**Assessing the role of the “estuarine filter” for emerging contaminants:
pharmaceuticals, perfluoroalkyl compounds and plasticisers in
sediment cores from two contrasting systems in the southern U.K.**

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ABSTRACT

The environmental occurrence, fate and ecotoxicity of emerging contaminants (ECs) has been the subject of increasing research, policy and public concern over the past two decades. While a wide range of publications have examined the environmental persistence and sediment/soil interactions of ECs following their discharge into aquatic environments, the extent to which ECs are sequestered in estuarine sediments, and the impact of this on their environmental persistence and supply to the ocean, in comparison remains unclear. This Article examines the environmental concentrations of seven, relatively water-soluble and environmentally mobile, ECs (including pharmaceuticals, perfluoroalkyl compounds, and plasticisers) in dated intertidal saltmarsh cores from two contrasting estuarine sites in the southern U.K. (one heavily urbanised/industrial, the other non-urbanised). Mean sediment EC concentrations are similar in both estuarine systems (in the range 0.1 (acetaminophen) to 17 (4-hydroxyacetophenone) ng/g dry weight). Despite their variable reported Log K_{ow} values (from *ca.* 0.5 to > 7), the ECs are all apparently mobile in the marsh systems studied, and where subsurface concentration maxima are present these most likely relate to local flushing or diffusive processes and cannot be clearly linked to likely input trends or changes in sediment geochemistry (including sedimentary organic carbon content). The “estuarine filter” here, at least with respect to intertidal saltmarsh sediments, shows reduced potential to sequester the seven ECs examined and mediate their supply to coastal and shelf environments.

46   **Keywords:** Emerging contaminants; saltmarsh; pharmaceuticals; perfluorinated compounds;
47   plasticisers; estuary.

49   **1. Introduction**

50   The environmental occurrence, fate and ecotoxicity of emerging contaminants (ECs - commonly
51   defined as any compound, both synthetic and natural, in the environment whose presence is
52   not routinely monitored and shows the potential to cause ecological disruption (Smital, 2008)),
53   has been the subject of increasing research, policy and public concern over the past two
54   decades (e.g. Kolpin et al., 2002; Petrie et al., 2015; Wilkinson et al., 2015; Costa et al., 2019;
55   Gaston et al., 2019). Emerging contaminants include a wide range of pharmaceutical residues
56   (*inter alia* illicit drug metabolites), perfluoroalkyl compounds, plasticisers, nanomaterials and
57   microplastics derived from various sources, notably waste water treatment works, but also
58   from non-point sources such as run-off from streets and agricultural land (Richardson and
59   Ternes, 2018). Despite their presence at typically µg/L or sub-µg/L concentrations, residues of
60   several ECs have been observed to cause biological disruption/dysfunction, and generational
61   effects, in exposed organisms via a number of mechanisms including endocrine dysfunction
62   (Chen et al., 2018; Thomas et al., 2018).

63   A wide range of publications have examined the environmental persistence, sediment/soil
64   interactions and breakdown processes of ECs once discharged into aquatic environments, with
65   several papers noting the interaction and burial / persistence of ECs in river bed and other
66   sediments. Indeed, Thiebault et al. (2017) note the preservation of general trends in historical
67   loading (over the last 50 years) of eight pharmaceutical products in dated sediment cores from
68   urban sediment in Orleans, France. However, and despite the expected “salting out” effects

69 observed for a range organic contaminants with increases in salinity (Turner, 2003; Munoz et
70 al., 2017), this apparent long-term sequestration and historical preservation may be less
71 effective in higher salinity settings such as estuaries (e.g. Labadie et al., 2007; Zhao et al., 2015).
72 This is important as estuaries, and estuarine sediments, play an important role in mediating the
73 transfer of a range of organic and inorganic contaminants to the ocean through the action of
74 the so-called “estuarine filter”, where elements and compounds are sequestered in fine
75 intertidal and subtidal sediments and thus prevented from directly entering marine
76 environments (Cundy and Croudace, 2017). While a number of authors have reported
77 sedimentary concentrations of various ECs in estuaries, the extent to which ECs are removed
78 and sequestered in estuarine sediments, and the impact of this on their degradation and
79 environmental persistence (particularly across the strong Eh/pH gradients observed in
80 subsurface estuarine sediments) remains relatively unclear. Here, we adapt a recently
81 developed analytical method (Wilkinson et al., 2016) using high performance liquid
82 chromatography (HPLC) tandem mass spectrometry (MS/MS) to simultaneously examine the
83 environmental concentrations of seven ECs (which have potential medium- to long-range
84 mobility through fluvial to marine systems due to their relative hydrophilicity, including
85 pharmaceuticals, perfluoroalkyl compounds, and plasticisers) in dated intertidal saltmarsh cores
86 from two contrasting estuarine sites in the southern U.K. We examine the downcore
87 distribution of these ECs to determine (a) to what extent they persist in the sediment column,
88 (b) whether downcore trends in EC concentration can be correlated with local industrial and
89 urban activity, and (c) the potential role of these sediments, and the estuarine filter as a whole,
90 in mediating EC supply to the coastal and shelf environments.

