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Spatial distribution of organic contaminants in three rivers of Southern England bound to suspended particulate material and dissolved in water☆

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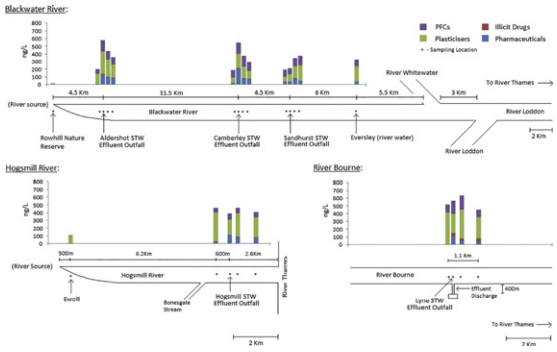
HIGHLIGHTS

- Per capita daily contribution of PPCPs/ECs entering English rivers was calculated.
- Long chain perfluorinated compounds more likely in SPM than other contaminants.
- Sewage effluent most significant source ($p < 0.05$) of most studied compounds.
- Low levels of plasticisers and perfluorinated compounds found in river headwaters.
- Environmental distribution coefficients for ECs between water/suspended matter.

GRAPHICAL ABSTRACT



Spatial distribution of the mean sum of studied perfluorinated compounds (PFCs), plasticisers, illicit drugs and pharmaceuticals (ng/L) through the course of three rivers in Greater London and Southern England.

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ABSTRACT

The spatial distribution of pharmaceuticals, personal care products (PPCPs) and other emerging contaminants (ECs) such as plasticisers, perflourinated compounds (PFCs) and illicit drug metabolites in water and bound to suspended particulate material (SPM) is not well-understood. Here, we quantify levels of thirteen selected contaminants in water ($n = 88$) and their partition to suspended particulate material (SPM, $n = 16$) in three previously-unstudied rivers of Greater London and Southern England during a key reproduction/spawning period. Analysis was conducted using an in-house validated method for Solid Phase Extraction followed by High-Performance Liquid Chromatography-Tandem Mass-Spectrometry. Analytes were extracted from SPM using an optimised method for ultrasonic-assisted solvent extraction. Detection frequencies of contaminants dissolved in water ranged from 3% (ethinylestradiol) to 100% (bisphenol-A). Overall mean concentrations in the aqueous-phase ranged from 14.7 ng/L (benzoylecgonine) to 159 ng/L (bisphenol-A). Sewage treatment works (STW) effluent was the predominant source of pharmaceuticals, while plasticisers/perfluorinated compounds may additionally enter rivers via other sources. In SPM, detection frequencies ranged from 44% (PFOA) to 94% (hydroxyacetophenone). Mean quantifiable levels of analytes bound to SPM ranged from 13.5 ng/g dry SPM (0.33 ng bound/L water) perfluorononanoic acid to 2830 ng/g dry SPM (14.3 ng bound/L water) perfluorooctanesulfonic acid. Long chain (>C7) amphipathic and acidic PFCs were found to more preferentially bind to SPM than short chain PFCs and other contaminants (Kd = 34.1–75.5 vs <5 respectively). Per capita

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daily contributions of studied contaminants entering rivers ranged from 0.157 μg/person/day of benzoylecgonine (cocaine metabolite) to 58.6 μg/person/day of bisphenol-A. The large sample size of this work ($n = 104$) enabled ANOVA followed by Tukey HSD post-hoc tests to establish significant trends in PPCP/EC spatial distribution from headwaters through downstream stretches of studied rivers. Novel findings include environmental Kd calculations, the occurrence of contaminants in river headwaters, increases in contaminant metabolite concentrations downstream of STW effluents revealing possible in-river degradation or de-conjugation, the influence of polarity and acidity in the partition of contaminants to particulate-material, among others.

1. Introduction

Modern medicine and other high-volume chemical products used on a day-to-day basis (such as plastics) have significantly elevated our quality of life over the last century. Such chemicals are an irreplaceable component of a healthy modern society. However, the ubiquitous use and disposal methods of such chemicals have led to their introduction into the environment. Since the late 1990s, pharmaceuticals were known to contaminate sewage treatment work (STW) effluent (Halling-Sørensen et al., 1998) and receiving streams and rivers (Kolpin et al., 2002). In the years following such findings, other so-called emerging contaminants (ECs) such as plasticisers and perflourinated compounds (PFCs) have been detected in areas far removed from human activity such as in remote alpine lakes (Veillette et al., 2012) and streams (Filipovic et al., 2015).

An interdisciplinary perspective on environmental toxicology and chemistry should not be lost in such study. Physiological response to environmental chemicals is likely to vary between organisms and sensitivity may vary between developmental stages of life (Weis, 2014; Wilkinson et al., 2016a). Some personal care products (PCPs) and other emerging contaminants (ECs) are found to mimic the action of endogenous hormones (particularly those interacting with estrogen receptors) and disrupt the physiology, behaviour and/or protein expression of exposed aquatic organisms (Vajda et al., 2008; Patisaul and Adewale, 2009; Vajda et al., 2011). Low concentrations of endocrine disruptors such as BPA, ethinylestradiol and some PFCs may be biologically active during sensitive periods of development or reproduction, which may only occur at certain times of year (Kjeldsen and Bonefeld-Jørgensen, 2013; Baumann et al., 2014; Little and Seebacher, 2015). Assessment of PPCP/EC occurrence and fate may be more significant if sampling campaigns coincide with significant biological events occurring in exposed organisms.

Despite significant research over the previous two decades, the spatial distribution of PPCPs/ECs discharged from STW effluent into rivers remains unclear, particularly when these contaminants associate with suspended particulate material (SPM). Similarly, the ultimate fate (not just the presence) of the organic contaminants found in rivers is largely unknown. Possible pathways may include distribution to river sediment or banks, suspended particulate material, bioaccumulation in aquatic organisms, volatilisation, and degradation. Furthermore, as such research is often conducted using grab sampling methods at a limited number of locations, an accurate and reliable estimation of contaminant distribution remains difficult to ascertain. Repeated sampling stretching over the course of rivers, temporal fluctuations of contaminants levels, changes in river hydrology, and association with other environmental compartments (such as SPM) however are rarely undertaken.

This work assesses the spatial distribution of thirteen PPCPs/ECs entering three rivers of southern England and their partitioning between dissolved and bound to SPM phases, a previously little-studied subject. Target contaminants included pharmaceuticals, illicit drugs, plasticisers, perfluorinated surfactants, and their metabolites/transformation products. Three rivers were selected for this work, of which two were evaluated from headwaters to first confluence with another river. Additionally, the effect of sewage treatment effluent outfall on concentrations of selected contaminants in three rivers was evaluated by comparison of upstream vs. downstream waters relative to five effluent outfalls. Specifically, we aim to:

a) Quantify the occurrence of target analytes in river headwaters;
b) Assess the influence of sewage treatment works discharge of PPCPs/ECs into rivers;
c) Assess the fate of PPCPs/ECs in the dissolved and bound to suspended particulate material phases of water along the course of whole-river systems during fish reproductive/spawning season (April–August); and
d) Determine environmental distribution coefficients (Kd) for the sorption of PPCPs/ECs to suspended particulate material along the course of studied rivers.

