

1 **Accepted copy of paper available from:** To cite this article: S. D. W. Comber, M. J. Gardner & B Ellor
2 (2019): Seasonal variation of contaminant concentrations in wastewater treatment works effluents and river
3 waters, *Environmental Technology*, DOI: 10.1080/09593330.2019.1579872
4 To link to this article: <https://doi.org/10.1080/09593330.2019.1579872>

5

6 **Seasonal variation of contaminant concentrations in wastewater treatment works effluents**
7 **and river waters**

8

9 **S. D. W. Comber¹, M. J. Gardner² and B Ellor³**

10 ¹ Plymouth University, B525 Portland Square, Drake Circus, Plymouth, Devon, PL4 8AA, UK

11 ² Atkins Limited, 500, Park Avenue, Aztec West, Almondsbury, Bristol BS32 4RZ, UK.

12 ³ UK Water Industry Research, 3rd floor, 36 Broadway, London, SW1 0BH, UK.

13

14 Corresponding author: sean.comber@plymouth.ac.uk

15 **Abstract**

16 Results are presented for 170 wastewater treatment works sites (20 per substance in influent,
17 effluent and 36 per substance in river water upstream and downstream of the WwTW discharge)
18 over a period of two years between 2015 and 2017; this comprises data for approximately 3,000
19 samples for effluent and 6,000 for river samples taken downstream of effluent discharges. Seasonal
20 trends in contaminant concentrations for several substances are reported. Two clear patterns of
21 seasonal variation are proposed over and above all of the variables associated with environmental
22 data including process technology, dilution and geography. Firstly, variation of riverine
23 concentrations caused by seasonal fluctuations in river flow (sewage flow being relatively consistent)
24 resulting in summer maxima and winter minima. Alternatively, variation is observed that is
25 attributable to the improved performance of wastewater treatment processes under warmer
26 conditions. This leads to lowest concentrations in autumn when surface water/sewage treatment
27 temperatures tend to peak. Seasonality for trace contaminants is more difficult to characterise than
28 that of sanitary parameters owing to the higher variability in concentration of the substances of
29 interest. The data also provide an insight into the amplitude of such variations. This makes it possible
30 to assess the likely effects of seasonality and its impact on aquatic life. For example, the existence
31 of seasonality (perhaps due only to dilution effects) might be demonstrated, but the amplitude might
32 be too small in relation to the potential ecotoxicological effects to be of any consequence.

33

34 **Key words:** priority chemicals; effluents; seasonality; water quality; rivers

35 **1. Introduction**

36 In the UK on each day, approximately 347,000km of sewers collect 11 billion litres of wastewater;
37 this is treated in approximately 9,000 wastewater treatment works (WwTW) that serve 96% of the
38 UK population [1]. WwTW effluents thus constitute the main discharges to surface waters and,
39 consequently, are the principal source of contaminant inputs to receiving river waters. Over the last
40 50 years, the water industry has made substantial investments in the improvement of wastewater
41 treatment, principally in response to legislation including the Dangerous Substances Directive [2],
42 Urban Wastewater Treatment Directive [3] and Water Framework Directive - WFD [4]. This has led
43 to marked reductions in the discharge of the contaminants conventionally associated with sewage
44 effluents, such as biochemical oxygen demand (BOD), suspended solids and ammonia. In more
45 recent years, however, focus on pollution has widened to include a greater range of trace substance
46 that did not feature in the original design criteria of treatment processes. Current concerns that are
47 reflected in directives such as the WFD, now extend to over 50 substances, including metals,
48 pesticides, industrial chemicals, solvents and other organic pollutants [5]. Reductions in
49 concentrations of these substances in wastewater can be achieved by conventional treatment via
50 biodegradation, volatilisation or adsorption to sludge solids. Indeed, for some contaminants removal
51 mechanisms can be highly effective [6]; in other cases, further or enhanced treatment might be
52 required.