2. Materials and Methods

2.1 Study area

Sediment cores were collected in 2016 from the Hythe saltmarsh system (on the western side of Southampton Water, U.K.), and the southern Beaulieu river (Figure 1). Southampton Water is a 10 km long and 2 km wide estuary that is one of the largest estuarine systems in the southern UK (Quaresma et al., 2007). The rivers Test and Itchen are the main contributors of fresh water to the estuary, supplying approximately $1.54 \times 10^6 \text{ m}^3$ of fresh water per day (Hydes, 2000) and 2×10^4 tons of total suspended sediment per year (Velegarakis et al., 1999). The estuary hosts a range of coastal ecosystems such as saline lagoons, saltmarshes and mudflats that support a range of breeding and migratory birds, crabs and other organisms (JNCC, 2017). The head of the estuary is highly urbanized, with the city of Southampton (population 256,459 (2018 data, Southampton City Council, 2019), covering an area approximately 51.8 km^2) and Southampton port (the second largest container terminal in the UK, which handles around 14 million tons of cargo each year). There is intensive industrial use of the western shore area with the large-scale Exxon Mobil oil refinery at Fawley and related industries that use the feedstock from the refinery. In contrast, the Beaulieu estuary is relatively undeveloped and lies in the New Forest National Park, an area of predominantly open heath and bog with little agriculture and very few urban areas (although it does receive sewage effluent discharges from 3 upstream continuous discharge WWTWs, with *E. coli* readings sufficiently high to historically close local clam fisheries (CEFAS, 2015).

The Hythe marsh is a *Halimione portulacoides* dominated marsh system, with patchy *Spartina* spp. and *Puccinellia maritima*, which is 1–2 km North West of the chemical industrial complex

113 and Exxon Mobil oil refinery at Fawley. This marsh area has been shown previously to retain
114 relatively undisturbed (and laterally consistent) geochemical records of temporal contaminant
115 input to Southampton Water (e.g. Cundy and Croudace, 2017). The Beaulieu site was a similar
116 mixed *Spartina spp.* and *Halimione portulacoides* marsh, located 200m north of the Royal
117 Southampton Yacht Club. Previous work in the Beaulieu marsh systems has also demonstrated
118 that these marshes retain a relatively complete and consistent record of past contaminant
119 inputs into the Beaulieu estuary (Cundy and Croudace, 1996; Thomson et al., 2002). Both sites
120 cored are significantly below the main freshwater:seawater mixing zone in each estuarine
121 system, and show near fully-marine salinities.

Figure 1. Study area: Southampton Water and the Beaulieu estuary, southern U.K. Aerial photographic images show detail of marsh areas sampled. Filled squares show locations of major wastewater treatment works (> 10,000 population equivalent) or site of smaller water company continuous wastewater discharge (Beaulieu river). Aerial photographic imagery Copyright 2020 Google. Map data Copyright 2020 Google.

2.2 Chemicals and materials

Solvents used for the extraction and chromatographic separation of the study compounds were of LC-MS grade (Honeywell Riedel-de Haën, Germany) and chemicals were of analytical quality (purity >96%) from Sigma-Aldrich (UK). The compounds selected for analysis, based on preliminary screening and chosen to represent a range of ECs chemistries, groups and potential sources (Table 1), and included the pharmaceutical acetaminophen; monomers bisphenol-S (BPS), bisphenol-A (BPA) (and its biotransformation product 4'-hydroxyacetophenone (HAP)), and the perfluoroalkyl (PFASs) compounds: PFOA, PFNA, and PFBS.

Stock solutions of each compound were prepared at 1000 mg/L in acetonitrile. Stock solutions were further diluted to intermediate solutions containing a mixture of all compounds (25 and 5 mg/L) in acetonitrile, and further diluted in the same solvent to achieve the concentration levels of 4; 20; 100; 250; and 500 µg BPA/L; 2; 10; 50; 125; 250; and 500 µg BPS and HAP/L and 0.2; 1; 5; 13; 25; 50 and 100 µg/L for the rest of the study compounds. Standards were stored at 4°C in a refrigerator until analysis.

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146 **Table 1:** List of compounds assessed, their pKa, log K_{ow} and production/usage history.