2. Materials and methods

Thirteen PPCPs/ECs were selected inter alia pharmaceuticals, illicit drugs/metabolites, plasticisers/metabolites and perfluorinated compounds (Table 1). The pharmaceuticals and illicit drug analytes were selected as specific markers of human-derived contamination which are commonly used and/or show the potential to be physiologically active in aquatic environments. While plasticisers and PFCs may enter STW effluent via household human-derived use, such compounds may additionally be used to examine inputs from industrial or transport-related activity (Zushi et al., 2008; Wilkinson et al., 2016b). Plasticiser BPA and its main biotransformation product HAP and replacement product BPS were selected based upon high production volume, persistent use and a significant body of research indicating ecotoxic potential to both humans and exposed non-target organisms (e.g., Kjeldsen and Bonefeld-Jørgensen, 2013; Rochester, 2013; Corsini et al., 2014). The illicit drug methamphetamine and metabolite amphetamine were selected due to a notable lack of information regarding their occurrence in rivers. Benzoylecgonine was selected due to its influence on the mitochondrial activity of aquatic plants at levels as low as 1 ng/L (García-Cambero et al., 2015).

All analytes were of at least 96% purity and purchased from Sigma Aldrich (Gillingham, Dorset, U.K.). Solid phase extraction cartridges (Strata-X 33 μm polymeric reversed phase 200 mg/6 mL) were purchased from Phenomenex in addition to a Phenomenex 2.6 μm C18-150 × 2.1 mm chromatography column used for all analysis. Whatman GF/F-grade glass microfibre filters of 47 mm diameter and 0.7 μm pore size were purchased from Fisher Scientific (Loughborough, Leicestershire, U.K.).

2.1. Sampling area

Selected rivers included the Hogsmill River (Greater London), Chertsey Bourne River and the Blackwater River (Fig. 1). These rivers were selected due to their accessibility, receiving only STW effluent outfalls (i.e., no confluence with another major river in the study area) and accessibility of river headwater sampling for the Hogsmill and Blackwater Rivers. Each river received input(s) from at least one STW. A total of six STWs were selected (Fig. 2): 3 discharging into the Blackwater River (Aldershot, Camberley and Sandhurst STWs), 1 into the Hogsmill (Hogsmill STW), 1 into the Chertsey Bourne (Chertsey STW) and 1

Table 1
Analytical parameters and pKa of studied contaminants.

Compound type	Compound	pKa	log Kow	LOD/LOQ		Recovery (%)	
				Water (ng/L)	SPM* (ng/L)	Aqueous 100 ng/L	SPM 100 ng/g
Pharmaceuticals	Acetaminophen	9.38	0.46a	0.28/0.93	6.67/22.1	93.3	45.2
	Diclofenac	4.15	4.51a	0.29/0.96	6.91/22.9	104	86.7
	Ethinylestradiol	10.7	3.67a	0.98/4.91	23.3/116	90.3	
Illicit drugs	Amphetamine	10.1	1.65a	0.22/1.09	5.24/25.9	83.4	
	Benzoylecgonine	3.15–9.54	3.32a	0.31/1.02	7.38/24.3	80.1	73.6
	Methamphetamine	9.87		0.32/1.06	7.62/25.2	90.3	
Plasticisers	Bisphenol-A	10.3	1.71a	1.17/3.87	27.8/92.1	113	82.4
	Bisphenol-S	8.2	1.76a	0.34/1.12	8.09/25.9	84.3	96.4
	4′-Hydroxyacetophenone	8.12	2.07a	0.31/1.04	7.38/24.8	83.2	73
Perfluorinated compounds	Perfluorobutanesulfonic acid	<1		0.33/1.13	7.86/26.9	93.1	75.5
	Perfluorononanoic acid	<1	7.27b	0.23/0.75	5.48/17.9	101	61.1
	Perfluorooctanoic acid	<1	6.30a	0.34/1.13	8.09/26.9	97.7	62
	Perfluorooctane sulfonate	<1	6.28a	0.51/1.52	12.1/36.2	99.7	79.4

* Mean LOD/LOQ: Mass of collected sample varied (based on organisms found at-location) thus LOD/LOQ was calculated for each extract and the means are presented here.

STW effluent-only site (Guildford STW). Mean daily discharge volume and flow in the studied STWs ranged from 9098 m^3 and 0.105 m^3/s at the Sandhurst STW to 58,180 m^3 and 0.673 m^3/s for the Hogsmill STW respectively (Supplementary Information Table 1). Headwaters were evaluated for the Hogsmill and Blackwater Rivers which enabled analysis of the entire course of the respective rivers, from source to the first confluence with another major river. In order to assess the spatial distribution of selected contaminants entering rivers via STW effluent, water samples were collected 50 m upstream from effluent outfalls, in the STW effluent outfall itself as well as 250 m and 1000 m downstream from the outfalls (Fig. 3). Suspended particulate material was collected using the same standard spatial distribution of samples (Fig. 3) however aqueous vs. bound distribution of selected contaminants was only assessed in 16 collected samples.

2.2. Collection of water samples

Grab samples (200 mL, $n = 88$) were collected in amber glass bottles on 3–4 separate occasions (depending on the site) from 23 sites: upstream and downstream of 5 STW effluent outfalls ($n = 76$), river source waters ($n = 6$), effluent-only from a 6th STW ($n = 3$), and from a location 6 km downstream from the last studied STW located on the Blackwater River ($n = 3$). Water was collected from the mid-course of respective rivers and brought to the laboratory within 4 h of collection. Water was subjected to vacuum filtration using a GF-F glass microfibre filter (pore size 0.7 μm). In order to eliminate any contamination or interference originating from the filter itself, every filter was soaked in 10% HNO_3 for 16 h and rinsed with 3 washes of 50:50 acetonitrile:acetone (*v*/v) to remove any potential contamination.

2.3. Collection of suspended particulate material (SPM)

Collection of SPM ($n = 16$) was achieved using vacuum filtration of collected water onto GF-D glass microfibre filters (pore size 2.7 μm). GF/D filters are commonly used for collection and extraction of SPM from water (Yang et al., 2016) and thus were selected for this work. The dry mass of each filter was recorded prior to filtration. At each collection site, 10 L of water was collected from the mid-course of the river into 10 L high density polyethylene carboys. Carboys were rinsed three times with 50:50 acetonitrile:acetone (*v*/v) then rinsed with river water prior to sample collection. Separation of the water and SPM was conducted within 3 h of collection. In order to maximise SPM mass, collected water was filtered through the GF-D filter until no additional water could pass (i.e., the filter became clogged). This step was repeated once more resulting in two filters containing SPM. The final volume of filtered water was recorded in order to determine the amount of SPM/L water and, after analysis, mass of analyte bound to SPM/L water. Filters containing SPM were air dried for 72 h in the dark at 21.3 ± 0.37 °C prior to extraction. This method resulted in the separation of 78.4% of total particulate material 0.45 μm ≥ Φ and mean loss of <21.6% SPM 2.7 μm ≥ Φ > 0.45 μm (see Supplementary Material Section 2.1 for full method details and calculation of recovery).

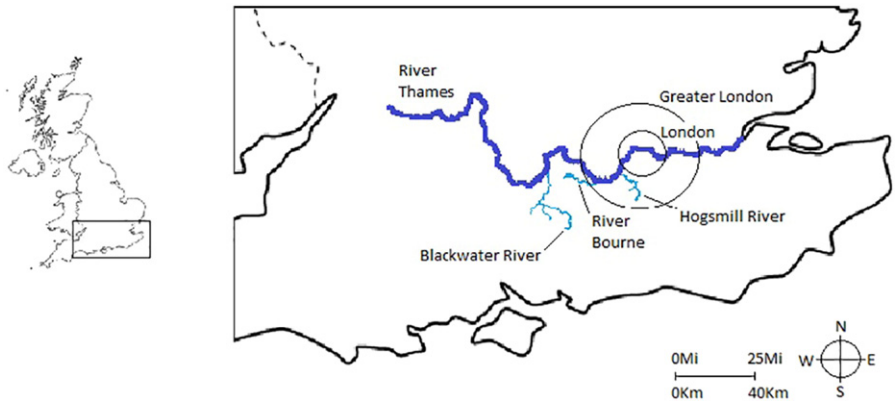

Fig. 1. Location of selected rivers and major urban boundaries in southeast England.

