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Concentrations, spatial and seasonal variations of Organophosphate esters in UK freshwater Sediment

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ABSTRACT

This study provides the first report of organophosphate esters (OPEs) in UK freshwater sediments with a focus on the possible impact of factors such as spatial/seasonal variation and wastewater treatment plants (WWTPs) on the measured OPE concentrations in surficial sediment from 3 UK rivers and 1 canal. Detection frequencies of: tris (chloroethyl) phosphate (TCEP), tris (2-chloroisopropyl) phosphate (TCIPP), tris (1,3-dichloro-2 propyl) phosphate (TDCIPP), tri-n-butyl phosphate (TNBP), tris (2-butoxyethyl) phosphate (TBOEP), 2-ethylhexyl diphenyl phosphate (EHDPP), tris (phenyl) phosphate (TPHP), and tri-m-tolyl phosphate (TmTP) ranged from 58% to 100%. The concentration of Σ_8 OPEs ranged from 107 ng g⁻¹ (dry weight - dw) (in the Worcester-Birmingham canal) to 52 ng g⁻¹ (dw) in both Rivers Severn and Sowe). The highest Σ_8 OPE concentration for all study locations was recorded during the autumn months (September, October, and November), and concentrations of Σ_8 OPEs in sediment samples from the River Severn, River Tame, and River Sowe all varied inversely with the river level and flow rate. The average concentrations of each target OPE in each study location were lower than those reported elsewhere but fell broadly within the range of concentrations reported from other countries. The potential risk posed by target OPEs in all study locations was found to be low, except for a moderate risk identified for EHDPP in the Worcester - Birmingham canal.

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1. Introduction

Organophosphate esters (OPEs) are of research interest because of their toxicity and increasing environmental presence [1–4]. These concerns are exacerbated by their extensive application as flame retardants, plasticisers, and anti-foaming agents [5–7]. As of 2018, cumulative global consumption of OPEs was reported to be approximately 1 million tonnes and the annual global production from the same 2018 was placed around 200,000 tonnes [8,9]. In Europe alone, an estimated total of 89,640 tonnes of phosphorus flame retardants was used in 2015 [10].

As OPEs are used as additives rather than reactive flame retardants, they are easily released into the environment [11–15], and wastewater treatment plants (WWTPs) have been reported as a major source of OPEs to the aquatic environment [16–18]. This is because most WWTPs are unable to efficiently remove OPEs (especially chlorinated alkyl-OPEs such as tris(2-chloroethyl)

phosphate (TCEP), tris(chloroisopropyl)phosphate (TCIPP), and tris(dichloropropyl)phosphate (TDCIPP)) [19,20]. By comparison, alkyl OPEs such as tri-n-butyl phosphate (TNBP), and tris(2-butoxyethyl) phosphate (TBOEP) can be more efficiently removed using processes like ozonation and biodegradation, applied in many WWTPs [21,22].

With sediments identified as major sinks for OPEs [12], it is surprising that relatively few studies (in Portugal, Spain and China) exist on the presence of OPEs in freshwater sediment samples [11–15]. To the best of our knowledge, no data exist on concentrations of OPEs in sediments in the UK. This study, therefore, reports concentrations of 8 OPEs: TCEP, TCIPP, TDCIPP, TNBP, TBOEP, EHDPP (2-ethylhexyl diphenyl phosphate), TPHP (tris (phenyl) phosphate), and TmTP (tri-m-tolyl phosphate) in surficial sediment samples from 4 waterways (3 rivers and 1 canal) in the UK. These OPEs were targeted because of their widespread application in everyday products such as polyurethane foam, textiles, furniture, electrical and electronic equipment, building materials, insulation materials, lacquers, glues, floor finish waxes as well as hydraulic fluids [23,24]. Sediment samples were collected every month for 12 months to evaluate spatial and seasonal variations in OPE concentrations in UK riverine

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sediment for the first time. Concentrations detected in this study are compared to those reported in freshwater sediments from other parts of the world and used to assess the ecological risk to aquatic organisms. Although evaluation of the impacts of WWTPs on OPE contamination was not a major objective of this study, we also analysed sediment samples collected upstream and downstream of 3 WWTPs discharging to our target rivers, thereby potentially providing some insight into the impact of these WWTPs on OPE contamination of receiving sediments.

2. Materials and methods

2.1. Reference standards and reagents

All solvents used during this study were High-performance liquid chromatography (HPLC) grade and purchased from Fisher Scientific (Loughborough, UK) and Sigma- Aldrich (St Louis, MO, USA). Individual chemical standards of 99.9% purity for eight native OPEs (TnBP, TCEP, TCIPP, TDCIPP, TBOEP, TPHP, EHDPP, and TMTP), recovery determination (or syringe) standard (RDS): 2,3,4,6- tetrachlorobiphenyl (PCB-62), and isotope-labelled internal (or surrogate) standards (TCEP-d₁₂, TDCIPP-d₁₂, and TPHP-d₁₅) were purchased from Wellington laboratories, (Guelph, ON, Canada). Standard reference material SRM 1944 (New York/New Jersey waterway sediment) was purchased from the US National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). Hypersep Florisil® SPE cartridges were purchased from Thermo Scientific (Rockwood, USA), and the nitrogen gas used for solvent evaporation was purchased from BOC gases, United Kingdom.