Compound	Compound type	pKa	Log K _{ow}	History
Acetaminophen	Pharmaceutical	9.38 ^a	0.46 ^a	Pain reliever and fever reducer, first discovered 1866. Introduced to the UK in 1956.
Bisphenol A (BPA)	Crosslinker in polymers and thermal paper	9.6 ^a , 9.44 ^b	3.32 ^a , 1.65 ^b	Cross-linker in polycarbonate plastics and epoxy resins production and additive in polyvinyl chloride. Invented in 1891, first synthesis in 1905, expanded use from 1930s (epoxy resins) and 1950s (polycarbonate plastics).
4-hydroxyacetophenone (HAP)	Metabolite and degradation product from BPA	8.12 ^a , 10.43 ^b	3.31 ^b	Used in cosmetics and personal care products, also metabolite and biotransformation product of BPA.
Bisphenol S (BPS)	Crosslinker in polymers and thermal paper	8.2 ^a , 8.47 ^b	1.65 ^a , 3.19 ^b	Close analogue of Bisphenol A, first manufactured in 1869 as a dye. BPS has been used as a recent substitute for BPA in an increasing number of products.
Perfluorobutane sulfonic acid (PFBS)	Perfluoroalkyl and Polyfluoroalkyl Substance (PFAS)	.-3.31 ^a	1.82 ^c	Surfactants used in various commercial and industrial applications since the 1940s.
Perfluorononanoic acid (PFNA)	Perfluoroalkyl and Polyfluoroalkyl Substance (PFAS)	<1 ^a , ~0 ^d	4.84- 7.27 ^e	
Perfluorooctanoic acid (PFOA)	Perfluoroalkyl and Polyfluoroalkyl Substance (PFAS)	2.8 ^a , ~0 ^d	6.30 ^a , 4.3 ^f	

147 ^a Derived from PubChem database, National Library of Medicine, National Center for Biotechnology Information, USA. <https://pubchem.ncbi.nlm.nih.gov/>, accessed July 2020.148 ^b Wang et al., 2002149 ^c <https://www.epa.gov/tsca-screening-tools>, accessed July 2020.150 ^d Goss, 2008151 ^e Howard and Meylan, 1997152 ^f Arp et al., 2006

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2.3 Sample preparation and extraction - ECs.

Following collection, cores were split vertically, sub-divided into 1cm depth increments and freeze-dried. Dried sediment samples (3g) were extracted with hexane and acetone (1:1) using microwave extraction (MARS 6 CEM microwave digester system, UK) following the EPA method 3546. For the determination of recovery rates in sediments from each site, and the repeatability of the extraction protocol and LC-MS analysis (Supporting Information), sediment samples (3g) were spiked with stock solution, containing a mixture of the study compounds to concentrations of 0, 50, 100, 200, and 300 ng contaminants/g sediment (in triplicate). Spiked samples were left in the dark for 24 hours before extraction to allow (a) for solvent evaporation and (b) for contaminant/sediment interaction. The slope between the amount of contaminant added and the amount found, expressed in %, was used to estimate recovery in the analysis and correct results for incomplete extraction and the effect of the matrix on the MS signal of the compounds. Enriched extracts obtained with microwave extraction were kept in 10 ml glass vials and preconcentrated to 0.5 ml with a gentle stream of nitrogen. The samples were then brought to 1 ml with methanol. Samples were analysed within 2 days and were kept in a refrigerator (4°C) until analysis. Extracts were filtered through Whatman GF/F-grade glass microfiber filters (diameter 47 mm, pore size 0.7 µm) from Fisher Scientific (Loughborough, U.K.) just before analysis. Recovery rates ranged between 7 and 28% (Table S1 – the relatively low recoveries are a consequence of the limited clean-up of compounds extracted from the sediments to ensure sub-LOD blank values – see further discussion in SI).

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179 **2.4 Sample analysis – LC-MS.**

180 The chromatographic separation of the study compounds was carried out using a C₁₈ (150 mm ×
181 2.1 mm) analytical column with a particle size of 2.6 µm, protected with a Securityguard
182 ULTRA™ UHPLC C₁₈ (4.6 mm ×2.1 mm) guard column, both from Kinetex® (Phenomenex,
183 Macclesfield, U.K.). The separation was carried out with a 1260 Infinity LC (Agilent
184 Technologies, US). Optimal separation was achieved with a binary mobile phase at a flow-rate
185 of 0.2 ml/min. The elution program was: 20-65% of acetonitrile in water (v/v), 0-15 min; and
186 return to the initial conditions in 5 min; followed by 5 min equilibration. The injection volume
187 was 10 µl. The detection of the study compounds was carried out with a 6430 triple quadrupole
188 mass spectrometer from Agilent Technologies (US), equipped with electrospray (ESI) ionisation
189 operating in positive and negative mode depending on the analyte being eluted. Data
190 acquisition was performed in multiple reaction monitoring (MRM) mode using the protonated
191 molecular ion (for ESI + mode) and the deprotonated molecular ion (for ESI – mode) as
192 precursor ion and two product ions for the quantification and confirmation of the analytes (See
193 Table S2). Optimised ionisation source working parameters for study compounds were:
194 capillary voltage, ±4 kV; nebulizer gas 15 psi; curtain gas, 11 L/min, gas temperature, 300°C.
195 Collision energy, fragmentor and electron multiplier voltage were optimised for two transition
196 ions per target analyte and internal standard using electrospray ionisation (Table S2). The
197 acquisitions software was Mass Hunter version B.04.00. The analytical method has previously
198 been validated following ICH guidelines (ICH, 2005; Wilkinson et al., 2016). Limits of detection

and limits of quantification for each of the target analytes are shown in Table S3. Quantification uncertainties ranged between 13 and 24% (Table S4).