53
54 Many exercises have been conducted to assess both seasonal and sustained longer term trends in
55 environmental variables. This is particularly the case for nutrients such as phosphate and nitrate,
56 BOD and ammonia, which are key determinands in assessing water quality status at specific sites
57 and catchments owing to the availability of long term datasets for routinely determined parameters
58 [7-9]. However, there is no overall analysis of seasonal trends taking account of aggregated data of
59 a substantial number of WwTW in order to analyse the seasonality of treatment for emerging
60 compounds such as pharmaceuticals or the generic influences of WwTW effluents on receiving
61 waters for substances of high concern but for which routine data is rarely collected (i.e. for priority
62 micropollutants chemicals known to be persistent, bioaccumulating and toxic).

63
64 Extensive monitoring over the past five years as part of the UK Water Industry Research (UKWIR)
65 Chemical Investigation Programme (CIP) phase 2 (described as CIP2 from here onwards) has
66 played a key role in the selection of substances and sites for future controls and remedial measures
67 [10,11]. The most recent elements of the CIP2 are scheduled to report on effluent and river quality
68 at over 600 sewage works in the period 2015-2020. Seasonal variation in contaminant
69 concentrations in sewage effluents and river waters impacted by effluents can be an important

70 feature of interest in this context. An understanding of seasonality is important if monitoring is to
71 provide accurate information on which to base water quality management decisions. Otherwise,
72 there is the potential for programme outputs (for example annual average concentrations) to be
73 biased, thereby calling into question the validity of the assessment of environmental quality and
74 compliance with standards.

75

76 Seasonality can also be of interest for several other reasons. Environmental impacts of contaminants
77 might only be of concern if the highest concentrations of contaminants coincide with the seasonal
78 presence of sensitive species or aquatic life stages in the surface water of interest. Furthermore,
79 various unsupported assumptions are often made regarding the nature of seasonal trends (for
80 example, that antibiotics or analgesics might be present at higher concentration in winter or,
81 conversely, that higher river flows in winter will reduce concentrations below those that prevail in
82 summer); such assumptions are rarely quantified or fully supported by reliable evidence. The 2015-
83 2017 output of CIP2 data provides a source of high quality analytical data over two years of sampling
84 for 170 WwTW and associated downstream sites across the whole geographic area of England. This
85 paper summarises findings on the basis of seasonality, through an analysis of results for up to 6000
86 samples, collected across of England and Wales. Determinands include nutrients, sanitary
87 parameters (BOD, ammonia) as well as a range of priority substances regulated under the Water
88 Framework Directive for which no previous seasonal patterns of environmental distribution has been
89 analysed. Furthermore, the density of the dataset has allowed conclusions to be drawn regarding
90 seasonal trends without the need to access data on flows, temperature and catchment
91 characteristics. Access to such a substantial dataset facilitates the illustration of trends and allows
92 conclusions to be drawn regarding the occurrence and magnitude of seasonal variation at an overall
93 national scale. It should be noted that whilst compliance levels with water quality standards are
94 important and are discussed elsewhere [12], this is not the focus of this paper and is therefore not a
95 major feature of the discussion below.

96 **2. Methodology**

97 **2.1 Substance selection**

98 The complete CIP2 programme included up to 73 individual determinands including dissolved and
99 total metals (not considered here), priority hazardous substances, priority substances and specific
100 pollutants identified under the Water Framework Directive, nutrients such as nitrate, phosphate
101 (soluble and total), ammonia, biochemical oxygen demand, chemical oxygen demand, total
102 suspended solids, pH, dissolved organic carbon and major ions. Not all determinands were analysed
103 in all samples, pharmaceuticals were only determined in influent and effluent from WwTW. A full list