2.2. Sample collection and preparation

Surficial sediment samples were collected from three rivers located in the West Midlands region of England, as well as from the Worcester-to-Birmingham Canal (~3 km southwest of Birmingham city centre) (Table S1 and Fig. S1). In each of the 3 sampled rivers, there was a WWTP, therefore paired samples (100 m distance) were collected upstream and downstream of the effluent discharge points of the WWTPs. For reasons of anonymity, the WWTPs will be referred to as WWTP1, WWTP2 and WWTP3, as shown in Fig. S1. The size of the population served by these WWTP, and the operation processes employed are summarised in Table S1.

Sediment samples were collected on the last week of the month from each location on 12 occasions (November 2019, December 2019, January 2020, February 2020, March 2020, April 2021, May 2021, June 2021, and July to November 2020). To provide samples from every month of the year, the April, May, and June sampling events were moved to 2021 because of the UK national COVID 19 lockdown period between mid-March 2020 to July 2020. At each sampling point, a stainless-steel extensible soil auger was used to collect surficial sediment samples to a depth of 6 cm. Collected sediment samples were then stored in pre-rinsed glass jars fitted with aluminium foil-lined lids for transportation to the laboratory at the University of Birmingham for analysis.

2.3. Sample extraction and purification

Samples were extracted in accordance with the method of [25] with slight modifications. One (1) g of sediment was mixed in a clean, dry test tube with 1 g of copper powder and spiked with 10 ng of internal (surrogate) standard mixture (d₁₂-TCEP, d₁₂-TDCIPP, and d₁₅-TPHP). The samples were then extracted by vortexing for 1 min with 5 mL of hexane: acetone (1:1 v/v), before ultrasonication for 10 min at 30 °C. Samples were centrifuged at 3500 rpm for 3 min, and the supernatant collected in a clean dry test tube. The steps from

extraction to collection of supernatants were repeated twice and the combined extracts evaporated under a gentle stream of nitrogen to ~1 mL. The crude extracts were loaded onto pre-conditioned Florisil cartridges (conditioned with 2 x 3 mL of hexane) and the extract washed with 10 mL of hexane before elution of OPEs with 8 mL of ethyl acetate. The eluate was then collected in a clean dry test tube and evaporated under a gentle stream of nitrogen until incipient dryness. The concentrate was then reconstituted in 100 µL of toluene containing 250 pg/µL of PCB 62 as recovery determination (syringe) standard before transferring into an inserted vial and stored in a freezer ready for GC-MS analysis.

2.4. Instrumental analysis

Analysis of OPEs was conducted on an Agilent 5975C GC coupled to an Agilent 5975C MSD fitted with a 30 m DB-5 MS column (0.25 mm ID, 0.25 µm film thickness) and operated in electron ionisation mode (EI) (Restek, USA). The carrier gas was helium at a constant flow rate of 1.0 mL/min. The injector temperature was set at 290 °C in split-less mode and the MS operated with a solvent delay of 5 min. Temperatures of the ion source, quadrupole and interface were set at: 230 °C, 150 °C and 300 °C respectively. The GC temperature programme was 65 °C, hold for 0.75 min, ramp 20 °C/min to 250 °C, hold for 1 min, ramp 5 °C/min to 260 °C, hold for 0 min, ramp 30 °C/min to 305 °C, and hold for 1 min. TnBP, TCEP, and TCIPP were quantified against d₂₇-TnBP, TDCIPP, TPHP, EHDPP, and TMPP against d₁₂-TPHP, while TDCIPP was quantified against d₁₂-TDCIPP (Table S2). The dwell time for each ion was 30 ms.

2.5. Quality assurance and quality control

To ensure accuracy and precision of the analytical data generated during this study, the following measures were taken. A full five-point calibration comprising concentrations of each individual native OPE of 50, 100, 250, 500, and 1000 pg/µL was conducted (with relative standard deviation (RSD) values for the relative response factors < 6.5% for all target OPEs. Concentrations of the internal standards in each calibration standard were 30 ng/µL and as an indication of the high efficiency of the extraction method, good recoveries (>77%) of the internal standards (d₁₂-TCEP, d₁₅-TPHP, and d₁₂-TDCIPP) were obtained in all samples (Table S3). Two procedural blanks (comprising 1 g Na₂SO₄ treated as a sediment sample), and one standard reference material (SRM 1944) were analysed for each batch of 20 sediment samples (Table S3). Low concentrations (5–20% of those found in samples from the same batch) of TCEP and TBOEP were detected in the procedural blanks (Table S3) and the average concentration detected in the blanks were subtracted from those in all samples from that batch. Table S3 provides the concentrations we detected in replicate analyses of SRM1944 to provide an indication of the reproducibility of our method and for the information of future researchers measuring OPEs in sediments. While to our knowledge no other data exist on OPEs in SRM1944 against which we can compare the accuracy of our method, our good internal standard recoveries and satisfactory blank levels provide reassurance of the quality of our data. The limit of detection (LOD) and the limit of quantification (LOQ) were calculated as the concentrations of analyte corresponding to signal to noise ratios of 3 and 10, respectively, except for TCEP and TBOEP where LOD and LOQ were calculated as 3 and 10 times the standard deviation of the blank levels (Table S4).