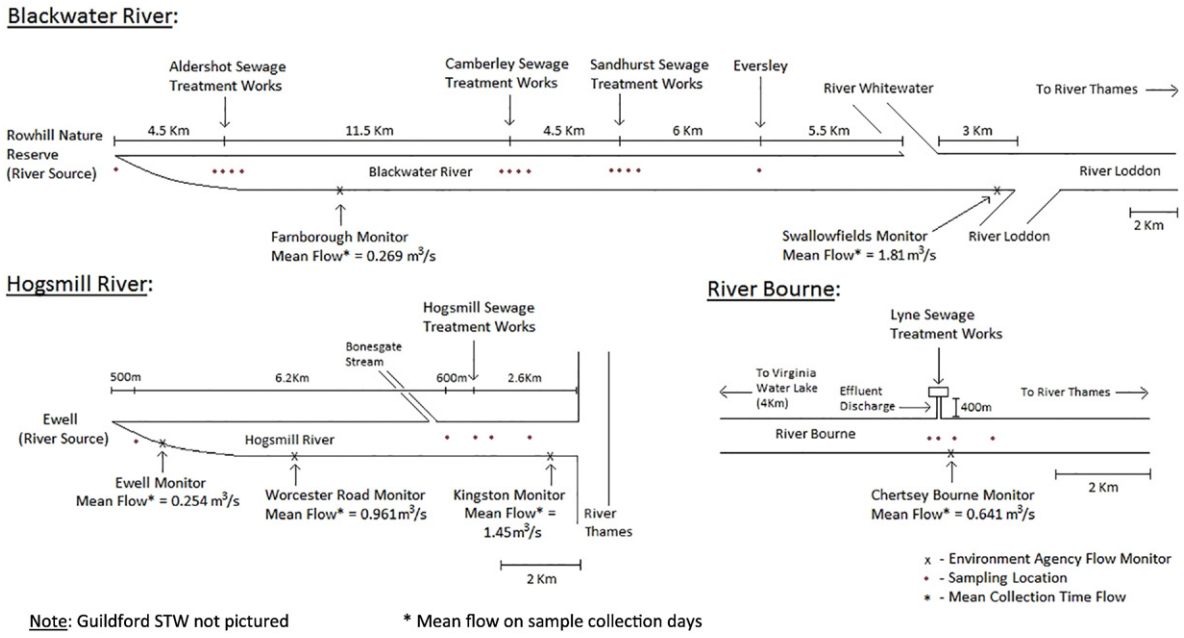

Fig. 2. Sampling locations and mean flow during sample collection days.

2.4. Extraction of selected analytes from suspended particulate material

Extraction of PPCPs/ECs from SPM was conducted using ultrasonic-assisted solvent extraction of the air-dried GF-D membrane filters containing the SPM sample. Dry filter + SPM mass was recorded before filters were sectioned into quarters and placed in a 100 mL 3 times solvent rinsed glass test tube. SPM containing filters were subjected to ultrasonication with 20 mL methanol:acetonitrile (25:75, *v*/v) with 1% acetic acid for 20 min at 40 °C. Separation of solid and liquid components of the extract was achieved using vacuum filtration through a GF-F glass mircofibre filter pre-washed three times in methanol:acetonitrile (25:75, *v*/v). Extracts were reduced to approximately 1.5 mL by rotary evaporation. An aliquot of 80 mL ultra-high purity, high performance liquid chromatography-grade water (HPLC-H_2O) was added to the reduced 1.5 mL extract making an aqueous solution with (<2% methanol:acetonitrile) suitable for solid phase extraction. The extract-solution was loaded onto an SPE cartridge (Oasis Strata™ X-33 μ, 200 mg/6 mL) at a rate of 5 mL/min, dried for 20 min under vacuum and eluted using 2x7mL aliquots of acetone:acetonitrile (50:50, *v*/v). SPE extracts were then rotary evaporated to dryness, reconstituted in 500 μL HPLC-H_2O:acetonitrile (80:20, *v*/v) and spiked with internal standards at 25 ng/mL prior to HPLC-MS/MS analysis. Due to the small amount of SPM in collected water, reconstitution occurred in half the amount of mobile phase than for water samples (500 μL vs. 1 mL respectively) in order to achieve lower detection limits. Spiked recoveries ranged from 45% (acetaminophen) to 96% (BPS) while the mean extraction recovery was 74% (Table 1).

2.5. Solid phase extraction (SPE) and high performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS)

SPE and HPLC-MS/MS analysis was conducted using a method previously developed and validated in-house for quantification of the specific 13 selected PPCPs/ECs in this study. Specific details relating to this method can be found in Supplementary Material Section 1.0 and elsewhere (Wilkinson et al., 2016b). Briefly, an Agilent Technologies 1260 Infinity HPLC coupled to an Agilent Technologies 6430 Series triple quadrupole mass spectrometer operated in multiple reaction monitoring mode was used for all quantitative analysis with a Phenomenex 150 × 2.1 mm (2.6 μm) chromatography column. Two transition ions were used to identify and quantify each target compound via electrospray ionisation. The method was previously validated (Wilkinson et al., 2016a, 2016b) using the International Conference on Harmonisation, Harmonised Tripartite Guideline Validation of Analytical Procedures: Text and Methodology Q2(R1) as a guideline (ICH, 2005).

Respective limits of detection (LOD) and quantification (LOQ) were lowest for contaminants found in water and varied for contaminants extracted from SPM (Table 1). Here, LODs/LOQs for contaminants extracted from SPM depended on the mass of SPM separated from the collected

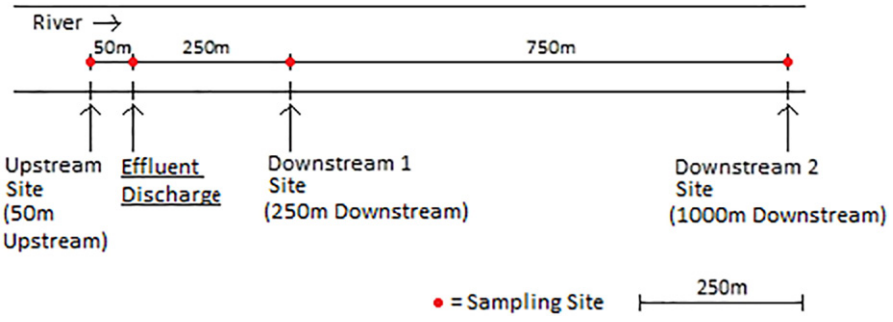

Fig. 3. Standard spatial distribution of sampling sites above and below sewage treatment effluent discharge.

river water, where lower LODs/LOQs corresponded to a higher mass of extracted SPM (see Table 1 for mean LODs/LOQs from SPM). LODs/LOQs for contaminants extracted from SPM were determined using the following equations:

$$LOD_{SPM} = LOD_{method}\ (SPM_{mass})/2$$

$$LOQ_{SPM} = LOQ_{method}\ (SPM_{mass})/2$$

where LOD_{SPM} and LOQ_{SPM} are the limit of detection and quantification for a specific compound extracted from the SPM, LOD_{method} and LOQ_{method} are the method-derived LOD and LOQ for the same compound (i.e., the same LOD/LOQ value as for water), SPM_{mass} is the mass of SPM separated from each collected water (i.e., in each 10 L carboy). LOD and LOQ calculations are divided by two as SPM extracts were reconstituted in 500 μL mobile phase rather than the standard 1 mL in order to improve detection limits/levels (see section 2.4).