Robust quality control measures were implemented throughout analysis. Before beginning each analytical run, the chromatography column was equilibrated using 15 injections of LC-MS grade water. Blanks, consisting of methanol, were injected after calibration standards and quality controls to ensure that cross contamination in the system did not occur. Furthermore, both quality controls and blanks were injected after every 5 environmental samples.

2.5 Sample analysis – radiometric dating, inorganic geochemistry, organic carbon and granulometry.

Sediment cores were vertically sub-sampled at 2 cm depth increments, and freeze-dried sediment samples counted for at least 16 hours on a Canberra well-type HPGe gamma-ray spectrometer to determine the activities of ^{137}Cs and other gamma-emitting radionuclides. Freeze-dried samples (as pressed pellets) were also analysed using a Philips Magix-Pro WD-XRF fitted with a 4 kW Rh target X-ray tube, to determine geochemical composition. Radiometric methods and XRF geochemical analysis methods are well established and reported in Croudace et al., 2012. Organic carbon content was estimated using the loss on ignition method (LOI, at 450°C for 24 hours), and a carbon conversion factor for saltmarsh soils (Craft et al., 1991). Particle size distribution within sediment samples was determined using a Malvern Mastersizer 2000 laser particle size analyser. One gram of homogenized sediment was mixed with 10 mL of

dispersant solution of sodium hexametaphosphate. The mixture was stirred for 5 min in order to deflocculate clay particles, after that time a small portion was taken for analysis.

2.6 Statistical analysis

A Pearson's correlation coefficient analysis was performed to evaluate the relationships between the principal sedimentary variables (granulometry, organic carbon content), and the organic micropollutants (BPA, BPS, acetaminophen, PFOA, PFNA, PFBS and HAP) for each site. Following this, a Principal Component Analysis (PCA) was conducted using the sedimentary characteristics (including bulk geochemical data) and pollution data for all samples from both sites to evaluate trends in the data between sites. A cluster analysis (Q-mode) of the environmental variables was also conducted using the sediment characteristics and organic pollutant data for each site to evaluate the relationship between these factors on a site basis and identify differences between the sites. Variables included the 34 core variables evaluated (granulometry, concentrations of major and trace elements organic carbon and emerging contaminants), which classified in a hierarchical structure using the complete linkage 1-Pearson r method. All statistical analyses were conducted using Minitab 17 (PA, USA).

3. Results and Discussion

3.1 Mean Emerging Contaminant (EC) concentrations.

Mean EC concentrations observed in saltmarsh sediments are statistically similar at Hythe and Beaulieu for all ECs examined (Table 2, p 0.05), ranging from 0.12 ng/g (acetaminophen),

241 through 0.2-5.3 ng/g (perfluoroalkyl compounds) to 7.9-16.5 ng/g (BPA, BPS and HAP). All ECs
242 examined, with the exception of PFBS, were detected at concentrations significantly above
243 instrumental detection limits in 95% of samples analysed. For acetaminophen, concentrations
244 observed at both Hythe and Beaulieu (Table 2) are significantly lower (< 10 times) than values
245 reported for urban river sediments by Thiebault et al. (2017) and Wilkinson et al. (2018), and in
246 estuarine and coastal sediments in New Zealand and South Korea (Kim et al., 2014; Stewart et
247 al., 2014). For perfluoroalkyl compounds, a number of authors have noted the presence of very
248 low (< 10 ng/g) concentrations of PFASs in estuarine and coastal sediments, near instrumental
249 detection limits or at non-detectable levels. For example, in a study of the north Bohai sea
250 region, China, Wang et al. (2011) recorded total concentrations of PFASs in sediments ranging
251 from < LOQ to 4.3 ng/g dw, with a mean of 0.62 ng/g dw. Perfluorooctane sulphonic acid (PFOS)
252 and PFOA were the dominant PFCs present. Mean sediment PFASs concentrations at Hythe and
253 Beaulieu show similar relative enrichment in PFOA compared to other PFASs, but overall
254 concentrations are significantly higher, and similar to concentrations at the upper range of
255 those previously reported for more contaminated estuarine or river systems (e.g. Kyoto, Japan
256 (Senthilkumar et al., 2007); Charleston, U.S.A. (White et al., 2015); sediments of three rivers in
257 greater London, U.K. (Wilkinson et al., 2018); and Beibu Gulf, China (Pan et al., 2020), Table 2).
258 Plasticizer concentrations (BPA, BPS, HAP) are broadly similar to those reported previously for
259 sediment cores from other coastal and marine areas, including the Pearl River Estuary (BPA up
260 to 12 ng/g, Peng et al., 2007), Sea of Japan (BPA up to 10 ng/g dw, Hong and Shin, 2009) and
261 the southern Baltic Sea (BPA < 1-32 ng/g, Lubecki and Kowalewska, 2019) (Table 2). In the
262 United Kingdom, Wilkinson et al. (2018) report mean concentrations of BPA, HAP and BPS