2.6. Statistical analysis

Excel (Microsoft Office 365) and IBM SPSS statistics software version 28.0.0. Were used for statistical analysis. Data distributions

were evaluated using the Kolmogorov-Smirnov test with all data log10 transformed to facilitate use of parametric statistical tests. To investigate spatial differences between concentrations at the four different waterways, a one-way analysis of variance (ANOVA) was used with a post hoc Tukey test. In addition, paired sample t-tests were conducted to compare OPE concentrations upstream and downstream of the WWTP discharge point in individual rivers. All OPE concentrations are presented on a dry weight (dw) basis and in situations where a compound is < detection limit, then such “non detects” are reported as being present at an assumed concentration calculated thus. Concentration of non-detect = $f \times \text{LOD}$; where f is the detection frequency of the OPE in question expressed as a decimal fraction such that the value of f for detection frequencies of 95%, 70% or 50% are expressed as 0.95, 0.70 and 0.50). Potential correlations between generated data were tested using Pearson correlations (all the data used were log transformed as test of homogeneity was not satisfied). In all cases, a p -value <0.05 was set as the level of statistical significance.

3. Results and discussion

3.1. Concentrations of OPEs in sediment samples

Table 1 provides a statistical summary of the concentration of all 8 OPEs (TnBP, TCEP, TCIPP, TDCIPP, TBOEP, TPhP, EHDPP, and TMTP) detected in sediment samples collected from the Worcester-Birmingham canal, and the Rivers Tame, Severn, and Sowe.

3.1.1. Worcester-Birmingham canal

Concentrations of $\Sigma_8\text{OPEs}$ in sediments from the Worcester-Birmingham canal ranged from 24 to 295 ng g^{-1} (dw), while mean concentrations of each individual target OPE ranged from 3 (TDCIPP) to 53 ng g^{-1} (dw) (TBOEP) (Table 2). Of the chlorinated OPEs, TCIPP had the highest mean concentration of 9.0 ng g^{-1} (dw) followed by TCEP (6.0 ng g^{-1} (dw)). The most abundant non-halogenated OPE was TBOEP (mean concentration = 53 ng g^{-1} (dw)) and the least TmTP with a mean concentration of 4 ng g^{-1} (dw). Detection frequencies were 100% for TCEP, TBOEP, TPhP, TDCIPP, and TmTP. For TCIPP and TnBP, it was 75%, while for EHDPP, the detection frequency was 92%.

3.1.2. River Severn, Worcester

For the River Severn at Worcester, concentrations of $\Sigma_8\text{OPEs}$ over the 12 months of sampling ranged from 21 to 98 ng g^{-1} (dw), with mean concentrations of each target OPE ranging from 1.0 (EHDPP, TMTP, TPhP and TDCIPP) to 31 (TBOEP) ng g^{-1} (dw) (Table 2). Consistent with our observations at the Worcester-Birmingham canal, TBOEP had the highest mean concentration of 31 ng g^{-1} (dw), and concentrations of Cl-OPEs fell in the order: TCIPP > TCEP > TDCIPP. However, the least abundant OPE at this

location (EHDPP) differed from that detected in the Worcester-Birmingham canal. Detection frequencies for TCEP, TBOEP, TPhP, TCIPP, and TDCIPP, were 100%; while for TnBP, TMTP, and EHDPP, detection frequencies were: 71%, 92%, and 83%, respectively.

3.1.3. River Tame in Water Orton

Concentrations of $\Sigma_8\text{OPEs}$ in surficial sediment from the River Tame at Water Orton over the 12 months period of sampling ranged from 19 to 109 ng g^{-1} (dw), with mean concentrations of individual OPEs ranging from 2.0 (TnBP, EHDPP, TMTP and TDCIPP) to 35 ng g^{-1} (dw) (TBOEP). As observed for the Worcester-Birmingham canal and the River Severn, the relative abundance of Cl-OPEs was TCIPP > TCEP > TDCIPP. Detection frequencies were: 100% for TCEP, TBOEP, and TPhP. For TCIPP, TDCIPP, and TmTP, it was 92%, while for EHDPP and TnBP, it was 83% and 58%, respectively.

3.1.4. River Sowe in Coventry

Concentrations of $\Sigma_8\text{OPEs}$ over the 12 months of monitoring ranged from 24 to 98 ng g^{-1} (dw), with mean concentrations of individual OPEs ranging from 1.0 (EHDPP and TPhP) to 32 ng g^{-1} (dw) (TBOEP). In line with our observations at other locations, the relative abundance of Cl-OPEs was TCIPP > TCEP > TDCIPP. Detection frequencies for TCEP, TBOEP, TMTP, TPhP, EHDPP, and TDCIPP were 100%, while for TCIPP and TnBP, detection frequencies were 83% and 67%, respectively.