2.6. Quality control

Significant measures were taken to reduce contamination and ensure as high quality results as possible when analysing environmental samples for chemicals as ubiquitous as plasticisers and PFCs. Such measures are thoroughly detailed in Supplementary Material Section 2.0. Briefly, all glassware was rinsed with acetonitrile:acetone (50:50, *v*/v) three times before and after every use, including rotary evaporators. At least once per week, glassware was additionally soaked in 10% HNO_3 overnight. All filters were soaked in 10% HNO_3 for 16 h and rinsed with three washes of 50:50 acetonitrile:acetone (*v*/v) in order to remove any contamination or interference originating from the filters themselves. Furthermore, in order to reduce the impact of method-derived contamination and minimise the effects of recovery on quantitative analysis, all calibrations for water samples were conducted by spiking 200 mL HPLC-grade water with respective levels of target contaminants followed by SPE, rotary evaporation, reconstitution and HPLC-MS/MS analysis.

Recoveries (Table 1) were assessed for water and SPM by spiking aliquots of respective matrix (200 mL river water filtered using a GF-F glass microfiber filter and SPM dried onto a GF-D glass microfiber filter) spiked with each respective analyte to a concentration of 100 ng/L for water and 100 ng/g dry weight for SPM respectively. Spiked SPM was allowed to dry for 3 h prior to extraction. Spiked aliquots of respective matrix used to assess recovery ($n = 3$ for water and $n = 3$ for SPM) were subjected to the same extraction, SPE and HPLC-MS/MS protocols as real samples and were blank offset (Table 1). Extracted concentrations were divided by those obtained by analysis of known standards ($n = 3$) to yield recovery, per standard methods.

2.7. Data analysis

Data analysis took place using IBM SPSS Statistics (Version 23) and is thoroughly detailed in Supplementary Material Section 3.0. The spatial distribution of each respective contaminant was evaluated using a One-Way ANOVA test using data from all rivers together (pooled) followed by a river-by-river analysis. Where a significant difference between means was found, further post-hoc analysis using Tukey's Honestly Significant Difference (HSD) test was applied in order to determine which paired means significantly differed. The specific contribution of STW effluent outfalls to the concentrations of contaminants in respective rivers was assessed using paired *t*-tests. Where contaminant concentrations fell between the LOQ and LOD, a value of half the LOQ was assigned for descriptive statistics. Non-detects were treated as zero-values in the calculations of overall means (e.g., mean of a contaminant's concentration over all collected STW effluent samples). This approach was chosen to avoid potential misrepresentation of the data. For example, ethinylestradiol (EE2) was detected in 3 of 22 STW effluent samples. Here, rather than report an overall EE2 mean in the 22 STW effluent samples as the average of the 3 quantifications, the overall sum of EE2 detected in effluent was divided by the total number ($n = 22$) of effluent samples analysed.

3. Results and discussion

3.1. Spatial distribution of PPCPs/ECs dissolved in water

Detection frequencies ranged from 3% (ethinylestradiol) to 100% (BPA) and no sample was found without any residue (clean) of selected target contaminants, including river source waters. Overall ($n = 88$) mean concentrations ranged from 0.23 ng/L (ethinylestradiol) to 158 ng/L (BPA). By location, mean concentrations (Table 2) in source/headwaters ($n = 6$) ranged from 0.97 ng/L (BPS) to 22.7 ng/L (BPA), in all other river water ($n = 79$) from 9.74 ng/L (BPS) to 137 ng/L (BPA) and in sewage treatment effluent outfalls ($n = 22$) from 1.12 ng/L (ethinylestradiol) to 242 ng/L (BPA). PFCs and plasticisers dominated levels of selected contaminants in sampled waters and pharmaceuticals were not detected upstream of the very first STW effluent outfall in respective rivers (Fig. 4).

Among overall pooled data, significant differences between mean contaminant concentrations at sampling locations were found (one-way ANOVA) for acetaminophen ($p = 0.044$), diclofenac ($p < 0.001$), BPS ($p = 0.010$), and PFOA ($p = 0.031$). Tukey's HSD post-hoc analysis revealed statistically different ($p < 0.05$) mean contaminant concentrations at river source/headwaters and/or upstream of STW effluent outfalls, which were both lower than those of the STW effluents and/or river water downstream of respective STW effluent outfalls (Table 3).

Investigation of similar patterns within individual rivers (non-pooled data) revealed differences among mean contaminant concentrations between sampling locations for diclofenac within the Hogsmill and Blackwater Rivers (one-way ANOVA $p < 0.001$ and $p = 0.038$ respectively) as well as benzoylecgonine (one-way ANOVA $p = 0.002$) and HAP (one-way ANOVA $p = 0.02$) in the Hogsmill river only.

In the Hogsmill River (Table 3), mean concentrations of benzoylecgonine and HAP were found to be higher upstream of STW effluents than in source/headwaters ($p = 0.002$ and 0.005 respectively). Similarly, upstream of STW effluent outfall mean concentrations for benzoylecgonine and HAP (31.3 ng/L and 75.4 ng/L respectively) were higher than those detected in the Hogsmill STW effluent itself (2.37 ng/L, $p = 0.004$ and 11.2 ng/L, $p = 0.004$ respectively), higher than those detected 250 m downstream from the Hogsmill STW effluent outfall (5.10 ng/L, $p = 0.043$ and 20.4 ng/L, $p = 0.048$ respectively), and higher than those detected 1000 m downstream from the Hogsmill STW effluent outfall (4.93 ng/L, $p = 0.038$ and 15.1 ng/L $p = 0.014$ respectively). Here (In the Hogsmill River), STW effluent appeared to dilute levels of both benzoylecgonine (a urinary metabolite of cocaine) and HAP (transformation product of BPA). The exact source of these contaminants upstream of the only STW effluent discharge into the Hogsmill River is not clear. However, hydroxyacetophenone was previously shown to enter rivers via street runoff, perhaps through contact with polycarbonate water pipes or as a result of vehicle (i.e., tyres) traffic (Wilkinson et al., 2016b). Although speculative, in addition to STW effluent, benzoylecgonine may also be introduced to rivers via untreated sources (e.g., campgrounds) as other PPCPs/ECs have been indicated to influence river chemistry via such sources (Kostich and Lazorchak, 2008). Furthermore, while metabolites are known to be eliminated from the body via conjugation (Kumar et al., 2012) and conjugates may be de-conjugated in both STWs and rivers (Kumar et al., 2012), higher concentrations of benzoylecgonine upstream of STW effluent outfalls may be explained by in-river de-conjugation of the conjugated metabolite. Similarly, higher levels of HAP may be explained by natural breakdown of BPA in rivers such as by aquatic bacteria (Omoike et al., 2013) or perhaps via photochemical degradation (López-Serna et al., 2012).

Table 2
Mean concentrations (ng/L) of selected contaminants in the aqueous phase of water ($n = 88$) at headwaters of respective rivers, upstream from STW effluent outfalls, in the STW effluent and downstream ('Down') of STW effluent outfalls by 250 m and 1000 m.