104 of determinands included within CIP2 are provided in Table S1. The data reported here are for a
105 subset of substances covering sanitary determinands (BOD, ammonium ion), nutrients (soluble
106 reactive phosphate), priority hazardous substances under the WFD (perfluorooctane sulphonic and
107 octanoic acids: PFOS, PFOA respectively; hexabromocyclododecane: HBCDD; cypermethrin and
108 benzo-a-pyrene in effluent and receiving waters. Furthermore, the seasonal trends of the
109 pharmaceuticals ethinyloestradiol, a hormonal steroid, the antibiotic, erythromycin, and the non-
110 steroidal anti-inflammatory drugs ibuprofen and diclofenac (the former available over the counter
111 and by prescription, the latter prescription only) in WwTW influent and effluent were assessed. These
112 12 chemicals were selected to be illustrative of certain types of substance characteristics as well as
113 seasonal trends associated with either WwTW efficiency or river dilution patterns. A full analysis of
114 all 73 CIP2 determinands was beyond the scope of this assessment.

115

116 **2.2 Sampling**

117 Results to date have been processed for 170 WwTW sites (20 occasions per substance in effluent
118 and 36 per substance in river water upstream and downstream of the effluent discharge – Table 1)
119 over a period of two years between June 2015 and June 2017 across the whole of England (Figure
120 1). Numbers of results per substance therefore corresponded to over 3000 for effluent and over
121 6,000 for river samples taken downstream of effluent discharges, outside of the mixing zone [13] at
122 the nearest practical bridge access point.

123

124 Samples were collected as random, single grab samples using clean telescopic dipper systems off
125 bridges in the middle of the flow from below the surface of the water. Sampling equipment was acid
126 and/or decon cleaned prior to use and rinsed thoroughly with sample (at least 3 times) prior to
127 collecting the sample for processing. Samples were taken at approximately evenly spaced time
128 intervals over the two-year sampling period, rather than as composite sampling. This latter approach
129 was precluded by concerns about sample stability raised in tests prior to the commencement of the
130 programme [14]. There are no internationally agreed specifications for determining when to take
131 samples during the course of a working day or week. However, it is widely accepted that taking
132 samples between working hours from Monday to Friday may not lead to a truly representative
133 estimate of the effluent or water at that site [15]. Therefore as a pragmatic and practical target, a
134 minimum of 15% of sampling was undertaken in non-working hours (evenings and weekends) which
135 was a sufficiently high frequency to account for any possible bias in the sample collection process;
136 whilst being practical in terms of staff availability and gaining access to sites (for WwTW sample
137 collection).

138

139

140

141

142

143 **Table 1 Summary of data used for this analysis**

CIP2 Driver Code	Name	Sample type	Total samples per site	Samples per sampling occasion	Substances*	Comments
C1a	Further effluent characterisation	Effluent from the works	20	1 sample at each of 20 events	Metals, P(H)Ss, sanitarries	Sampled at same time as C1e
C1b	Emerging substances	Influent and effluent to the works	20	1 sample at each of 20 events	Pharmaceuticals and sanitarries	Sampled at same time as C1a
C1e	River sampling	Upstream and downstream of effluent discharge	36	1 sample at each of 36 events	Metals, P(H)Ss, sanitarries	Sampled at same time as C1a

144

* P(H)S = Priority and Priority Hazardous Substances under the Water Framework Directive

145

Sanitarries = BOD, ammonium ion, Chemical Oxygen Demand, suspended solids

146

147

148



149
150
151
152

Figure 1 Location of sampling sites for CIP2

153 **2.3 Sample treatment and analysis**

154 The samples were collected in stainless steel samplers, stored in glass containers and transported
 155 at 4° C to the analytical laboratories. The maximum sample storage period was determined for key
 156 determinands prior to the beginning of the programme by undertaking tests of sample stability. A
 157 period of 3 to 5 days storage for trace determinands (depending on substance) was shown not to
 158 lead to more than a 20% change in concentration. Detailed sampling, filtration and preservation
 159 requirements are provided in S2. Analytical work was commissioned from contracted laboratories,
 160 who used their own in-house analytical methodologies, which were not standardised but had to meet
 161 a minimum and exacting performance criteria. Given the variety of potential methods used and
 162 allowing for commercial sensitivities it is not possible to detail specific Gas and/or Liquid
 163 Chromatographic-Mass Spectrometry techniques employed by the laboratories. However, to ensure
 164 analytical quality was paramount the programme management team demanded a number of criteria
 165 for laboratories to meet before participating. This included ISO17025 accreditation, the requirement
 166 to undertake tests of analytical performance to demonstrate that they met the stated programme
 167 requirements for limit of detection (LOD), precision and recovery in relevant sample matrices at
 168 relevant concentrations (Table 2, S1) that is, proof of performance was required, rather than methods
 169 being stipulated. See section S1 and Table S1 of the electronic supporting information for more
 170 detail.

