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

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26 **ABSTRACT**

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

45

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

48

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 $\mu\text{g/L}$ or sub- $\mu\text{g/L}$ 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.

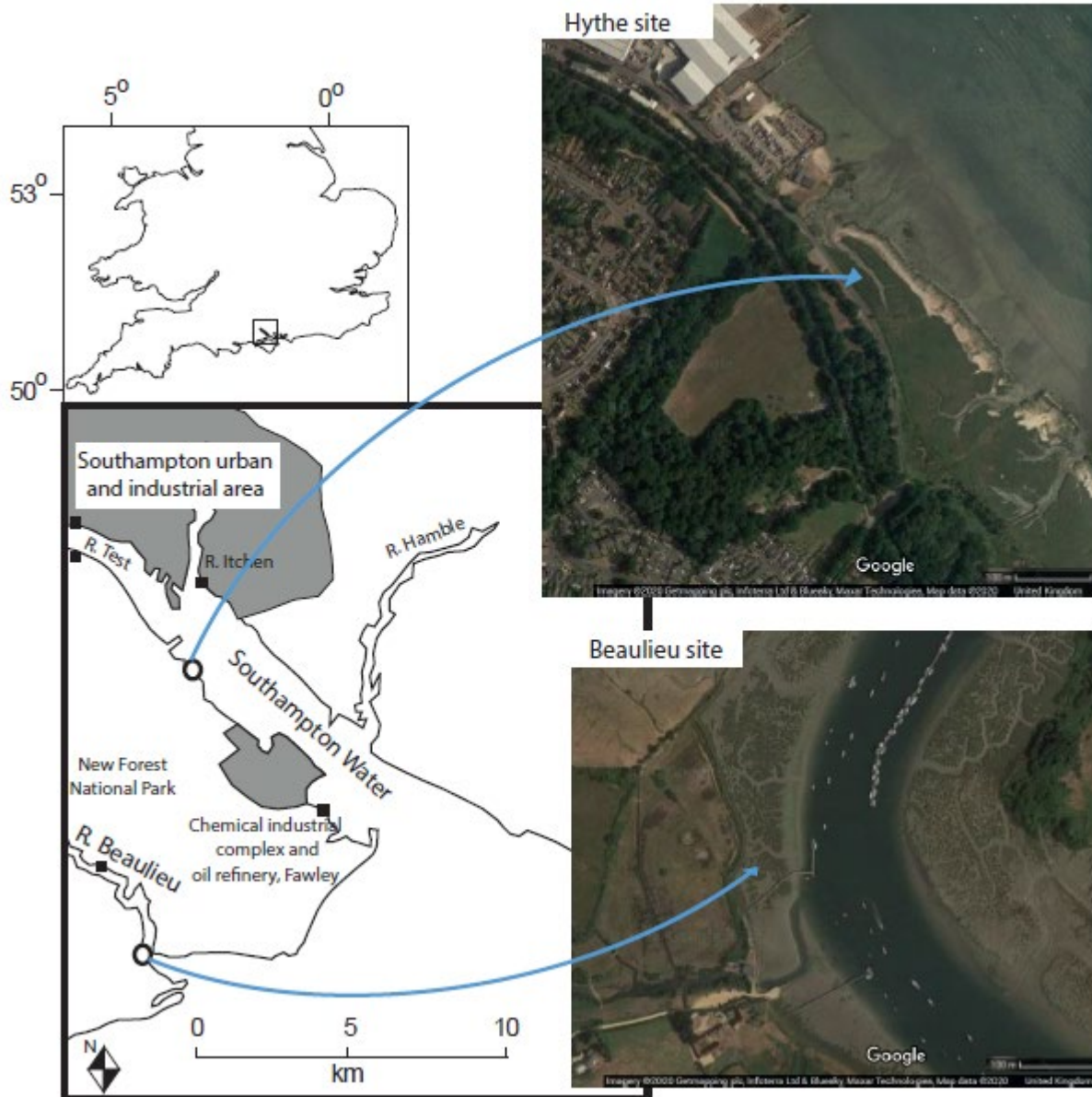
91 2. Materials and Methods

92 2.1 Study area

93 Sediment cores were collected in 2016 from the Hythe saltmarsh system (on the western side
94 of Southampton Water, U.K.), and the southern Beaulieu river (Figure 1). Southampton Water is
95 a 10 km long and 2 km wide estuary that is one of the largest estuarine systems in the southern
96 UK (Quaresma et al., 2007). The rivers Test and Itchen are the main contributors of fresh water
97 to the estuary, supplying approximately $1.54 \times 10^6 \text{ m}^3$ of fresh water per day (Hydes, 2000) and
98 2×10^4 tons of total suspended sediment per year (Velegrakis et al., 1999). The estuary hosts a
99 range of coastal ecosystems such as saline lagoons, saltmarshes and mudflats that support a
100 range of breeding and migratory birds, crabs and other organisms (JNCC, 2017). The head of the
101 estuary is highly urbanized, with the city of Southampton (population 256,459 (2018 data,
102 Southampton City Council, 2019), covering an area approximately 51.8 km^2) and Southampton
103 port (the second largest container terminal in the UK, which handles around 14 million tons of
104 cargo each year). There is intensive industrial use of the western shore area with the large-scale
105 Exxon Mobil oil refinery at Fawley and related industries that use the feedstock from the
106 refinery. In contrast, the Beaulieu estuary is relatively undeveloped and lies in the New Forest
107 National Park, an area of predominantly open heath and bog with little agriculture and very few
108 urban areas (although it does receive sewage effluent discharges from 3 upstream continuous
109 discharge WWTWs, with *E. coli* readings sufficiently high to historically close local clam fisheries
110 (CEFAS, 2015).

111 The Hythe marsh is a *Halimione portulacoides* dominated marsh system, with patchy *Spartina*
112 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.



122

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

128

129 **2.2 Chemicals and materials**

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

137

138 Stock solutions of each compound were prepared at 1000 mg/L in acetonitrile. Stock solutions
139 were further diluted to intermediate solutions containing a mixture of all compounds (25 and 5
140 mg/L) in acetonitrile, and further diluted in the same solvent to achieve the concentration