(ng/L)										
Compound type	Compound	Headwaters $n = 6$	Upstream $n = 19$	STW effluent $n = 22$	Down[a] 250 m $n = 19$	Down[a] 1000 m $n = 19$	Overall Mean $n = 88$	Detection Freq. (%)	Range (ng/L)	SD (ng/L)
Pharmaceuticals	Acetaminophen	ND	20.8	47.5	15.1	10.4	21.9	82.8	<0.93–415	64.1
	Diclofenac	ND	11.4	86.5	60.3	52.9	50.6	73.9	<0.96–253	63.5
	Ethinylestradiol	ND	ND	0.932	ND	ND	0.23	3.13	<0.98–10.2	1.57
Illicit drugs	Amphetamine	ND	ND	ND	ND	ND	ND	0		
	Benzoylecgonine	ND	11.4	12.4	11.7	11.0	10.8	81.3	<1.06–107	22.8
	Methamphetamine	ND	ND	ND	ND	ND	ND	0		
Plasticisers	BPA	22.7	121	242	154	131	159	100	<3.87–1420	251
	BPS	0.970	9.18	30.8	11.7	9.18	14.7	95.3	<1.02–306	41.5
	HAP	4.89	70.0	75.9	56.2	49.6	59.7	96.9	<1.04–327	85.7
Perfluorinated compounds	PFBS	ND	20.4	42.7	40.3	41.4	34.9	77.8	<1.13–115	32.4
	PFNA	2.75	16.7	25.3	32.5	23.9	23.8	93.8	<0.75–209	44.5
	PFOA	2.33	23.7	33.5	24.6	21.5	25.9	90.7	<1.13–189	31.6
	PFOS	2.41	17.7	27.5	23.8	17.8	20.3	87	<1.52–119	32.5

[a] Downstream from sewage treatment work effluent outfal.

STW effluents largely dominated contributions of human pharmaceuticals acetaminophen and diclofenac ($p = 0.044$ and $p < 0.001$ respectively) to downstream flow with other compounds not presenting significant differences among location means in both overall (pooled) and river-by-river analysis (Tables 3 and 4). *t*-tests pairing upstream contaminant concentrations to those at 250 m and 1000 m downstream of STW effluent discharges (Table 4) showed that STW effluent affected mean downstream concentrations for diclofenac ($p < 0.001$), HAP ($p < 0.05$), BPA ($p < 0.04$), PFBS ($p < 0.005$) and PFOS ($p < 0.015$). Mean HAP concentrations upstream of STW effluents (40.7 ng/L) were higher than those at 1000 m downstream (25.7 ng/L, $p = 0.043$) indicating STW effluent diluted mean HAP levels. Other than HAP, all statistically different mean concentrations were higher than those at respective upstream locations than those at 250 m ($p < 0.05$) and 1000 m ($p < 0.05$) downstream of STW effluent discharges. Positive differences in mean downstream levels of diclofenac, BPA, PFBS and PFOS indicate that STW effluent discharges may be the most significant source of these contaminants into the studied river systems. However, it should be noted that in whole river systems, ANOVA followed by Tukey HSD tests only revealed STW effluent-dependent contributions between upstream and subsequent downstream locations (vs. source/headwaters and subsequent downstream locations) for diclofenac. Although speculative, such findings may be explained by three possibilities: 1) contributions of diclofenac via STW effluent are more significant than other compounds, 2) conjugated diclofenac may enter rivers via STW effluents which become deconjugated downstream, and 3) diclofenac is not immobilized by other environmental compartments (i.e., suspended particulate material, sediment, aquatic plants and organisms) as preferentially as other contaminants.

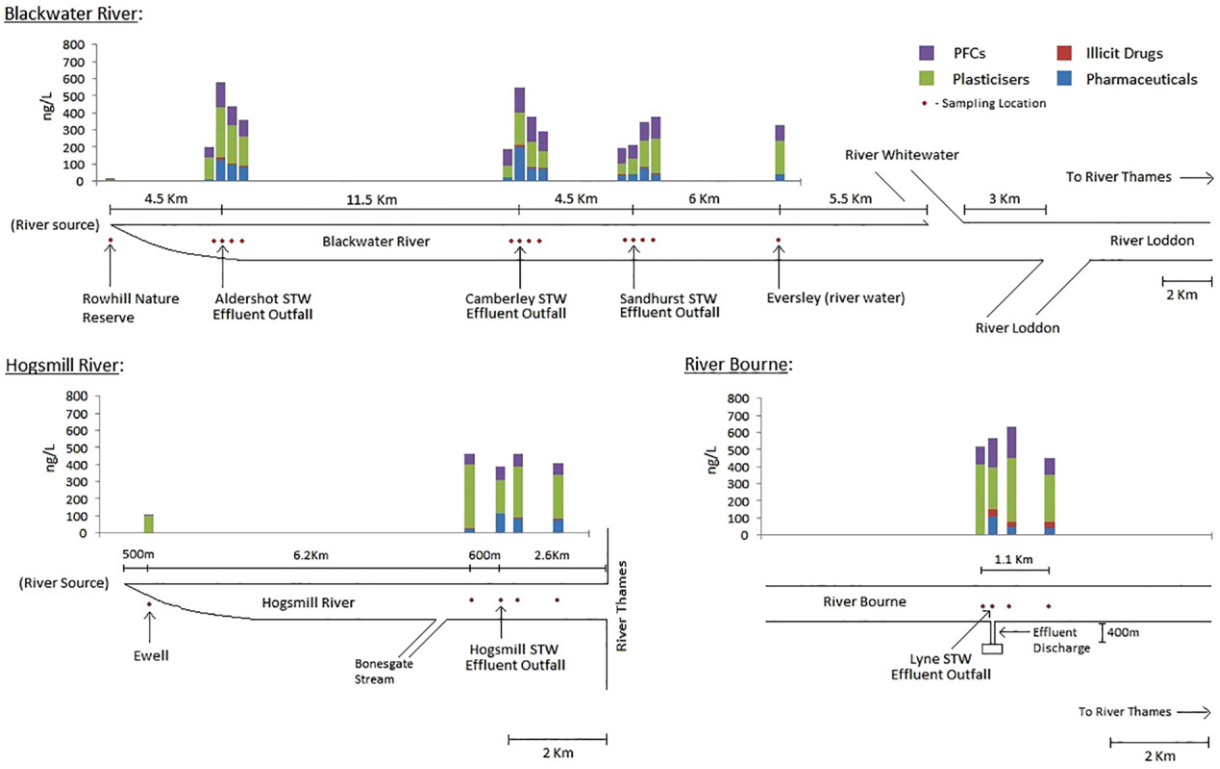

Fig. 4. Spatial distribution of aqueous cumulative PPCPs/ECs classes (Σ_{aq} PFCs, Σ_{aq} plasticisers, Σ_{aq} illicit drugs and Σ_{aq} pharmaceuticals).

Table 3
Statistically significant ANOVA followed by Tukey post-hoc test results.