ranging from 4.62-14.69 ng/g d.w. sediment, ND-5.65 ng/g d.w., sediment and ND-1.4 ng/g d.w sediment respectively in three freshwater rivers in greater London. Unlike in the Wilkinson et al. (2018) study of urban freshwater rivers, however, concentrations of the biotransformation product 4'-hydroxyacetophenone were generally higher than those of its parent BPA in the estuarine systems studied here (discussed further below).

Table 2: Mean concentrations of each analyte at Hythe and Beaulieu saltmarsh sites. Previously reported data for other locations are also shown (see text for discussion).

Compound	Mean (SD) ng/g		Previously reported data (other locations) ng/g
	Hythe	Beaulieu	
Acetaminophen	0.12 (0.02)	0.13 (0.03)	<2-35 (Thiebault et al., 2017); <0.93–1.11 (Wilkinson et al., 2018); 5.5-88.5 (Kim et al., 2014); <50-145 (Stewart et al., 2014).
Bisphenol A (BPA)	10.6 (4.8)	7.9 (2.1)	1-12 (Peng et al., 2007); <LOQ-10 (Hong and Shin, 2009); <1-32 (Lubecki and Kowalewska, 2019); 4.62-14.69 (Wilkinson et al., 2018).
4-hydroxyacetophenone (HAP)	16.5 (3.7)	11.9 (2.9)	<LOQ-5.65 (Wilkinson et al., 2018).
Bisphenol S (BPS)	8.0 (1.4)	7.94 (2.2)	<LOQ-1.4 (Wilkinson et al., 2018).
Perfluorobutane sulfonate (PFBS)	0.2 (0.04)	0.2 (0.06)	<1.13–10.7 (Wilkinson et al., 2018).
Perfluorononanoic acid (PFNA)	3.6 (1.3)	4.1 (0.7)	<0.75–78.6 (Wilkinson et al., 2018).
Perfluorooctanoic acid (PFOA)	5.3 (1.2)	4.9 (1.3)	<LOQ–0.54 (Wang et al., 2011); 1.3-3.9 (Senthilkumar et al., 2007); 0.02–2.52 (White et al., 2015); <1.13–15.4 (Wilkinson et al., 2018); <0.01-0.25 (Pan et al., 2020).

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273 The similar mean concentrations ($p < 0.05$) found between the Hythe and Beaulieu cores for all
274 seven ECs examined indicates a relative ubiquity of these ECs in estuarine waters on the central
275 southern UK coast, which are readily measurable even in less industrialised and urbanised
276 settings (i.e. the Beaulieu estuary). The lack of clear enrichment in ECs in the heavily urbanised
277 and industrialised Southampton Water system over those found in the Beaulieu estuary is most
278 likely a consequence of (a) ECs input from a range of catchment sources, rather than a single
279 main or point source, and (b) mixing of these inputs on the tidal circulation prior to deposition
280 in the marsh systems. Pharmaceuticals and personal care products (e.g. acetaminophen) are
281 most likely to enter these estuaries via wastewater treatment plants and overflows from
282 combined sewers (Munro et al., 2019). There are five WWTPs directly discharging treated
283 effluent into the wider Southampton Water system with a combined population equivalence of
284 359,489 people (Portswood WWTP- p.e. 72657, Millbrook WWTP- p.e. 134433, Marchwood
285 WWTP- p.e. 74266, Woolston WWTP- p.e. 63622 and Ashlett Creek/Fawley WWTP- p.e. 14511).
286 In addition, there are at least five more discharging into rivers within 10 km of Southampton
287 Water. There are also at least nine combined sewage overflow points which will discharge
288 untreated sewage directly into Southampton Water during times of heavy rainfall. In the
289 Beaulieu River there are fewer wastewater sources, but there is a small WWTP just south of
290 Beaulieu village and 4-6 domestic properties or farms along the Beaulieu river with discharge
291 licences. There is also the Boldre WWTP which discharges into the Hatchet Stream which joins
292 with the Beaulieu River near the Southampton Yacht Club. These (and other) sources have been
293 linked with historical closure of local bivalve fisheries. In addition to inputs via WWTP discharge,