171
172

173 **Table 2 Determinand abbreviations, required limits of detection and total error for WFD**
 174 **priority chemicals assessed**

Code	Determinand	Required LOD effluent	Required LOD river	P % (i)
PFOS	Perfluorooctane sulfonic acid (µg/l)	0.00065	0.00009	50
PFOA	Perfluorooctanoic acid (µg/l)	0.00065	0.00009	50
HBCD	Hexabromocyclododecane (µg/l)	0.0016	0.00023	50
BAP	Benzo(a)pyrene (µg/l)	0.00017	0.00002	50
CYP	Cypermethrin (µg/l)	0.00008	0.00001	50
DCF	Diclofenac (µg/l)	0.01	0.01	50
IBPF	Ibuprofen (µg/l)	0.01	0.01	50
EE2	17α ethinyloestradiol (µg/l)	0.00003	0.00003	50
ERMY	Erythromycin (µg/l)	0.1	0.1	50
AMON	Ammoniacal nitrogen (as N) (mg/l)	0.1	0.1	50
BOD	Biochemical Oxygen Demand (mg/l)	2	2	50
TP	Total phosphorus (as P) (mg P/l)	0.01	0.01	50
SRP	Soluble reactive phosphate (as P) (mg P/l) (filtrable (0.45 µm pore size) and molybdate reactive phosphate)	0.01	0.01	50

175 ¹ P% is the target maximum tolerable error and is equal to:

176
$$\left[(targetLOD)^2 + \left(\frac{A \times P\%}{100} \right)^2 \right]^{\frac{1}{2}}$$

177 Where the target maximum LOD and P% are given in the Table 1 and A is the determinand concentration in the sample.
178

179 Performance testing was designed to demonstrate that the tolerable total error limit is achieved by
180 showing that precision (2 x standard deviation) and bias was respectively no larger than half the
181 target maximum total error. Thus, for example, for a total tolerable error limit of 100 units, standard
182 deviation should be shown not to be larger than 25 and bias should not exceed 50. The LOD was
183 defined as 3.3x the standard deviation of blank-corrected results of determinations made on a
184 sample containing essentially no determinand (where possible in a relevant sample matrix) [16]. In
185 some cases, it was not possible to find effluent samples free from determinands in which case a
186 synthetic sample was used.

187

188 Within laboratory QC analyses were undertaken for both laboratory tests and field sampling.
189 Laboratories also took part in a bespoke proficiency testing scheme. Details of the proficiency testing
190 scheme used to confirm data quality is provided in S1 of the Electronic Supplementary Information
191 (ESI). Where reported concentrations were below the required LOD, the result was substituted at
192 half face value - as stipulated in the relevant Directive [17]. As part of the proficiency testing scheme
193 Z scores were calculated. A Z-score is a numerical measurement of a value's relationship to the
194 mean in a group of values. If a Z-score is 0, it represents the score as identical to the mean score.
195 Z-scores may also be positive or negative, with a positive value indicating the score is above the
196 mean and a negative score indicating it is below the mean. Positive and negative scores also reveal
197 the number of standard deviations that the score is either above or below the mean [18]. Of the
198 approximately 250 z-scores calculated for the above pharmaceuticals tested there were only eleven
199 instances of z-scores greater than 2. Of these only three were larger than 3 (rated as
200 "unsatisfactory"). There were no instances of continued or consistent patterns of error. Hence
201 proficiency test results indicate a very positive picture, with CIP laboratories performing to a high
202 standard with respect to CIP requirements. Consequently, it was concluded that for the substances
203 considered here, there were no important instances of inter-laboratory bias or inter-regional variation
204 (data not shown), which would indicate important bias in the methodology of sample handling and
205 analysis.