141 levels of 4; 20; 100; 250; and 500 µg BPA/L; 2; 10; 50; 125; 250; and 500 µg BPS and HAP/L and
142 0.2; 1; 5; 13; 25; 50 and 100 µg/L for the rest of the study compounds. Standards were stored at
143 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)	-.331 ^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,
148 USA. <https://pubchem.ncbi.nlm.nih.gov/>, accessed July 2020.149 ^b Wang et al., 2002150 ^c <https://www.epa.gov/tsca-screening-tools>, accessed July 2020.151 ^d Goss, 2008152 ^e Howard and Meylan, 1997153 ^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

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

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

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208 **2.5 Sample analysis – radiometric dating, inorganic geochemistry, organic carbon and**
209 **granulometry.**

210 Sediment cores were vertically sub-sampled at 2 cm depth increments, and freeze-dried
211 sediment samples counted for at least 16 hours on a Canberra well-type HPGe gamma-ray
212 spectrometer to determine the activities of ^{137}Cs and other gamma-emitting radionuclides.
213 Freeze-dried samples (as pressed pellets) were also analysed using a Philips Magix-Pro WD-XRF
214 fitted with a 4 kW Rh target X-ray tube, to determine geochemical composition. Radiometric
215 methods and XRF geochemical analysis methods are well established and reported in Croudace
216 et al., 2012. Organic carbon content was estimated using the loss on ignition method (LOI, at
217 450°C for 24 hours), and a carbon conversion factor for saltmarsh soils (Craft et al., 1991).
218 Particle size distribution within sediment samples was determined using a Malvern Mastersizer
219 2000 laser particle size analyser. One gram of homogenized sediment was mixed with 10 mL of

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

222

223 **2.6 Statistical analysis**

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

236

237 **3. Results and Discussion**

238 **3.1 Mean Emerging Contaminant (EC) concentrations.**

239 Mean EC concentrations observed in saltmarsh sediments are statistically similar at Hythe and
240 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

263 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.
 264 sediment respectively in three freshwater rivers in greater London. Unlike in the Wilkinson et
 265 al. (2018) study of urban freshwater rivers, however, concentrations of the biotransformation
 266 product 4'-hydroxyacetophenone were generally higher than those of its parent BPA in the
 267 estuarine systems studied here (discussed further below).

268

269 **Table 2:** Mean concentrations of each analyte at Hythe and Beaulieu saltmarsh sites. Previously
 270 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,