ANOVA and Tukey's post hoc test were used to check the statistical significance of observed variability in $\Sigma_8\text{OPE}$ concentrations across the studied locations. The test revealed no significant difference in $\Sigma_8\text{OPE}$ concentrations across the four study locations ($P = 0.669$). The highest average $\Sigma_8\text{OPE}$ concentration was recorded in the Worcester-Birmingham canal (110 ng g^{-1} (dw)) (Fig. 2). Higher concentrations of most individual target OPE were also recorded at the Worcester-Birmingham canal with this location providing the highest average concentration for 7 out of the 8 target OPEs analysed in the present study. This can be attributed to the urban location of this site and proximity to potential sources of contamination such as recreational uses and dumping of domestic rubbish or waste. Possible low flow rates in this waterway might also aid the partitioning of OPEs to sediment [34]. The second highest average $\Sigma_8\text{OPE}$ concentration was for the River Tame, where the sampling points were up and down stream of a WWTP servicing the highest population of all three sampling locations (approximately 2.5 million people). There was only a minor difference between $\Sigma_8\text{OPE}$ concentrations measured at the Rivers Severn and Sowe, although sediment samples collected from the River Sowe (close to WWTP 2 which serves a population of 420,000) show a slightly higher concentration of $\Sigma_8\text{OPEs}$ than samples from River Severn (close to WWTP3 which services a total population of 50,000 to 200,000 people).

Although visual observation shows higher concentrations in the

Table 1
Average concentrations (range in parentheses) of target OPEs in sediment samples from the Worcester – Birmingham canal, and the Rivers Tame, Severn, and Sowe.

OPE	Average (range) concentration ng g^{-1} (dw)			
	Worcester-Birmingham Canal	River Severn ^a	River Sowe ^a	River Tame ^a
TnBP	18 (0.02–73)	3 (0.02–10)	2 (0.02–12)	2 (0.02–9)
TCEP	6 (0.5–22)	4 (0.3–13)	5 (1–14)	4 (0.5–12)
TCIPP	9 (0.02–37)	9 (0.8–16)	7 (0.02–20)	13 (0.02–27)
TBOEP	53 (6–170)	31 (10–16)	32 (8–81)	35 (10–92)
EHDPP	9 (0.02–29)	1 (0.02–4)	1 (0.3–4)	2 (0.7–4)
TMTP	4 (0.2–16)	1 (0.04–4)	3 (0.1–14)	2 (0.04–9)
TPhP	4 (0.1–26)	1 (0.3–8)	1 (0.4–2)	2 (0.3–9)
TDCIPP	3 (1–8)	1 (0.2–4)	2 (0.4–5)	2 (0.03–4)
$\Sigma_8\text{OPEs}$	107 (24–300)	52 (21–98)	52 (24–98)	62 (19–110)

^a Values given are for all samples collected from that waterway – i.e., upstream, and downstream of a WWTP.

Table 2Comparison between OPE concentrations (ng g^{-1} (dw)) in surficial freshwater sediments in this study and results from other parts of the world.

Study	Location	TnBP	TCEP	TCIPP	TBOEP	EHDPP	TmTp	TPhP	TDCIPP
This study	River Tame	2.3	4.0	13.3	35.0	1.8	2.4	1.9	1.6
This study	River Sowe	2.2	4.6	6.7	32.4	1.0	2.6	0.9	1.9
This study	River Severn	3.1	3.8	9.0	30.6	1.1	1.2	1.5	1.4
This study	Worcester and Birmingham Canal	18.3	6.4	9.0	53.3	8.8	4.1	4.2	3.1
[26]	River Besòs (River Sediment)	8.4	7.1	164.7	< LOD	37.7	–	13.3	8.8
[27]	Luoma Lake, China (Lake Sediment)	0.02	0.4	0.1	0	0.1	0.06	0.01	–
[14,28]	Lake Taihu, China (Lake sediment)	0	3.0	1.2	0	0.4	0.4	1.7	0.1
[29]	Evrotas River Sediment (Greece)	2.4	1.8	4.6	1.5	4.8	4.8	0.4	1.6
[29]	Adige River (Italy)	5.5	2.5	14.9	2.4	37.3	37.3	0.9	2.3
[29]	Sava River (Slovenia, Croatia, Bosnia and Herzegovina and Serbia)	7.7	0.8	6.6	3.2	4.8	4.8	–	0.4
[30]	Lakes Superior (Sediment)	0.3	0.2	0.2	0.03	0.01	0.01	0.04	–
[30]	Lake Michigan. (Sediment)	0.5	ND	0.4	1.5	0.03	0.03	0.2	–
[30]	Lake Ontario (Sediment)	1.4	ND	0.7	7.3	0.3	0.3	2.6	–
[31]	Vaal River, South Africa.	37.5	2.6	1.1	26.2	–	–	2.9	0.7
[32]	Kathmandu valley, Nepal. (River Sediment)	76.4	18.5	112.6	–	135.6	–	39.6	5.7
[33]	The Arctic	–	1.3	1.2	2.6	0.2	–	0.4	0.4

Worcester-Birmingham Canal for most target OPEs (Table 1 and Fig. 2), only EHDPP showed significantly higher concentrations in the Worcester-Birmingham Canal compared to the Rivers Severn ($p = 0.003$), Tame (0.007), and Sowe (0.002). No other statistically significant differences were observed between concentrations of individual OPEs in the 4 studied locations. TBOEP displayed the highest concentrations of all targeted OPEs (Fig. 1), while TCIPP was the chlorinated OPE detected at the highest concentration across all four sampling locations. This high concentration of TBOEP can be attributed to its high production volume and wide range of applications [35,36].

3.2. Seasonal variations

The highest $\sum_8\text{OPE}$ concentration for all study locations was recorded during the autumn months (September, October, and November), while the lowest concentrations were all recorded in the winter months (December, January, and February) (Fig. S2 and Table S5).