PFASs are associated with areas of train traffic, airports, military and other training installations, port and boat activity and in storm runoff from built developments and roads (Zushi and Masunaga, 2009; Xiao et al., 2012; Ahrens et al., 2015; Yan et al., 2015; Anderson et al., 2016; Wilkinson et al., 2016). While Southampton Water is a much more urbanised and industrialised system, both study estuaries share a range of these input sources, particularly boating activity and boatyards. Similarly, another important source of plastic degradation products and PFASs are plastic water pipes (Schaefer et al., 2006; Wilkinson et al., 2016). These sources are likely to provide a continual discharge to both estuarine systems, which are then mixed by tidal and other currents prior to deposition in the marsh systems.

3.2 EC distribution with sediment depth, and retention of temporal trends in contaminant input.

The distribution of ECs with depth in each sediment core (Figure 2) is relatively irregular (Hythe-BPA and HAP, and PFASs) or quasi-linear with a slight decline in concentration with depth (remaining profiles). Acetaminophen shows a near-exponential decline in concentration with depth in the Beaulieu marsh, from surface concentrations of 0.2-0.24 ng/g dw to *ca.* 0.1 ng/g dw at -20cm depth, although this pattern is not replicated in the Hythe marsh core. At both sites sampled, the seven ECs are present above respective LOD throughout the cored depth of 35+ cm. While slight inflections in the profiles frequently occur at similar depths, particularly when comparing different PFASs, where clear subsurface concentration maxima are present (e.g. Hythe core, for BPA, at -26 cm depth) these do not correlate with peaks in other

contaminants, or with subsurface maxima in organic carbon content (Figure 2, Table S5). As noted above, concentrations of the biotransformation product HAP were generally higher than those of BPA, shown by a ratio > 1 at most sampled depths throughout the sediment cores (Figure 3). Higher ratios of HAP to the BPA parent compound (HAP:BPA ratio) may indicate greater transformation of BPA within WWTW, in-estuary or in-marsh degradation of BPA into HAP, or additional HAP sources in these systems. There is no evidence however of consistent changes of HAP:BPA with burial depth that may indicate increasing biotransformation of BPA with burial time in the marsh. At Hythe, HAP:BPA ratios increase to >4 at -15cm depth, then decrease to <1 due to the prominent subsurface maximum in BPA at -26 cm depth. Although similar HAP:BPA ratios were previously observed within the first 5cm of sediment depth in semi-rural stretches of the River Bourne in the U.K., those observed here were generally higher than in sediment of small urban rivers (Wilkinson et al., 2018). This may be partially driven by (a) diverse inputs of BPA into urban rivers (Osenbrück et al., 2007; Proctor et al., 2020) increasing the amount of the parent compound relative to metabolites and (b) degradation of BPA into HAP via sediment dwelling bacteria such as *Pseudomonas putida* (Eltoukhy et al., 2020) and *Sphingomonas* sp. (Zhang et al., 2013). BPA to BPS ratios were generally close to 1 (or less), with the exception of two samples at depth in the Hythe core – no consistent recent decrease in this ratio was observed which might record the documented replacement of BPA with BPS in industrial and commercial products.

Figure 2: PFNA, PFOA, BPA, HAP, BPS, PFBS, acetaminophen and organic carbon (via LOI analysis) distribution with depth in Beaulieu (top) and Hythe (bottom) saltmarsh cores. Profiles are arranged from high to low K_{ow} (left to right). Dashed vertical line on selected graphs shows limit of detection, determined at a signal-to-noise ratio of 3 from injection of spiked soil sample extracts (Table S3).

Beaulieu River - Yacht club

Hythe

339

340 **Figure 3:** HAP/BPA and BPA/BPS ratios, and organic carbon (via LOI analysis), distribution
 341 with depth in Beaulieu (top) and Hythe (bottom) saltmarsh cores. Dashed vertical line on
 342 HAP/BPA and BPA/BPS graphs shows one to one ratio.