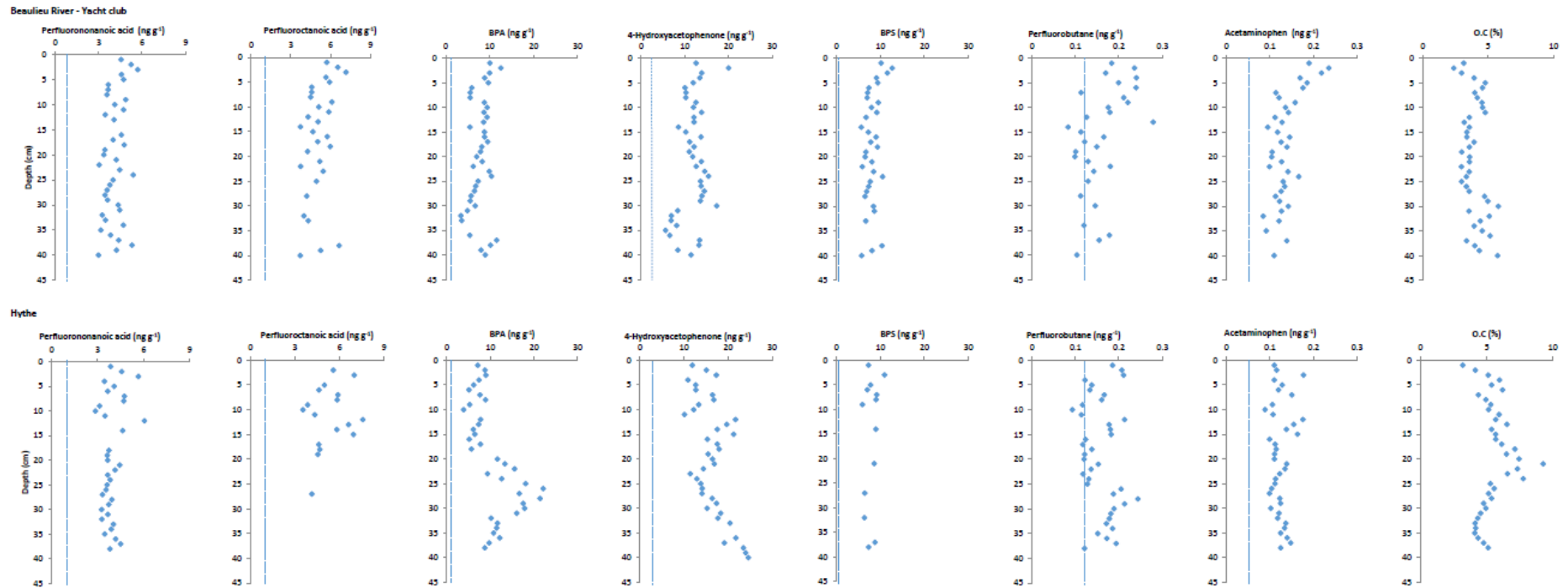
294 PFASs are associated with areas of train traffic, airports, military and other training installations,
295 port and boat activity and in storm runoff from built developments and roads (Zushi and
296 Masunaga, 2009; Xiao et al., 2012; Ahrens et al., 2015; Yan et al., 2015; Anderson et al., 2016;
297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

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304 **3.2 EC distribution with sediment depth, and retention of temporal trends in contaminant** 305 **input.**