To further understand the observed seasonal variations in concentrations of OPEs, we examined the relationship between OPE concentration and two parameters that display seasonal variation: river flow rates [37] and water levels [38] during each season, as previous studies have reported notable variations in pollutant concentration in sediments with such hydrodynamic parameters [39–41].

Concentrations of $\sum_8\text{OPEs}$ in sediment samples from the River Severn, River Tame, and River Sowe all varied inversely with the river level and flow rate (Figs. S3–S8). The highest flow rates and river levels were observed in winter and spring, the seasons displaying the lowest $\sum_8\text{OPE}$ concentrations. More specifically, we observed a significant negative correlation between $\sum_8\text{OPE}$ concentration and river flow rate ($r = -0.68$, $p = 0.03$). In contrast, the inverse relationship between $\sum_8\text{OPE}$ concentrations and river level, was not statistically significant ($r = -0.51$, $p = 0.09$). At the River Tame, the negative correlation between $\sum_8\text{OPE}$ concentrations and flow rate was near significant ($r = -0.61$, $P = 0.06$) with a similar observation made for river level ($r = -0.54$, $P = 0.07$). Similar observations were made between $\sum_8\text{OPE}$ concentrations and river level ($r = -0.559$, $p = 0.059$) and flow rate ($r = -0.627$, $p = 0.07$) at the River Sowe.

For the fourth sampling location (Worcester-Birmingham canal), flow rate and water level data were not available. However, as this is a canal with many locks, the flow rate and water level are expected to have minimal variation. The observed relationships between river level, flow rate, and OPE concentrations can be

attributed to the diluting effect of higher river levels as a result of higher rainfall and the fact that slow flowrate facilitates contaminant partitioning/adsorption to sediment particles [41]. Another possible explanation is the overflow caused by more abundant precipitation in winter which might lead to chemical loss in pipes before they reach the WWTPs.

3.3. Comparison of OPE concentrations in freshwater sediments collected up and downstream of WWTP discharge points

To investigate any possible impact of wastewater treatment plants on OPE concentrations in UK riverine sediment, paired samples were collected upstream and downstream of the effluent discharge points of three WWTPs – one each along the River Severn, River Sowe, and River Tame.

Although variations were observed in the concentration of $\sum_8\text{OPEs}$ measured upstream and downstream of all 3 WWTPs over the 12 months period (Figs. S10–S12), as well as the mean concentration of individual target OPEs upstream and downstream of all 3 WWTPs (Fig. 3), a paired sample t -test revealed no statistically significant difference between the concentrations of $\sum_8\text{OPEs}$ upstream and downstream of WWTP 3 (River Severn) and 1 (River Tame). However, for WWTP 2 (River Sowe), a paired sample t -test revealed $\sum_8\text{OPE}$ concentrations downstream of the WWTP were significantly higher than those upstream ($p = 0.005$). Furthermore, to eliminate the possibility that using $\sum_8\text{OPEs}$ for the paired t -test might obscure some differences for individual OPEs, the paired t -test was repeated for the 8 individual target OPEs. This showed significantly higher concentrations of TnBP downstream than upstream of WWTP3 (River Severn) ($p = 0.04$) and significantly higher concentrations of TPhP and TCEP downstream than upstream of WWTP 2 (River Sowe) ($p = 0.02$ and 0.05 respectively). For the River Tame, no statistically significant difference between the concentrations of any of the 8 target OPEs upstream and downstream of WWTP1.

Similar to some previous studies [18,42], the results presented here (especially for the Rivers Severn and Sowe) do not reveal a significant contribution of WWTPs to concentrations of OPEs in the sampled sediments [43]. This is likely due to a combination of factors including: efficient removal of OPEs by the treatment operations of the WWTPs in this study, as well as potential degradation of parent OPEs (since they are not highly resistant to aerobic and anaerobic degradation) and their excretion as metabolites (di- and mono-esters) in humans and other animals, which were not quantified in the present or previous studies [43–45].