Compound	ANOVA	Tukey		Mean	*p*-value	95% CID	Mean 95%
	p-value	Multiple comparisons		(ng/L)		(ng/L)[a]	CID (ng/L)[a]
Overall analysis (data from all rivers analysed together):							
Acetaminophen	0.044	River source	vs…	ND			ND
			STW upstream	5.22	NSD		
			STW effluent	9.71	0.026	1.19–79.1 (less)	9.71 (less)
			STW down 250 m	8.4	0.043	1.04–67.8 (less)	8.40 (less)
			Farthest downstream	5.56	NSD		
Diclofenac	<0.001	River source	vs…	ND			
			STW upstream	7.07	NSD		
			STW effluent	73.8	0.001	6.04–217 (less)	73.8 (less)
			STW down 250 m	44.8	0.023	0.35–164 (less)	44.8 (less)
			STW down 1000 m	39.4	0.04	0.03–153 (less)	39.4 (less)
		Upstream	vs…	5.07			
			STW effluent	73.8	<0.001	7.24–99.8 (less)	40.2 (less)
			STW down 250 m	44.8	0.007	0.71–64.7 (less)	19.7 (less)
			STW down 1000 m	39.4	0.019	0.18–58.2 (less)	16.2 (less)
BPS	0.010	River source	vs…	1.55			
			STW upstream	7.91	0.012	1.29–20.4 (less)	5.10 (less)
			STW down 250 m	8.91	0.005	1.44–22.9 (less)	5.74 (less)
			STW down 1000 m	6.73	0.032	1.08–17.4 (less)	4.33 (less)
			Farthest downstream	5.37	NSD		
PFOA	0.031	River source	vs…	1.15			
			Farthest downstream	53.6	0.009	1.18–130 (less)	39.0 (less)
River-by-river analysis:							
Blackwater River:							
Diclofenac	0.038	Upstream	vs…	9.95			
			STW effluent	79.6	0.046	0.001–132 (less)	33.3
Hogsmill River:							
Diclofenac	<0.001	River source	vs…	ND			
			STW effluent	111	<0.001	40.9–214 (less)	111 (less)
			STW down 250 m	77.7	<0.001	22.0–167 (less)	77.7 (less)
			STW down 1000 m	70.9	<0.001	18.5–157 (less)	70.9 (less)
		Upstream	vs…	1.85			
			STW effluent	111	<0.001	33.6–157 (less)	83.9 (less)
			STW down 250 m	77.7	<0.001	16.7–117 (less)	55.6 (less)
			STW down 1000 m	70.9	<0.001	13.7–109 (less)	49.8 (less)
Benzoylecgonine	0.002	River source	vs…	ND			
			STW upstream	31.3	0.002	3.60–271 (less)	31.3 (less)
		Upstream	and…	31.3			
			River source	ND	0.002	3.60–271 (more)	31.1 (more)
			STW effluent	2.37	0.004	2.24–77.6 (more)	13.2 (more)
			STW down 250 m	5.1	0.043	1.05–35.5 (more)	6.13 (more)
			STW down 1000 m	4.93	0.038	1.09–37.2 (more)	6.35 (more)
HAP	0.002	River source	vs…	7.76			
			STW upstream	75.4	0.005	1.95–47.9 (less)	9.72 (less)
		Upstream	vs…	75.4			
			River source	7.76	0.005	1.95–47.9 (more)	9.72 (more)
			STW effluent	11.2	0.004	1.82–25.1 (more)	6.72 (more)
			STW down 250 m	20.4	0.048	0.00–13.8 (more)	3.69 (more)
			STW down 1000 m	15.1	0.014	1.35–18.6 (more)	4.98 (more)

CID–confidence interval of the difference, NSD–not significantly different, ND–not detected.
Note: Only statistically significant results are shown in Table 3.
[a] 'Less' signifies that the 95% CID range is below that of the other respective paired mean.

3.2. Spatial distribution of PPCPs/ECs bound to suspended particulate material (SPM)

Six of the thirteen selected analytes were identified in SPM extracts (Table 5) above analytical detection limits and only four above quantifiable limits (diclofenac, HAP, PFNA and PFOS). Among identified compounds, detection frequencies ranged from 44% (PFOA) to 94% (HAP). Maximum levels ranged from 119 ng diclofenac/g dry SPM (0.72 ng/L, when corrected for SPM mass/L) and 250 ng PFNA/g dry SPM (0.07 ng/L, when corrected for SPM mass/L) to 425 ng HAP/g dry SPM (1.76 ng/L, when corrected for SPM mass/L) and 6800 ng PFOS/g dry SPM (44.0 ng/L). It should be noted that the amount of SPM >2.7 μm in diameter in collected water was consistently low. Furthermore, fine SPM (2.7 μm ≥ Φ > 0.7 μm) has been shown to contain greater amounts of some PPCPs such as BPA and ethinylestradiol than course (Φ ≥ 2.7 μm) SPM (Yang et al., 2016). However, here, fine SPM (of a particle diameter between 0.45 μm and 2.7 μm) was shown to account for <22% of total SPM mass. The protocol for extraction of PPCPs/ECs presented here may thus slightly under-represent the bound-fraction and should be further investigated.

Mass of SPM separated from collected water ranged from 1.8 mg/L to 11.2 mg/L (mean 6.12 mg/L). Using scanning electron microscopy (SEM), particulate material showed a relatively uniform and compacted consistency when dried on glass microfibre filters (Fig. 5). Highest levels of SPM were found in the upper Blackwater River and lowest in the Hogsmill River (Supplementary Table 3). For this reason, concentrations of selected analytes extracted from SPM are reported here in both ng analyte/g dry weight (dw) SPM and ng analyte/L of water the SPM was extracted from. Where the amount of SPM in water is low, ng/L units may provide a more efficient perspective on the level of present

Table 4
Statistically significant *t*-tests results pairing sampling locations up- and downstream from STW effluent discharges.

Compound	Pairs		p–Value	Mean (ng/L)	95% CID (ng/L)	Mean 95% CID (ng/L)
Acetaminophen	NSD					
Diclofenac	Upstream	Vs.		3.89		
		Effluent	<0.001	65.5	18.9–62.3 (less)	37.4 (less)
		250 m Down	<0.001	39.6	8.24–33.3 (less)	18.6 (less)
		1000 m Down	<0.001	35.3	6.71–28.4 (less)	15.7 (less)
Ethinylestradiol	Insufficient data					
Benzoylecgonine	NSD					
Amphetamine	ND					
Methamphetamine	ND					
HAP	Upstream	Vs.		40.7		
		Effluent	0.007	17.8	1.29–4.07 (higher)	2.29 (higher)
		250 m Down	NSD	30.5	NSD	NSD
		1000 m Down	0.043	25.7	1.02–2.45 (higher)	1.57 (higher)
BPA	Upstream	Vs.		46.1		
		Effluent	0.018	102	1.16–4.22 (less)	2.22 (less)
		250 m Down	0.002	95.3	1.35–3.24 (less)	2.07 (less)
		1000 m Down	0.035	79.3	1.04–2.84 (less)	1.72 (less)
BPS	NSD					
PFBS	Upstream	Vs.		21.7		
		Effluent	<0.001	47.6	13.3–38.7 (less)	25.9 (less)
		250 m Down	0.001	43.6	10.5–33.5 (less)	22.0 (less)
		1000 m Down	0.003	40.9	7.3–31.2 (less)	19.3 (less)
PFNA	NSD					
PFOA	NSD					
PFOS	Upstream	Vs.		9.14		
		Effluent	<0.001	18.2	1.48–2.69 (less)	1.99 (less)
		250 m Down	0.002	14.3	1.21–2.02 (less)	1.56 (less)
		1000 m Down	0.014	12.4	1.07–1.71 (less)	1.35 (less)

CID–confidence interval of the difference, NSD–not significantly different, ND–not detected.

'Less' signifies that the 95% CID range is below that of the other paired mean.

'Higher' signifies that the 95% CID range is above that of the other paired mean.

Table 5
Levels of studied PPCPs/ECs in aqueous and bound phases of river water upstream from STW effluent outfalls, in the STW effluent, as well as downstream ('Down') of STW effluent outfalls by 250 m and 1000 m.