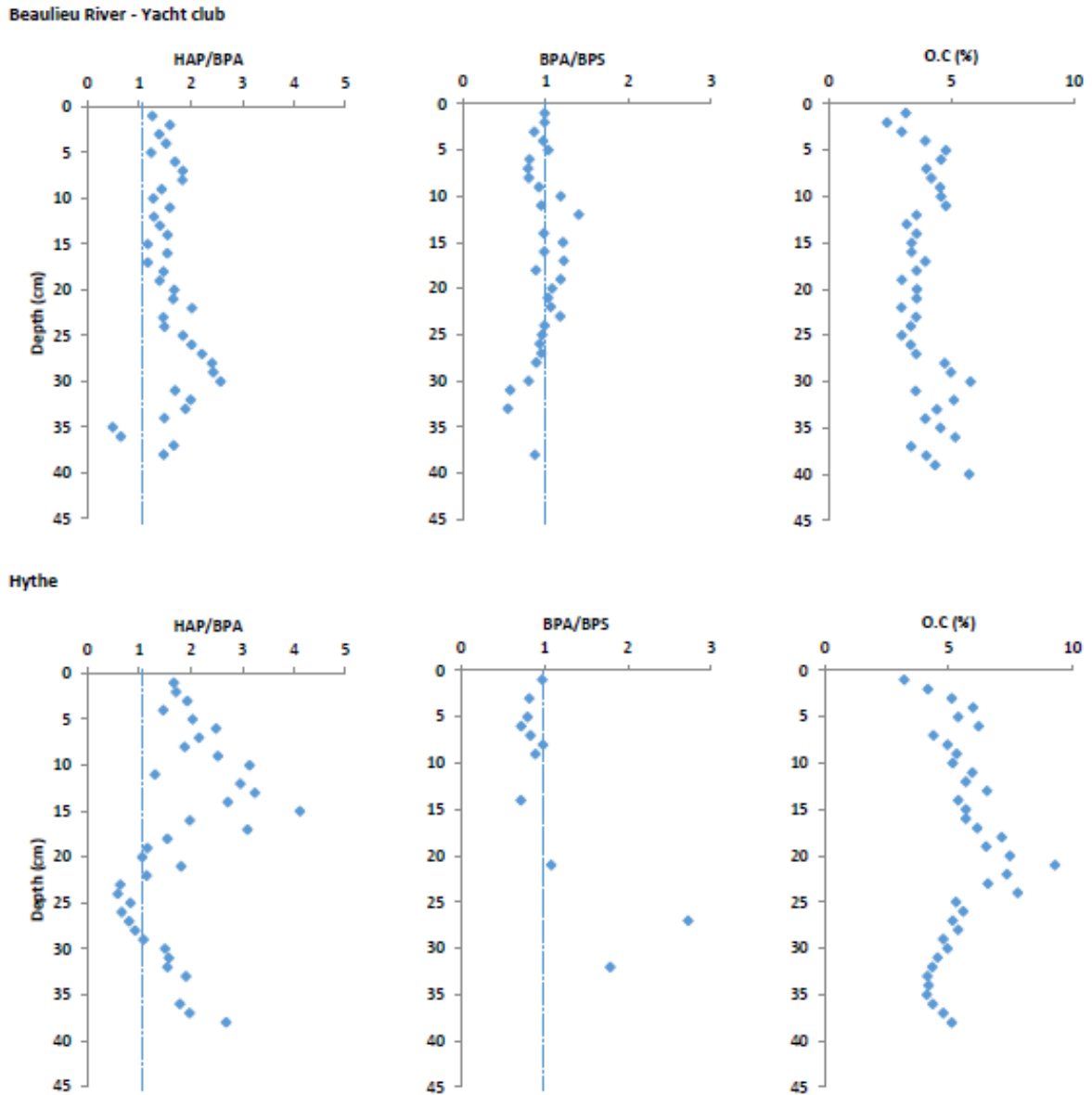
306 The distribution of ECs with depth in each sediment core (Figure 2) is relatively irregular (Hythe-
307 BPA and HAP, and PFASs) or quasi-linear with a slight decline in concentration with depth
308 (remaining profiles). Acetaminophen shows a near-exponential decline in concentration with
309 depth in the Beaulieu marsh, from surface concentrations of 0.2-0.24 ng/g dw to *ca.* 0.1 ng/g
310 dw at -20cm depth, although this pattern is not replicated in the Hythe marsh core. At both
311 sites sampled, the seven ECs are present above respective LOD throughout the cored depth of
312 35+ cm. While slight inflections in the profiles frequently occur at similar depths, particularly
313 when comparing different PFASs, where clear subsurface concentration maxima are present
314 (e.g. Hythe core, for BPA, at -26 cm depth) these do not correlate with peaks in other

315 contaminants, or with subsurface maxima in organic carbon content (Figure 2, Table S5). As
316 noted above, concentrations of the biotransformation product HAP were generally higher than
317 those of BPA, shown by a ratio > 1 at most sampled depths throughout the sediment cores
318 (Figure 3). Higher ratios of HAP to the BPA parent compound (HAP:BPA ratio) may indicate
319 greater transformation of BPA within WWTW, in-estuary or in-marsh degradation of BPA into
320 HAP, or additional HAP sources in these systems. There is no evidence however of consistent
321 changes of HAP:BPA with burial depth that may indicate increasing biotransformation of BPA
322 with burial time in the marsh. At Hythe, HAP:BPA ratios increase to >4 at -15cm depth, then
323 decrease to <1 due to the prominent subsurface maximum in BPA at -26 cm depth. Although
324 similar HAP:BPA ratios were previously observed within the first 5cm of sediment depth in
325 semi-rural stretches of the River Bourne in the U.K., those observed here were generally higher
326 than in sediment of small urban rivers (Wilkinson et al., 2018). This may be partially driven by
327 (a) diverse inputs of BPA into urban rivers (Osenbrück et al., 2007; Proctor et al., 2020)
328 increasing the amount of the parent compound relative to metabolites and (b) degradation of
329 BPA into HAP via sediment dwelling bacteria such as *Pseudomonas putida* (Eltoukhy et al.,
330 2020) and *Sphingomonas* sp. (Zhang et al., 2013). BPA to BPS ratios were generally close to 1 (or
331 less), with the exception of two samples at depth in the Hythe core – no consistent recent
332 decrease in this ratio was observed which might record the documented replacement of BPA
333 with BPS in industrial and commercial products.



334
 335 **Figure 2:** PFNA, PFOA, BPA, HAP, BPS, PFBS, acetaminophen and organic carbon (via LOI analysis) distribution with depth in Beaulieu (top) and
 336 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
 337 detection, determined at a signal-to-noise ratio of 3 from injection of spiked soil sample extracts (Table S3).

