y., Zhang, G., Jones, K.C., 2010. Past, present, and future controls on levels of persistent organic pollutants in the global environment. Environ. Sci. Technol. 44, 6526–6531.
Ormerod, S.J., Tyler, S.J., 1990. Environmental pollutants in the eggs of Welsh Dipper; Cinclus cinclus: a potential monitor of organochlorine and mercury contamination in upland rivers. Bird Study 37, 171–176.
Ormerod, S.J., Tyler, S.J., 1993. Further studies of the organochlorine content of Dipper Cinclus cinclus eggs: local differences between Welsh catchments. Bird Study 40, 97–106.
Ormerod, S.J., Tyler, S.J., Jüttner, I., 2000. Effects of point-source PCB contamination on breeding performance and post-fledging survival in the dipper Cinclus cinclus. Environ. Pollut. 110, 505–513.
Pountney, A., Filby, A.L., Thomas, G.O., Simpson, V.R., Chadwick, E.A., Stevens, J.R., Tyler, C.R., 2015. High liver content of polybrominated diphenyl ether (PBDE) in otters (Lutra lutra) from England and Wales. Chemosphere 118, 81–86.
R Core Team, 2015. R: A Languages and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria.
Rasmussen, J.J., Wiberg-Larsen, P., Baattrup-Pedersen, A., Cedergreen, N., McKnight, U.S., Kreuger, J., Jacobsen, D., Kristensen, E.A., Friberg, N., 2015. The legacy of pesticide pollution: an overlooked factor in current risk assessments of freshwater systems. Water Res. 84, 25–32.
Ravera, O., 2001. Monitoring of the aquatic environment by species accumulator of pollutants: a review. J. Limnol. 60, 63–78.
Schäfer, S., Buchmeier, G., Claus, E., Duester, L., Heininger, P., Körner, A., Mayer, P., Paschke, A., Rauert, C., Reifferscheid, G., Rüdel, H., Schlechtriem, C., Schröter-Kermani, C., Schudoma, D., Smedes, F., Steffen, D., Vietoris, F., 2015. Bioaccumulation in aquatic systems: methodological approaches, monitoring and assessment. Environ. Sci. Eur. 27, 5.
Schwarzenbach, R.P., Escher, B.I., Fenner, K., Hofstetter, T.B., Johnson, C.A., von Gunten, U., Wehrli, B., 2006. The challenge of micropollutants in aquatic systems. Science 313, 1072–1077.
Sumpter, J.P., 2009. Protecting aquatic organisms from chemicals: the harsh realities. Philos. Trans. Seri. A Math. Phys. Eng. Sci. 367, 3877–3894.
Sun, R.-X., Luo, X.-J., Tan, X.-X., Tang, B., Li, Z.-R., Mai, B.-X., 2015. Legacy and emerging halogenated organic pollutants in marine organisms from the Pearl River Estuary, South China. Chemosphere 139, 565–571.
Thomas, R., Lello, J., Medeiros, R., Pollard, A., Seward, A., Smith, J., Vafidis, J., Vaughan, I., 2015. Data Analysis with R Statistical Software: A Guidebook for Scientists. Eco-Explore, Newport, UK.
Van der Oost, R., Beyer, J., Vermeulen, N.P.E., 2003. Fish bioaccumulation and biomarkers in environmental risk assessment: a review. Environ. Toxicol. Pharmacol. 13, 57–149.
Ver Hoef, J.M., Peterson, E.E., Clifford, D., Shah, R., 2014. SSN: an R package for spatial statistical modeling on stream networks. J. Stat. Softw. 56, 1–45.
Viganò, L., Mascolo, G., Roscioli, C., 2015. Emerging and priority contaminants with endocrine active potentials in sediments and fish from the River Po (Italy). Environ. Sci. Pollut. Control Ser. 22, 14050–14066.
Viganò, L., Roscioli, C., Erratico, C., Guzzella, L., Farkas, A., 2009. Polybrominated diphenyl ethers (PBDEs) in gammarids, caddisflies, and bed sediments of the lowland River Po. Bull. Environ. Contam. Toxicol. 82, 200–205.
Wang, Y., Naumann, U., Wright, S.T., Warton, D.I., 2012. Mvabund - an R package for model-based analysis of multivariate abundance data. Methods Ecol. Evol. 3, 471–474.
Wasi, S., Tabrez, S., Ahmad, M., 2013. Toxicological effects of major environmental pollutants: an overview. Environ. Monit. Assess. 185, 2585–2593.
Weber, R., Gaus, C., Tysklind, M., Johnston, P., Forter, M., Hollert, H., Heinisch, E., Holoubek, I., Lloyd-Smith, M., Masunaga, S., Moccarelli, P., Santillo, D., Seike, N., Symons, R., Torres, J.P.M., Verta, M., Varbelow, G., Vijgen, J., Watson, A., Costner, P., Woelz, J., Wycisk, P., Zennegg, M., 2008. Dioxin- and POP-contaminated sites — contemporary and future relevance and challenges. Environ. Sci. Pollut. Control Ser. 15, 363–393.
Windsor, F.M., Ormerod, S.J., Tyler, C.R., 2018. Endocrine disruption in aquatic systems: up-scaling research to address ecological consequences. Biol. Rev. 93, 626–641.
Zoumis, T., Schmidt, A., Grigorova, L., Calmano, W., 2001. Contaminants in sediments: remobilisation and demobilisation. Sci. Total Environ. 266, 195–202.
Zuur, A.F., Leno, E.N., Smith, G.M., 2007. Analysing Ecological Data. Springer, New York, USA.