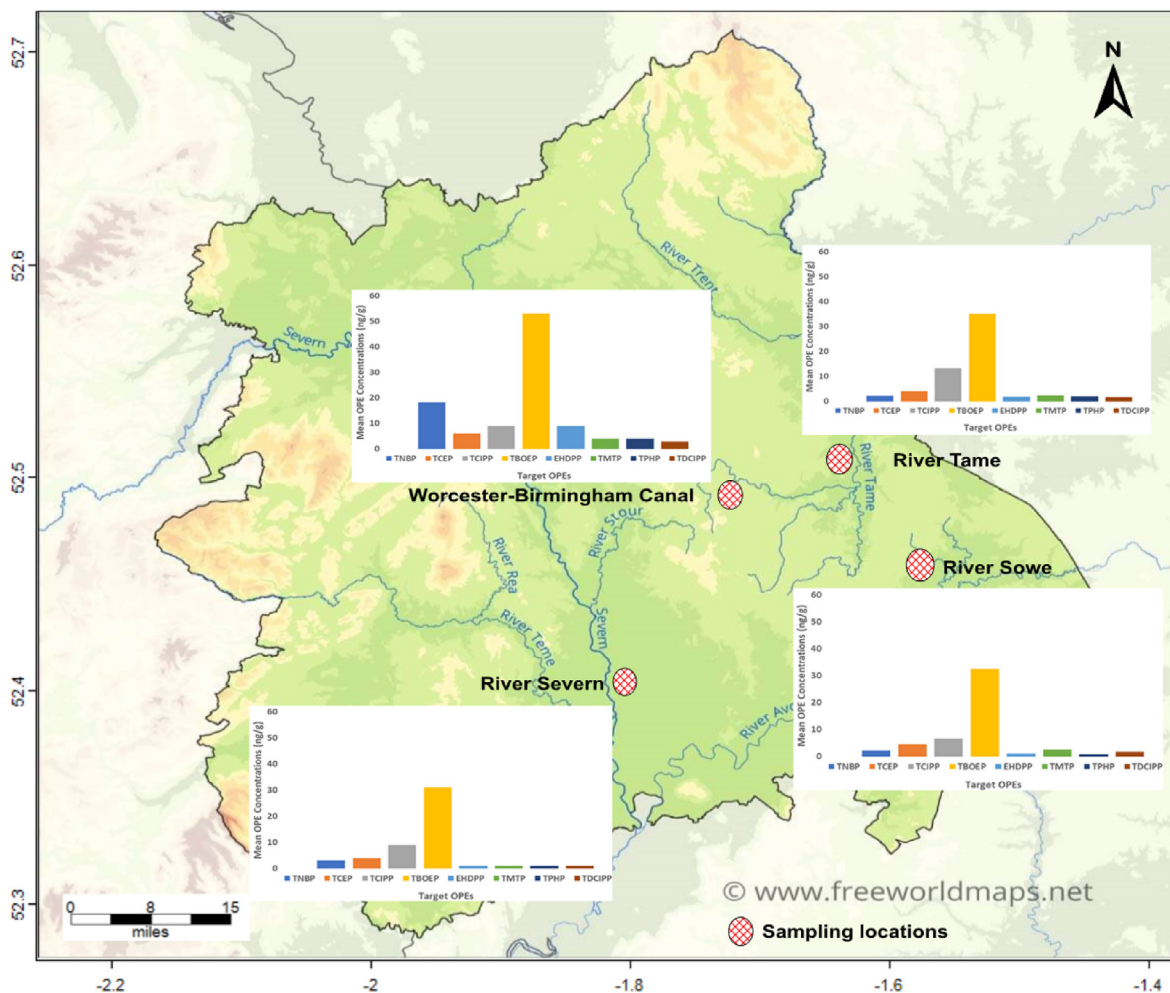


Fig. 1. Map of West Midlands showing concentrations/composition of OPEs at sampling sites (freeworldmaps.net).

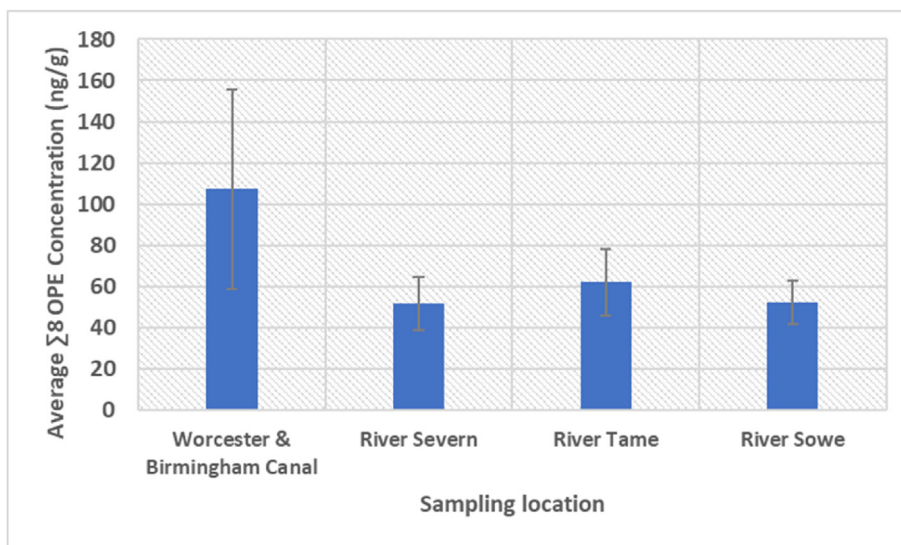


Fig. 2. Comparison of average Σ_8 OPE concentrations (y-error bar denotes standard deviation) at the Worcester and Birmingham canal, River Severn, River Sowe, and River Tame.

3.4. Ecological risk assessment

To assess the risk of the target OPEs on aquatic organisms, the risk quotient (RQ) method was used [32,33,46]. The RQ is calculated

as the ratio of the measured environmental concentration (MEC) and the predicted no effect concentration (PNEC) as shown in equation (1).