338

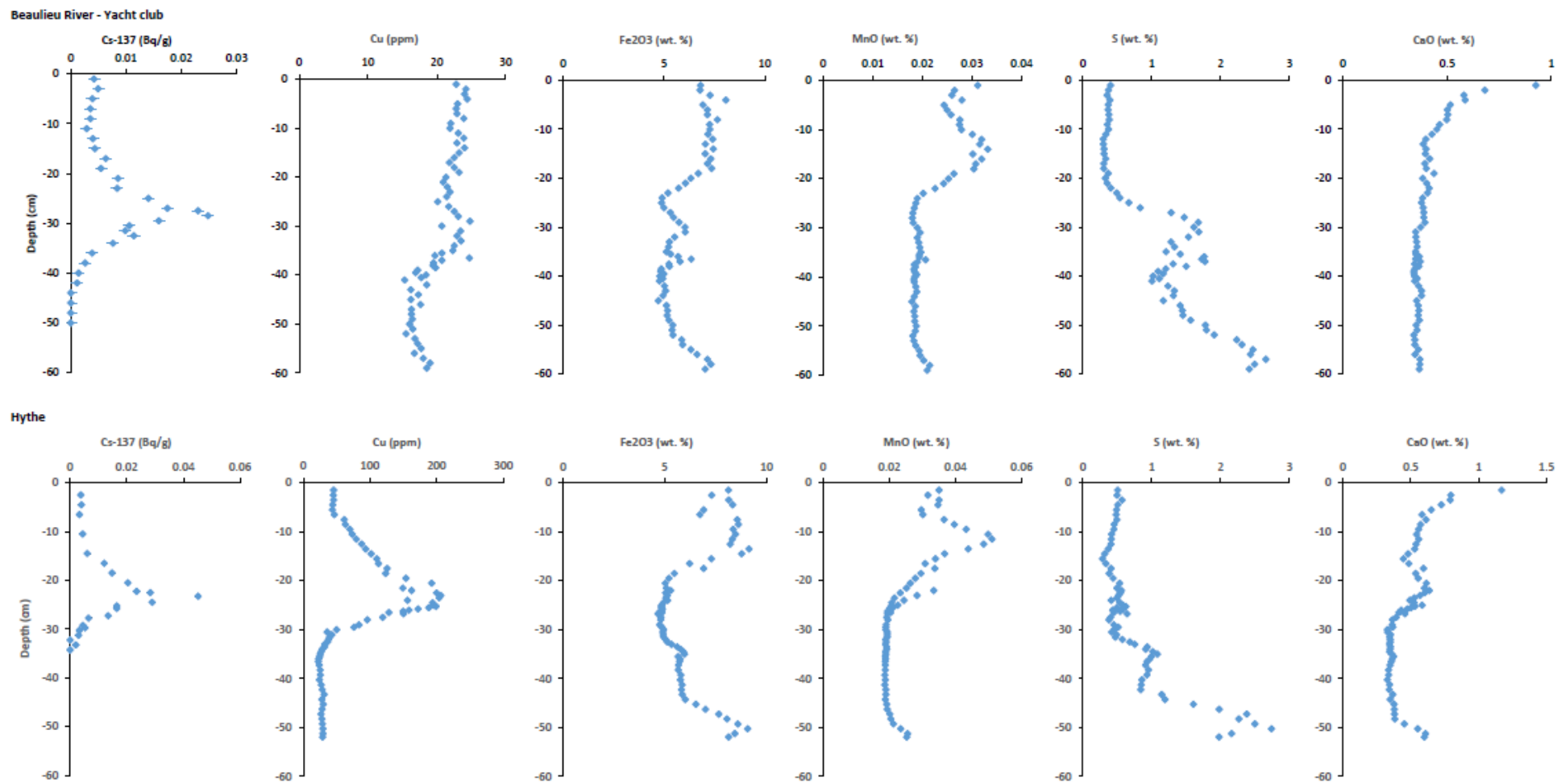


339

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.



381

382 **Figure 4:** ^{137}Cs , Cu, Fe_2O_3 , MnO, S, and CaO distribution with depth in Beaulieu (top) and Hythe (bottom) saltmarsh cores.