		Dissolved in Water (ng/L)				Bound to SPM (ng/L)				Bound to SPM (ng/g dry SPM weight)				Detection Freq. (%) in SPM
Compound Type	Compound	Upstream of STW	STW Effluent	Down 250 m	Down 1000 m	Upstream of STW	STW Effluent	Down 250 m	Down 1000 m	Upstream of STW	STW Effluent	Down 250 m	Down 1000 m	
Pharmaceuticals	Acetaminophen	<LOQ	11.6	<LOQ	<LOQ	ND	ND	ND	ND	ND	ND	ND	ND	0
	Diclofenac	3.23	95.9	50.0	40.9	ND	<LOQ	<LOQ	0.72	ND	<LOQ	<LOQ	119	56.3
	Ethinylestradiol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0
Illicit Drugs	Benzoylecgonine	<LOQ	6.38	1.63	<LOQ	ND	ND	ND	ND	ND	ND	ND	ND	0
	Amphetamine	<LOQ	<LOQ	<LOQ	<LOQ	ND	ND	ND	ND	ND	ND	ND	ND	0
	Methamphetamine	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0
Plasticisers	HAP	86.7	47.7	26.5	21.9	0.88	0.84	0.53	<LOQ	137	123	84.2	<LOQ	93.8
	BPA	13.4	85.2	38.3	40.4	ND	ND	ND	ND	ND	ND	ND	ND	0
	BPS	7.94	4.33	5.76	4.62	ND	ND	ND	ND	ND	ND	ND	ND	0
Perfluorinated	PFBS	10.7	71.6	58.7	71.4	ND	<LOQ	<LOQ	<LOQ	ND	<LOQ	<LOQ	<LOQ	50
Compounds	PFNA	1.46	1.55	1.27	1.00	0.33	0.29	0.36	<LOQ	13.5	48.6	91.4	<LOQ	75.0
	PFOA	6.12	8.38	6.64	6.28	ND	ND	<LOQ	<LOQ	ND	ND	<LOQ	<LOQ	43.8
	PFOS	11.0	23.8	15.9	15.5	3.55	14.3	6.32	1.35	754	2830	1490	336	81.3

LOQ – level of quantification, ND – not detected.

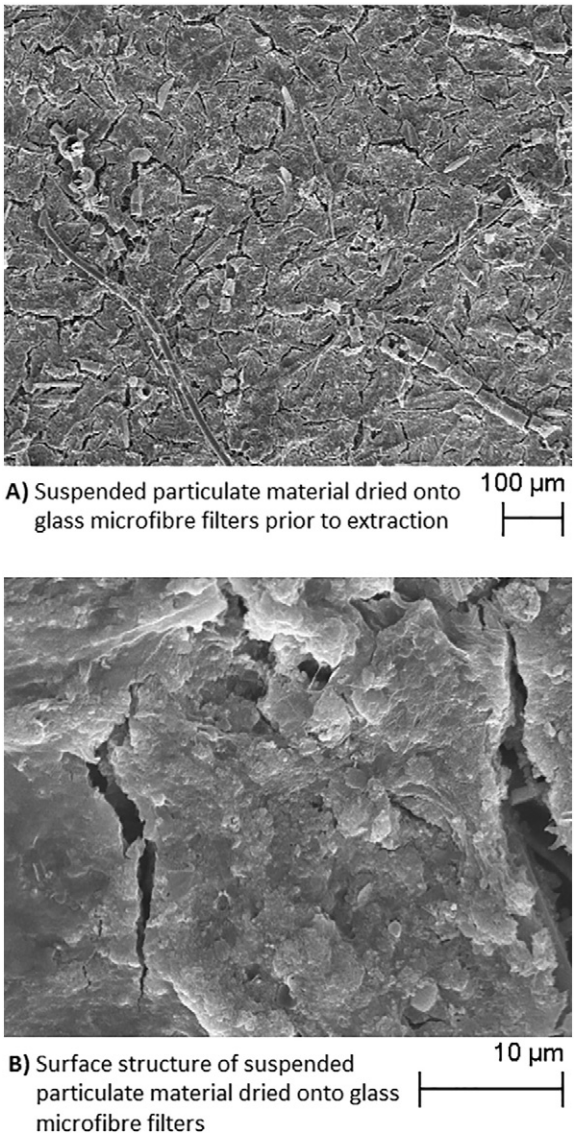

Fig. 5. SEM micrograph showing the uniformity of dried SPM on glass microfibre filters (A) and surface structure (B) using scanning electron microscopy.

contaminants bound to suspended material. For example, where 6.12 mg/L SPM is present in water, 163 L of water would be necessary to extract 1 g of SPM. Here a ng/g dw unit may potentially be misleading when considering relative amounts of target analytes bound to suspended material vs. dissolved in water.

Overall, levels of selected contaminants bound to SPM were dominated by PFCs and plasticisers while human pharmaceuticals were only marginally associated with suspended material, perhaps due to hydrophobicity (Table 5). No significant trend was identified in the spatial distribution of SPM-bound contaminants up- and downstream of STW effluent discharges using one-way ANOVA tests. Using a paired *t*-test, levels of bound PFOS upstream of STW effluent discharges (mean = 754 ng/g dw SPM, 3.55 ng/L when corrected for SPM mass/L) were found to be statically different from levels in STW effluent ($p = 0.033$, mean = 2830 ng/g dw, 14.3 ng/L when corrected for SPM mass/L) and near statistically different from levels found 250 m downstream from STW effluent discharges ($p = 0.054$, mean = 1490 ng/g dw, 6.32 ng/L when corrected for SPM mass/L). No other significant distribution trend was identified for bound contaminants.

3.3. Partition between bound and dissolved phases

Selected analytes were almost exclusively found dissolved in sampled waters (Table 5). Of the compounds detected bound to SPM above respective limits of detection, only PFNA (Kd = 31.4) and PFOS (Kd = 75.5) showed mean partition coefficients >30 (Table 6). Mean partition coefficients for diclofenac (Kd = 0.26) and HAP (Kd = 1.84) were consistently >2, while mean Kd values were lowest for both PFNA and PFOS 1000 m downstream of respective STW effluent discharges (Kd = 24.1 and 21.7 respectively). Mean bound PFOS accounted for 9% (1000 m downstream of STW effluent discharges) to 60% (in STW effluents) of all detected PFOS (bound PFOS plus aqueous PFOS) in respective water samples. Similarly, bound PFNA accounted for 16% (1000 m downstream of STW effluent discharges) to 28% (250 m downstream from STW effluent discharges) of all detected PFNA (bound PFNA plus aqueous PFNA).

PFCs showed the greatest association with SPM in addition to the lowest pKa values (<1) and highest log Kow values (>6) of studied compounds (Table 1). Here, length of a fluorinated carbon chain, increased hydrophobicity and acidity appeared to be associated with contaminant adsorption to SPM. Amphipathic compounds containing a relatively long and linear hydrophobic region (8 or more carbons) and an acidic hydrophilic region showed greatest association with SPM. The fluorinated 8-carbon chained PFOS and 9-carbon PFNA were the only PFCs presenting Kd values > respective limits of analytical quantification. Such findings are consistent with those reported elsewhere and suggest short chain PFCs are likely to occur primarily in the aqueous phase (e.g., Ahrens et al., 2010; Kwadijk et al., 2010; Knepper and Lange, 2011; Zhao et al., 2016; Nguyen et al., 2016). Interestingly, unlike previous studies where conflicting results are, at times, presented regarding adsorption to aquatic solid material such as sediment (e.g., Higgins and Luthy, 2006; Kwadijk et al., 2010) and SPM (e.g., Nguyen et al., 2016) between carboxylic vs. sulfonic acid PFCs, no clear relationship was observed here with adsorption to aquatic SPM. This finding may indicate that

Table 6
Distribution coefficient (Kd) of selected PPCPs/ECs between bound and aqueous phases of collected water upstream from STW effluent outfalls, in the effluent and downstream ('Down') of the effluent outfalls (250 m and 1000 m).

Compound type	Compound	Upstream of STW	STW effluent	Down 250 m	Down 1000 m	Mean Kd	Mean % bound
Pharmaceuticals	Acetaminophen	ND	ND	ND	ND		
	Diclofenac	ND	ND	<LOQ	1.03	0.26	<1
	Ethinylestradiol	ND	ND	ND	ND		
Illicit drugs	Benzoylecgonine	ND	ND	ND	ND		
	Amphetamine	ND	ND	ND	ND		
	Methamphetamine	ND	ND	ND	ND		
Plasticisers	Hydroxyacetophenone	1.58	2.58	3.18	<LOQ	1.84	1.41
	Bisphenol-A	ND	ND	ND	ND		
	Bisphenol-S	ND	ND	ND	ND		
Perfluorinated compounds	PFBS	ND	<LOQ	<LOQ	<LOQ	<LOQ	
	PFNA	9.20	31.4	71.9	24.1	34.1	21.5
	PFOA	ND	ND	<LOQ	<LOQ		
	PFOS	68.3	119	93.3	21.7	75.5	38.5

Table 7
Per capita contribution of studied contaminants to receiving rivers (μg/person/day).