343 The sediment cores examined were dated via ^{137}Cs dating, supported (at Hythe only) by
344 matching the vertical distribution of Cu in the sediment with the known discharge history of
345 this heavy metal from the Fawley refinery (e.g. Cundy and Croudace, 2017). In both cores
346 examined ^{137}Cs shows a prominent subsurface maximum at -28 cm (Beaulieu) and -23 cm
347 (Hythe) (Figure 4), which in this region of the southern UK has been previously established
348 to correspond to the 1963 fallout maximum from above ground nuclear weapons testing
349 (Cundy and Croudace, 1996; Cundy et al., 1997; Cundy and Croudace, 2017). This provides a
350 defined age marker in the sediment column, indicating a sediment accumulation rate of *ca.*
351 5 mm/year (Beaulieu) and *ca.* 4 mm/year (Hythe), in agreement with previously reported
352 data for these and surrounding marsh systems (Cundy and Croudace, 1996; Cundy et al.,
353 1997; Thomson et al., 2002; Cundy and Croudace, 2017). The broad subsurface maximum in
354 Cu in the Hythe core between -20 and -25cm reflects increasing Cu discharges from the
355 Fawley refinery prior to additional effluent control measures in 1970/71 (Cundy and
356 Croudace, 2017), indicating a sediment accumulation rate of 4 mm/year at Hythe,
357 corroborating the ^{137}Cs -derived rate (NB. Cu concentrations at Beaulieu conform with local
358 geogenic background, Croudace and Cundy, 1995). Given these dates and sediment
359 accumulation rates, it is clear that all ECs analysed are present at above-LOD concentrations
360 in sediments deposited prior to 1960, and potentially (if constant sediment accumulation
361 rates are assumed) in pre-1950 sediments. Some ECs therefore are found at depths which
362 pre-date their widespread environmental introduction (e.g. acetaminophen, PFASs, Table 1),
363 which indicates their diffusion or transport to deeper, older sediment core horizons,
364 possibly driven by tidal flushing (i.e. horizontal and vertical percolation of incoming water
365 associated with tidal inundation). This, and the lack of any consistent subsurface maxima or
366 trends in concentration (or in EC ratios, e.g. BPA:BPS) that can be correlated with their

367 increasing production and use, industrial development or urbanisation activities (e.g. known
368 timing of population increases, port and port traffic development, boating activity and
369 WWTW construction) highlights that these sediments do not contain a record of likely
370 historical contaminant loading each estuary, and do not record temporal trends in estuarine
371 EC inputs. This finding contrasts both with sediment core data for ECs in freshwater
372 (riverine) sediments presented by Thiebault et al., (2017) (and more recently by Mourier et
373 al., 2019), and with the recorded retention of trends in historical inputs of various heavy
374 metals, radionuclides and (for Southampton Water) hydrocarbon residues in the two
375 estuaries studied here (Little et al., 1988; Croudace and Cundy, 1995; Cundy and Croudace,
376 1996; Thomson et al., 2002; Cundy and Croudace, 2017). Similar mobility for estrone (E1)
377 has however been observed in clay-rich estuarine sediments in the Ouse estuary, UK
378 (Labadie et al., 2007), while Peng et al., (2007) found that nonylphenol was quantifiably
379 detected in sediments predating its widespread application (1940s) in the Pearl River
380 estuary, suggesting the downward penetration of NP in the sediment column.

Beaulieu River - Yacht club

Hythe

381

382 **Figure 4:** ¹³⁷Cs, Cu, Fe₂O₃, MnO, S, and CaO distribution with depth in Beaulieu (top) and Hythe (bottom) saltmarsh cores.

3.3 Geochemical associations of ECs, and effectiveness of the “estuarine filter”.

Consideration of bulk geochemical data for the redox-sensitive elements Fe, Mn and S (Figure 4) indicates that there is a relatively well-developed redox zonation in each core, with increases in solid phase sulphur at depth (>25 cm depth, Beaulieu, greater than 30 cm depth, Hythe) reflecting the development of anoxic conditions in deeper sections of the marsh, resulting in sulphate reduction and precipitation of Fe sulphides. This redox zonation shows no apparent relationship with ECs distribution or with HAP:BPA ratio. Calcium distribution shows a decline with depth from a surface maximum value, as observed elsewhere (e.g. Spencer et al., 2003) due to decalcification, which occurs in oxic saltmarsh sediments in response to a lowering of pH resulting from nitrification and decomposition of organic matter.

The application of PCA highlighted clear differences in composition and contaminant geochemistry between the sites, with higher scores along axis 1 identified for the Hythe site and lower values for the Beaulieu site (Figure 5). Axis 1 however only accounted for 35.9% of the variation in the data, and axis 2 accounted for 18.2% of the variation, which shows (a) the multiparametric character of the data, and (b) the lack of clear association of ECs with any one defined component of the sediment. The main factors influencing axis 1 were: K₂O, V, Pb, MgO, TiO₂, Ba, Sand, Al₂O₃, and S, whereas the main factors influencing axis 2 were Cl, I, Na₂O, P₂O₅, MnO, CaO, Cu, and OC (Figure 5). The principal factors that were found to differentiate the sites were those concerning sedimentary characteristics (e.g. granulometry, mineralogy, organic carbon, redox processes) with minor differences in the observed values of the organic pollutants between each studied estuary. This suggests that chemistry and contaminant binding is more complex than direct correlation (or direct

interaction) of ECs with sedimentary particulate organic carbon – regardless of the individual contaminant’s functionality and hydrophobicity (Table 1, and Table S5). As observed by other authors, this may at least partly be an effect of colloidal association and transport of these ECs (e.g. Kalmykova et al., 2013). Cluster analysis noted two main groupings in each studied system. At Beaulieu, ECs are related with clay and silt (Figure 6a); whereas at Hythe they are distributed across all sediment fractions such as sand, silt and clay (Figure 6b). This suggests some degree of fine sediment association at Beaulieu, with supply of ECs associated with fine suspended material that may have been sourced from other areas in the estuary more impacted by industrial and leisure (e.g. boating) activity or WWTWs.