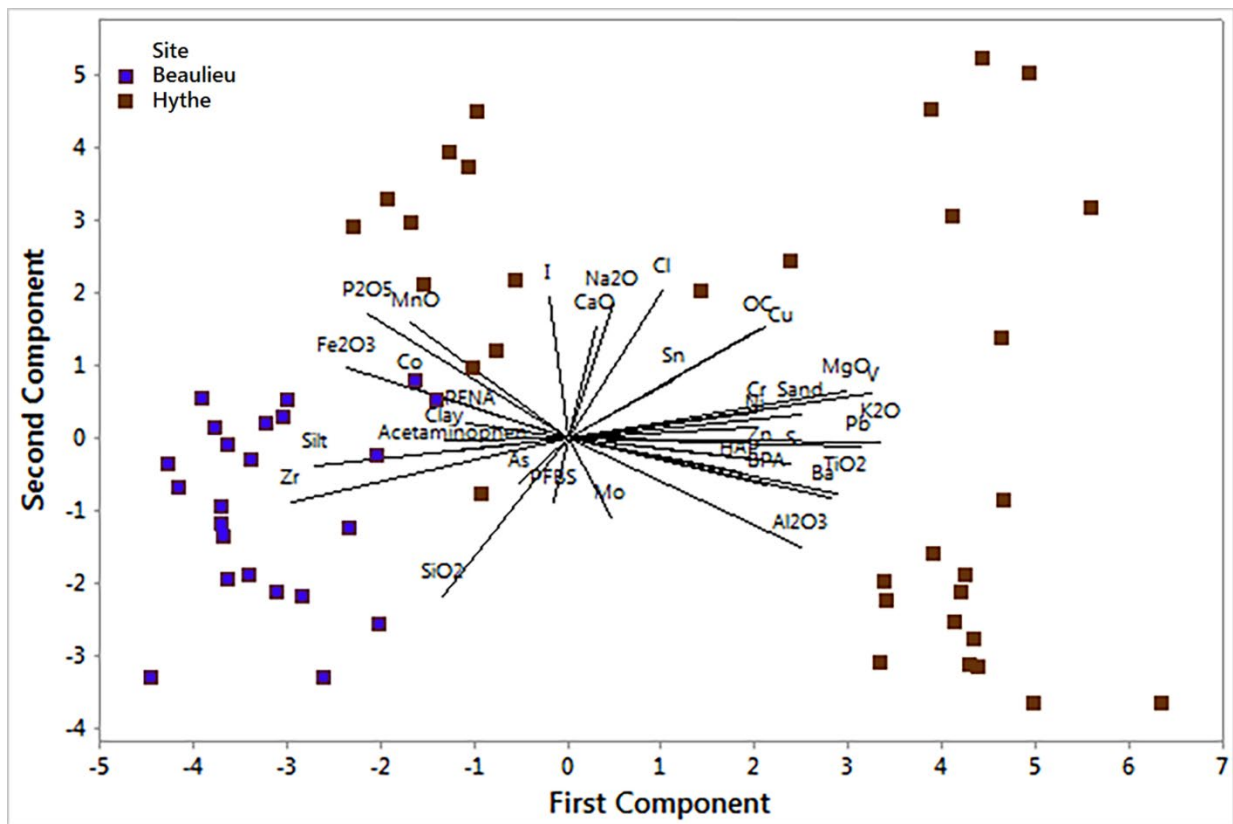
383 3.3 Geochemical associations of ECs, and effectiveness of the “estuarine filter”.