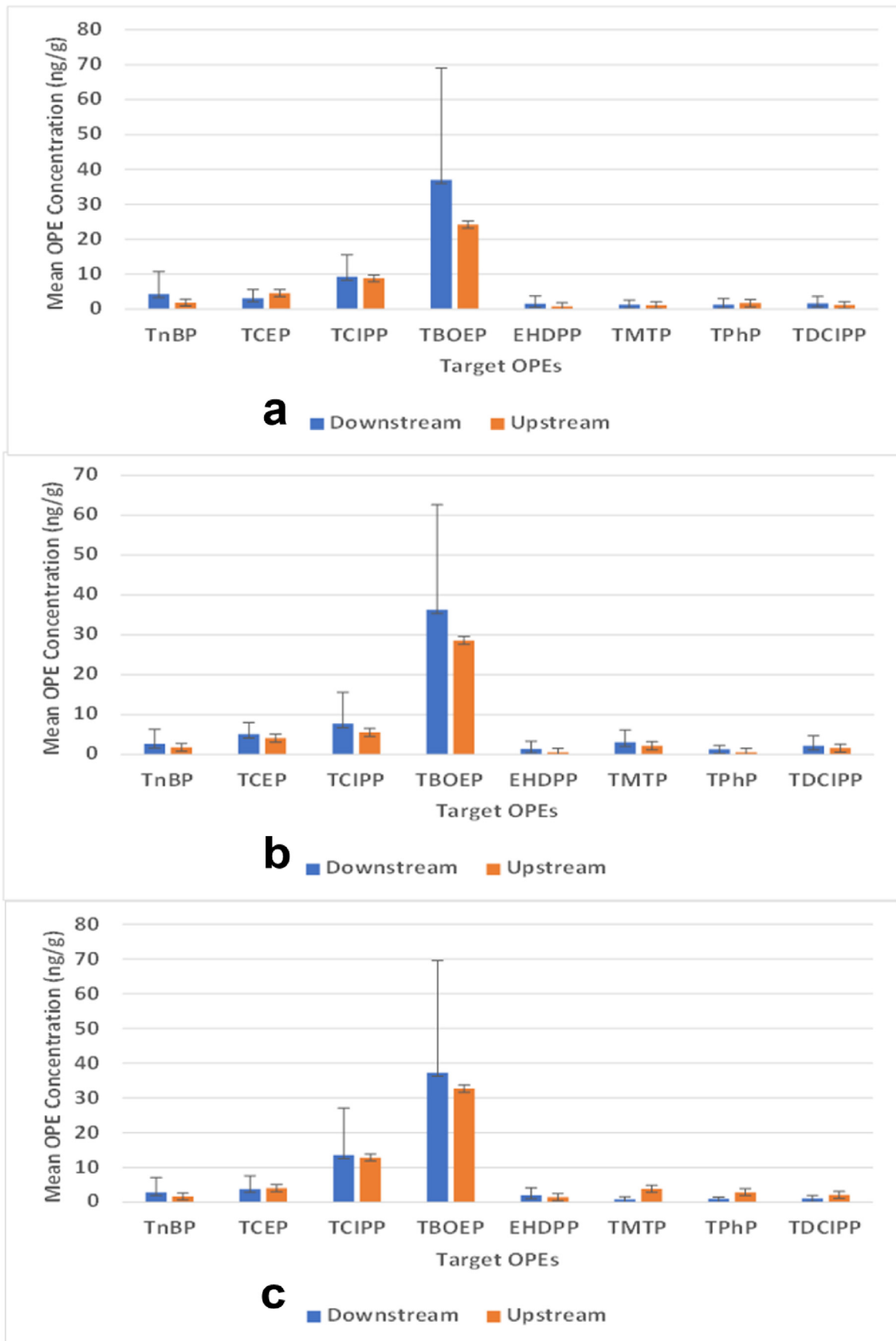


Fig. 3. Mean concentrations of each target OPE upstream and downstream of a WWTP in surficial sediments from River Severn (a), River Sowe (b) and River Tame (c).

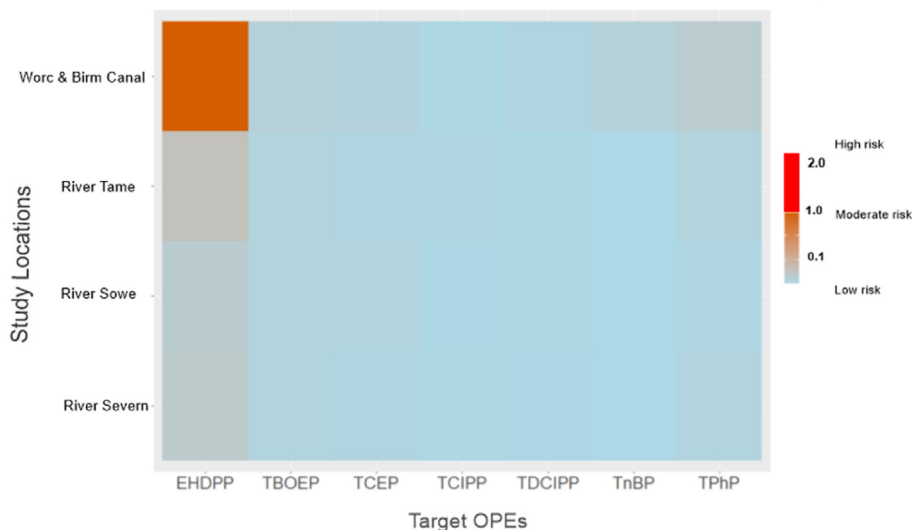


Fig. 4. Risk classification of the OPEs in the four study locations.

$$RQ = \frac{MEC}{PNEC} \quad 1$$

$$PNEC = \frac{EC_{50} \text{ or } LC_{50}}{f} \quad 2$$

where f is an assessment factor (1000 was used in this study) while EC_{50} and LC_{50} stand for effective concentration and Lethal concentration respectively.