418 **Figure 5:** PCA ordination plot showing all subsamples from cores at Beaulieu and Hythe with
419 environmental vectors.

421

422 **Figure 6:** Tree diagram for the 34 core variables studied, derived from a cluster analysis

423 using the complete linkage 1-Pearson r method. (a) shows data for Beaulieu and (b) shows

424 data for Hythe site.

At the seawater pHs observed around the sampling sites (7-8.5), both ionised and non-ionised forms of acetaminophen and the bisphenols will be present, although the neutral species will be the most abundant. In contrast, the anionic form of the perfluoroalkyl acids will dominate (ITRC, 2020). Hence the perfluoroalkyl species will be expected to have a more amphiphilic character under these environmental conditions: with a fluorinated tail participating in van der Waals and hydrogen bonding interactions with organic matter and negatively charged carboxylic groups, with a capacity also to participate in hydrogen bonding and/or interact ionically with cations (e.g. amino groups from organic matter or free metals). In addition, sorption (e.g. to organic carbon) generally increases with increasing perfluoroalkyl tail length, indicating that long-chain PFASs (for example, PFOA) would be expected to be more strongly sorbed than their shorter-chain counterparts (e.g. PFBS) (ITRC, 2020). Despite these likely differences in sediment binding potential, the data presented here show little apparent long-term sequestration in intertidal sediments for any of the seven ECs examined – while sediments are clearly labelled with these contaminants, the ECs are apparently relatively mobile in the marsh systems studied, and a contaminant chronology or record of temporal inputs is not retained in the sediment cores. Where subsurface maxima are present (most prominently here for BPA at the Hythe marsh) these most likely relate to local flushing or diffusive processes and cannot be clearly linked to likely input trends or changes in sediment geochemistry. Unlike radionuclides and heavy metals, which are effectively sequestered and buried for long periods (depending on longer term sediment accumulation and marsh erosion trends, e.g. Cundy and Croudace (2017)), the “estuarine filter” here, at least for these intertidal saltmarsh sediments, shows reduced potential to sequester the seven ECs examined and mediate their supply to coastal and shelf environments.

449

450   **4. Conclusions**

- 451   • Seven, relatively water-soluble and environmentally mobile, ECs were examined and
452   found to be present in the ng/g range in both Hythe and Beaulieu saltmarsh
453   sediments, with concentrations ranging from 0.12 ng/g (acetaminophen), through
454   0.2-5.3 ng/g (perfluoroalkyl compounds) to 7.9-16.5 ng/g (BPA, BPS and HAP).
- 455   • Broadly similar mean concentrations were found between the Hythe and Beaulieu
456   sediment cores for all ECs examined, indicating a relative ubiquity of these ECs in
457   estuarine waters on the central southern UK coast. The lack of clear enrichment in
458   ECs in the heavily urbanised and industrialised Southampton Water (Hythe) system
459   over those found in the non-urbanised Beaulieu estuary is most likely a consequence
460   of ECs input from a range of catchment sources, rather than a single main or point
461   source, and mixing of these inputs on the tidal circulation prior to deposition in the
462   marsh systems.
- 463   • The ECs are apparently relatively mobile in the marsh systems studied, and where
464   subsurface concentration maxima are present these most likely relate to local
465   flushing or diffusive processes and cannot be clearly linked to likely input trends or
466   changes in sediment geochemistry (including in sedimentary organic carbon
467   content).
- 468   • Despite their likely differences in sediment binding potential (with reported Log K_{ow}
469   values ranging from *ca.* 0.5 to > 7), the data presented here show little apparent
470   long-term sequestration in intertidal sediments for any of the ECs assessed. Unlike
471   radionuclides and heavy metals, which can be effectively sequestered and buried for

long periods, the “estuarine filter” here, at least for these intertidal saltmarsh sediments, shows reduced potential to sequester the ECs examined and mediate their supply to coastal and shelf environments.

SUPPORTING INFORMATION.

Further information on background contamination and analyte recovery, and tables of quality parameters in the determination of ECs, mass spectrometry acquisition conditions, limits of detection and quantification for each studied EC analyte, uncertainties in the quantification of the study compounds, and correlation matrix including granulometry, organic carbon and organic pollutants for study sites.

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494

495   **NOTES.**

496   The authors declare no competing financial interest.

497

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670 GRAPHICAL ABSTRACT

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