Compound type	Compound	Aldershot effluent	Camberley effluent	Chertsey effluent	Hogsmill effluent	Guildford effluent
	Location	*Rural*	*Suburban*	*Suburban*	*Urban*	*Suburban*
	Population equivalent	*37,000*	*140,000*	*88,400*	*383,000*	*86,800*
	Treatment	*AST*	*AST*	*TFC*	*AST*	*AST/TFC*[a]
Pharmaceuticals	Acetaminophen	1.53	19.4	20.6	2.64	39.2
	Diclofenac	15.5	33.4	12.2	ND	9.27
	Ethinylestradiol	ND	ND	ND	2.85	1.50
Illicit drugs	Amphetamine	ND	ND	ND	ND	ND
	Benzoylecgonine	1.60	2.48	12.2	0.157	5.86
	Methamphetamine	ND	ND	ND	ND	ND
Plasticisers	BPA	25.9	22.1	58.6	0.836	143
	BPS	1.96	4.98	0.987	11.6	59.2
	HAP	11.6	21.8	11.8	3.05	62.6
Perfluorinated compounds	PFBS	7.39	13.2	9.75	1.38	6.18
	PFNA	7.01	16.9	6.75	0.888	1.61
	PFOA	1.75	5.15	19.7	2.92	6.52
	PFOS	3.21	2.99	15.7	15.4	9.25

AST - Activated Sludge Treatment, TFC - Trickling Filter Contact.
[a] 50/50 AST/TFC.

compound hydrophobicity is more influential on adsorption to SPM than acidity, however this finding warrants further investigation.

3.4. Daily loads of studied contaminants

Four sites were selected to monitor contaminant loads up- and downstream from STW effluent outfalls, Aldershot, Camberley, Hogsmill and Chertsey (Fig. 2). These sites were chosen based on their proximity to Environment Agency UK river flow monitors and information available on STW discharge flow rates. Contaminants introduced into the aquatic environment solely via human use (e.g., the cocaine metabolite benzoylecgonine, and pharmaceuticals acetaminophen, diclofenac and ethinylestradiol) showed highest mean loads in STW effluent. Here, 0.812 ± 0.81 g/day benzoylecgonine, 1.42 ± 1.1 g/day acetaminophen, 2.77 ± 3.2 g/day diclofenac and 0.273 ± 0.21 g/day ethinylestradiol entered the rivers via the studied STW effluent outfalls (Supplementary Information Table 3). Loads of pharmaceuticals and benzoylecgonine decreased in downstream flow, indicating either these compounds degraded or distributed to other aquatic compartments (e.g., SPM, sediment or biota).

Plasticiser loads were generally more variable than those of pharmaceuticals. Here, BPA and its main transformation product HAP exhibited lowest loads in STW effluent outfall (2.72 ± 2.1 g/day BPA and 1.57 ± 0.99 g/day HAP) while loads in river water ranged from 8.92–13.88 g/day BAP and 2.45–3.37 g/day HAP, generally not varying >20% (Supplementary Information Table 3). As these compounds have previously been shown to enter rivers via runoff from streets and runoff collection ponds near streets (e.g., Wilkinson et al., 2016a, 2016b) such variability present in these data may be due to the presence of non-STW inputs within the course of studied rivers. It should be noted that a comprehensive evaluation of such poorly-characterised, non-STW, sources was not within the scope of this work but warrants further investigation.

Perfluorinated compounds typically showed highest loads 250 m downstream of STW effluent discharges and lowest upstream (Supplementary Information Table 3). Between 250 m and 1000 m downstream of STW effluent discharges, largest decreases in loads was observed for long-chain (>7 carbons) PFCs. Here, mean PFNA and PFOS loads decreased by 38% and 31% respectively between 250 m and 1000 m downstream from STW effluent outfalls. This finding may indicate that increased hydrophobicity and PFC chain length may influence either compound partition to other compartments in the aquatic environment or environmental degradation. These variables were associated with compound partition to SPM in this work and may explain the decrease in PFC loads downstream loads here.

Contaminant loads in STW outfall were normalised to population equivalent of each facility giving a per capita contribution of target contaminants into receiving rivers (Table 7). Mean daily contributions per person ranged from 0.157 μg of benzoylecgonine/person/day (a cocaine metabolite) in the urban Hogsmill STW effluent to 58.6 μg of BPA/person/day in the suburban Chertsey STW effluent. Overall, highest contributions per capita were demonstrated for pharmaceuticals and plasticisers and contributions were generally lowest from facilities using activated sludge treatment over a trickling filter contact process.

4. Conclusions

Here, we present one of largest and most detailed studies of the spatial distribution and fate of PPCPs/ECs focusing on both dissolved and bound fractions of studied waters, from headwaters through the course of respective rivers. This large work ($n > 100$) highlights the need to view river systems as dynamic and responsive carriers of environmental pollutants. Notable findings include six key determinations: 1) plasticisers and PFCs are present in studied source/headwaters (a novel finding); 2) pharmaceutical compounds are largely introduced into rivers via STW effluent outfalls; 3) selected non-pharmaceutical compounds, such as PFCs, may enter rivers through significant sources not related to STW effluent outfalls; 4) transformation products such as hydroxyacetophenone (BPA transformation product) may occur at higher concentration upstream of STW effluent outfalls and become diluted in downstream flow (another novel finding), 5) the establishment of environmental Kd-values for partition to SPM, and 6) other than amphipathic and acidic long chain PFCs (C > 7), studied contaminants are found almost exclusively dissolved in the collected, non-turbid, water (another novel finding).

The data presented here uniquely highlights the need to elucidate the occurrence and fate of conjugated pharmaceuticals and metabolites in river water and STW effluent. Although speculative, conjugated chemicals originating from STW effluent outfalls may become de-conjugated in the aquatic environment thereby increasing respective downstream concentrations as compared to effluent itself. Such a pattern may have been observed here with acetaminophen and benzoylecgonine, the first of similar studies to observe this phenomenon. The possibility of in-river de-conjugation of acetaminophen originating from STW effluent outfalls may slowing the overall net rate of downstream attenuation is an overlooked and poorly researched subject. Similarly, in-river processes such as photochemical degradation and biotransformation should be considered for their potential roles in increasing concentrations of transformation products between STW

effluent outfalls and subsequent downstream sampling points. For example, here, this may be demonstrated by the observed higher concentrations of BPA transformation product hydroxyacetophenone in samples collected upstream of STW effluent outfall and subsequent downstream dilution. This is again the first work to quantify this trend in multiple river systems.

An interdisciplinary approach to the study of environmental chemistry is paramount to delivering well-informed, high-impact and relevant research. Here, the levels of 13 selected PPCPs/ECs were not found above those commonly associated with biological significance. However, synergistic effects of those contaminates evaluated here and others not studied is likely to affect biological disruption thresholds. Furthermore, grab sampling conducted in conjunction with passive sampling may result in a more reliable and less time-intense option for assessing relative time-weighted average spatial distribution of organic contaminant concentrations that may be of biological significance (Jones-Lepp et al., 2012; Vystavna et al., 2012). Such research is the nexus between environmental chemistry and toxicology and likely to dominate research in years to come.

Conflict of interests

Nothing to declare.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2017.03.167.

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