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

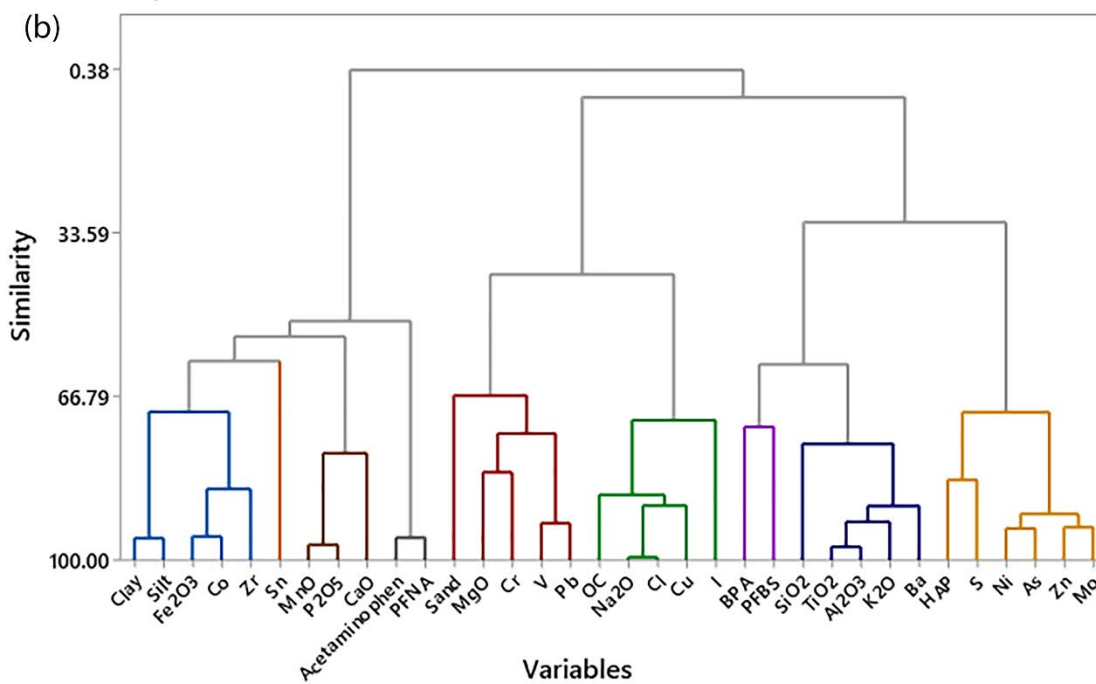
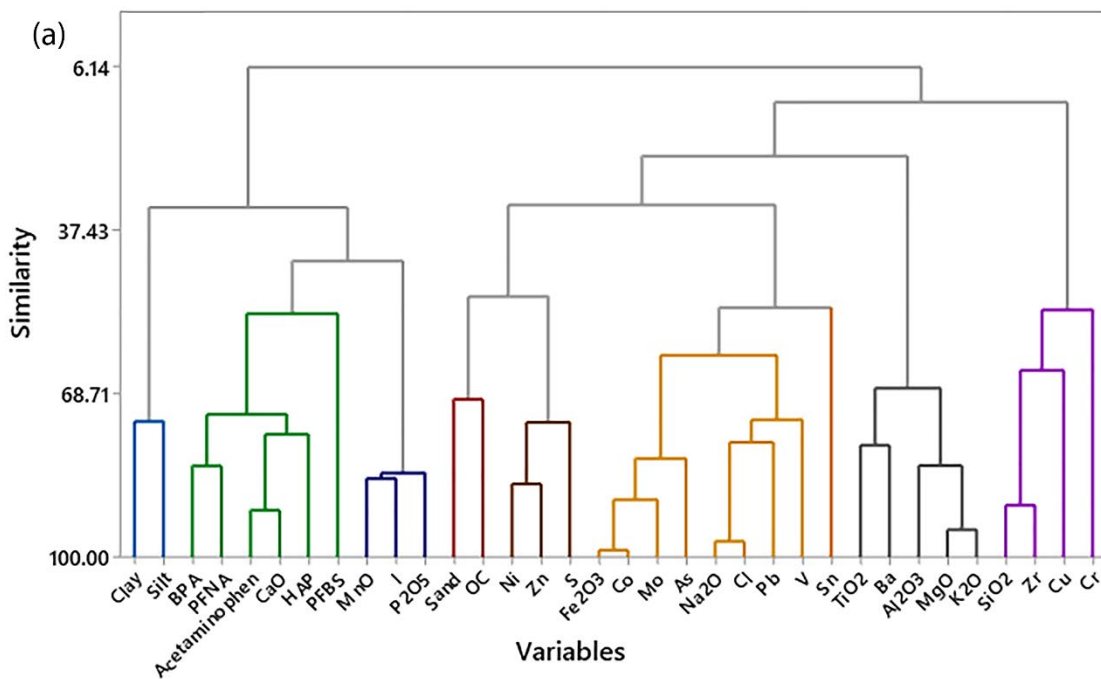
394 The application of PCA highlighted clear differences in composition and contaminant
395 geochemistry between the sites, with higher scores along axis 1 identified for the Hythe site
396 and lower values for the Beaulieu site (Figure 5). Axis 1 however only accounted for 35.9%
397 of the variation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

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

416



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.

425 At the seawater pHs observed around the sampling sites (7-8.5), both ionised and non-
426 ionised forms of acetaminophen and the bisphenols will be present, although the neutral
427 species will be the most abundant. In contrast, the anionic form of the perfluoroalkyl acids
428 will dominate (ITRC, 2020). Hence the perfluoroalkyl species will be expected to have a
429 more amphiphilic character under these environmental conditions: with a fluorinated tail
430 participating in van der Waals and hydrogen bonding interactions with organic matter and
431 negatively charged carboxylic groups, with a capacity also to participate in hydrogen
432 bonding and/or interact ionically with cations (e.g amino groups from organic matter or free
433 metals). In addition, sorption (e.g. to organic carbon) generally increases with increasing
434 perfluoroalkyl tail length, indicating that long-chain PFASs (for example, PFOA) would be
435 expected to be more strongly sorbed than their shorter-chain counterparts (e.g. PFBS) (ITRC,
436 2020). Despite these likely differences in sediment binding potential, the data presented
437 here show little apparent long-term sequestration in intertidal sediments for any of the
438 seven ECs examined – while sediments are clearly labelled with these contaminants, the ECs
439 are apparently relatively mobile in the marsh systems studied, and a contaminant
440 chronology or record of temporal inputs is not retained in the sediment cores. Where
441 subsurface maxima are present (most prominently here for BPA at the Hythe marsh) these
442 most likely relate to local flushing or diffusive processes and cannot be clearly linked to
443 likely input trends or changes in sediment geochemistry. Unlike radionuclides and heavy
444 metals, which are effectively sequestered and buried for long periods (depending on longer
445 term sediment accumulation and marsh erosion trends, e.g. Cundy and Croudace (2017)),
446 the “estuarine filter” here, at least for these intertidal saltmarsh sediments, shows reduced
447 potential to sequester the seven ECs examined and mediate their supply to coastal and shelf
448 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