Just like several existing studies where PNEC values were obtained from previous studies [9,28,47], the PNEC values used in this study were obtained from Wang et al., 2019 and Fu et al., 2017 (Table S7). For the CI-OPEs, PNEC values were as reported by the European Commission (EC) based on the lowest effect concentrations in some biota (*Folsomia*, *L. sativa* seedlings, and *Eisenia foetida*) (Wang et al., 2019, Fu et al., 2017). For TPHP and EHDPP, PNEC values were estimated based on equilibrium partitioning model such that $(PNEC_{soil} = K_{soil-water}/P_{sed} \times PNEC_{aquatic} \text{ organisms} \times 1000)$; where $K_{soil-water}$ = soil/water partition coefficient, P_{sed} = bulk density of wet sediment (Wang et al., 2019, Fu et al., 2017). The RQ for all study locations are shown in Table S6.

The potential risk from these OPEs to aquatic organisms were evaluated from the RQ values. RQ values ranging from 0.01 to 0.1 are classed as low risk, those between 0.1 and 1 as moderate risk, while RQ values above 1 are classed as high risk [48] as such values indicate the PNEC is exceeded [27,49,50]. All target compounds in all study locations in this study fall within the low-risk category except for EHDPP in the Worcester-Birmingham canal which poses a moderate risk due to the RQ value of 0.29 (Fig. 4).

Moreover, while lower than in the canal, RQs for EHDPP in the Rivers Sowe and Tame approach the moderate risk level. This result is very similar to previous work where EHDPP was also reported as a predominant contributor to ecological risk in surface water [27]. As a cautionary note, we highlight that the PNEC value used for any ecological risk assessment plays a key role in the evaluation of the risk and the fact that this value can vary significantly depending on the PNEC derivation methodology used, has been described as of concern [51]. It has been reported that the two approaches proposed for deriving the PNEC value of chemicals (the assessment factor (AF) approach and the species sensitivity distribution (SSD) approach) can both lead to overestimation or underestimation of

risk [51]. Furthermore, the lack of knowledge on the toxicological impact of exposure to chemical mixtures must be considered. The toxic effect of chemicals can change as a result of the influence of other chemicals on their biological action as well as other possible interactions between chemicals (synergistic or antagonistic effects) [52,53]; however, most current risk assessments are based on single chemicals [53].

3.5. Comparison with results from other parts of the world

Although there are several studies on OPEs in environmental media such as: water [54,55], air [56,57], indoor dust [25,58], and food [59,60]; there are presently few data on concentrations of OPEs in freshwater sediment [3].

Table 2 compares concentrations of OPEs detected in freshwater sediments in this study with those reported for 12 other studies from different parts of the world. The average concentrations of each target OPE in each study location (for this study) are lower than those reported in some previous studies [26,27] but fall broadly in the middle of the range previously reported from other countries (Table 2). The OPE detected at the highest average concentration in all locations in the present study was TBOEP, with our concentration exceeding that reported for all 12 previous studies considered here. TBOEP was also reported as one of the OPEs detected at the highest concentrations in sediments of the Vaal River in South Africa [31]. This likely reflects greater use of and emissions to rivers of TBOEP than for our other target OPEs. For TCEP and TCIPP, the average concentration in all the locations in this study (River Tame, River Sowe, River Severn, and the Worcester-Birmingham canal) exceeded those reported in most of the studies considered. Also, the inverse relationship between river flow rate and OPE concentration reported in this study is similar to the findings of a study targeting 10 OPEs in sediment from the industrially-impacted and highly urbanised River Besòs in Spain [26].

4. conclusion

This study provides the first report of OPEs in UK freshwater sediments. All target OPEs were detected at all four study locations with detection frequencies ranging from 58% to 100%. The average concentration of Σ_8 OPEs ranged from 107 ng g⁻¹ (dw) (in the

Worcester-Birmingham canal) to 52 ng g⁻¹ (dw) (in both rivers Severn and Sowe) with TBOEP and TCIPP displaying the highest concentrations of all target analytes and chlorinated OPEs respectively, in all four sampling locations.

The results of this study suggest that freshwater contamination with OPEs varies seasonally because of seasonal variations in hydrodynamic factors (flow rate and river level). Specifically, the highest concentrations of Σ_8 OPEs at all study locations was recorded in the autumn months (September, October, and November) which coincide with the lowest flow rates and river levels. Furthermore, urbanisation and proximity to potential anthropogenic sources of contamination might have a greater influence on freshwater sediment contamination with OPEs than WWTPs. This is because concentrations of most OPEs in the 3 rivers studied were not significantly greater downstream of WWTP discharge points; moreover, the highest average Σ_8 OPE concentration over the 12 months period was recorded in the Worcester and Birmingham canal (the most urban location and the only location in this study that does not receive direct input from a WWTP).

The potential risk posed by the target OPEs in all study locations was found to be low except for a moderate risk identified for EHDPP in the Worcester-Birmingham canal. As a cautionary note however, risk assessments based on single chemicals, do not adequately account for possible synergistic and antagonistic effects of the complex chemical mixtures present in sediments.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.emcon.2023.100243>.

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