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

475

476 **SUPPORTING INFORMATION.**

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

482

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488

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494

495 **NOTES.**

496 The authors declare no competing financial interest.

497

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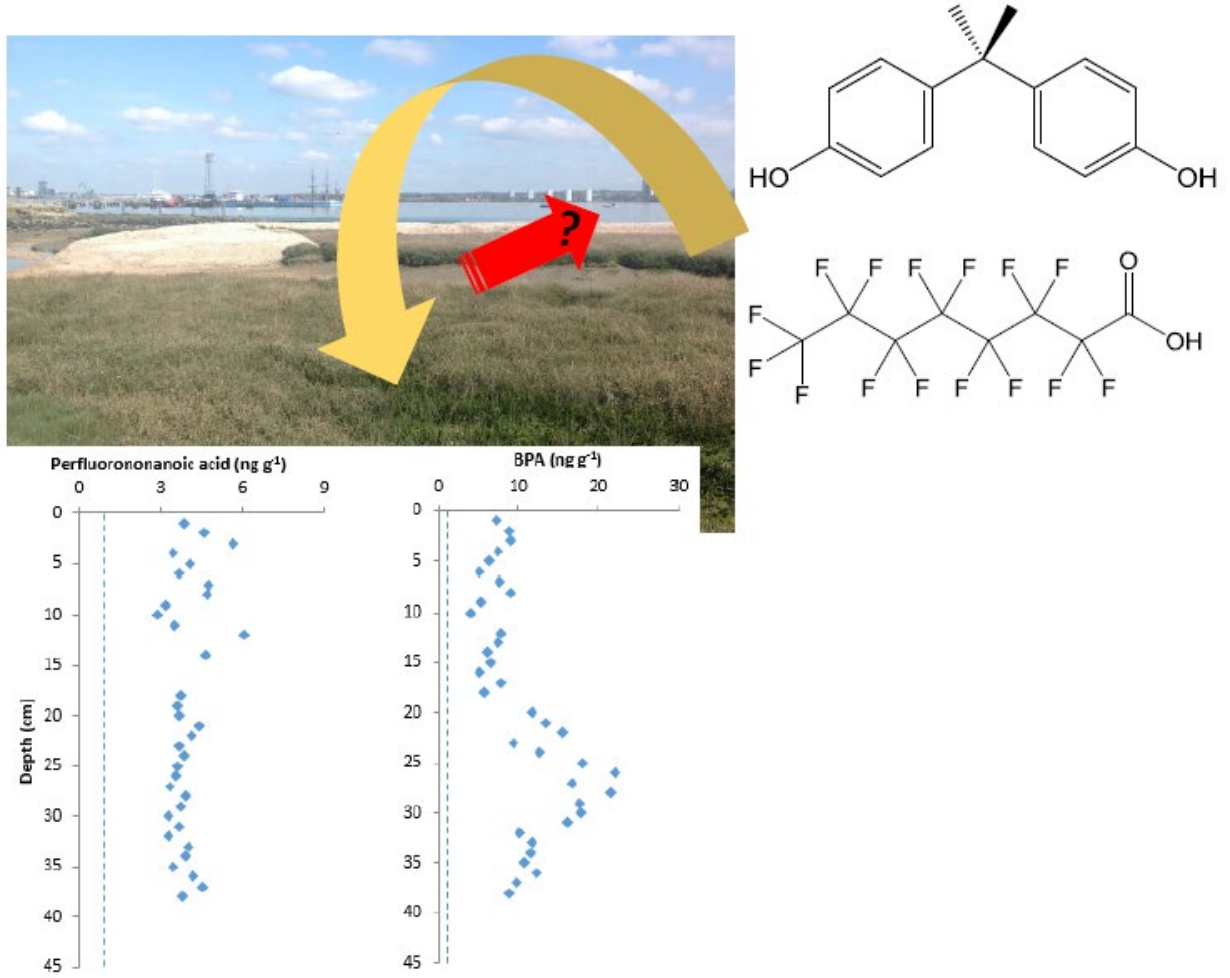
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670 GRAPHICAL ABSTRACT



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