206

207 The approach to the assessment of seasonality was to list all reported results for a given determinand
208 in order of sampling date, to group the resulting string of data into monthly sets and to calculate the
209 mean and 90% confidence interval for each month (combining information of a given calendar month
210 in each of the two years of sampling). Results were also in some cases assessed as single series
211 over the sampling period to examine whether or not an annual variation was repeated over the two
212 years of sampling.

213

214

215 **2.4 Data analysis principle and methodology**

216 The purpose of the analysis carried out on this dataset was to determine whether or not seasonal
217 trends could be observed using measured concentrations alone, independent of environmental
218 variables such as dilution in the river, temperature affecting WwTW performance, time of sampling,
219 type of WwTW etc. In order to undertake this analysis it was necessary to condense the large dataset
220 into monthly averages to achieve this a Locally weighted scatter-plot smoother (LOESS) smoothing
221 curve [19] was plotted where appropriate. The results of this analysis are shown below. Values
222 plotted are monthly averages (of approximately 300 results for effluents and 500-600 results for river
223 waters) with an associated 90% confidence interval.

224

225 **3. Results and discussion**

226 Samples were collected from 170 sites across the whole of England from Pegswood in
227 Northumberland to Fraddon in Cornwall, a distance of approximately 750 km, encompassing large
228 (e.g. Thames, Severn and Humber) catchments as well as much smaller rivers where previous
229 assessments have considered WwTW to have a potential impact on downstream contaminant
230 concentrations. Sampling not only covered geographic extent and catchment size, but also widely
231 varying geology (chalk through to granite), demographics (urban to rural) and climatic conditions
232 (Figure S1). WwTW size sampled varied from serving a population of less than 1,000 to almost 1.5m.
233 Average dilution of the CIP2 WwTW varies but sites were selected on the basis of likely to have
234 lower dilution and hence a higher priority for monitoring the impacts of effluents on receiving waters.
235 A mean estimated dilution from previous work was approximately 150 times but the median much
236 lower at around 8 times dilution [20]. Met Office data [21] for the whole of England suggests that
237 2016 was a slightly warmer (mean of 10.2 vs degrees Celsius) than the long term trend but typical
238 for overall average rainfall (821mm).

239

240 By aggregating and analysing the full data it was possible to examine concentrations across the
241 sampling period to determine trends in concentrations which might therefore have an impact on
242 reported annual averages against environmental quality standards as well as assessing the
243 magnitude of impact that WwTW may have on downstream observed concentrations. This approach
244 of plotting monthly data provides three clear types of annual profiles associated with seasonal trends
245 in observed concentrations within river water receiving WwTW effluent. These trends may be
246 explained in the following way:

247

248 **Type A:** concentrations influenced primarily by in-river dilution rather than WwTW treatment
249 efficiency;

250 **Type B:** concentrations that follow seasonal (largely temperature-based) WwTW efficiency
251 patterns;

252 **Type C:** concentrations with relatively seasonally invariant patterns

253 Although quite simplistic in concept, dividing the observed trends up into these three types is
254 designed to illustrate the potential significance of impact a WwTW effluent might have on observed
255 downstream concentrations. The data analysis shows that in fact for some substances discussed
256 below, it is the performance of the WwTW (largely related to temperature changes and hence
257 microbiological activity and/or efficiency) which determines the observed seasonal profiles, not
258 environmental factors such as in-river dilution.

259 Although a full analysis of river flows associated with each individual WwTW would be helpful in
260 determining dilution factors available, obtaining such data for 170 WwTW locations across
261 catchments extending across the whole of England was far beyond the scope of this project. Such
262 data have formed part of the source apportionment analysis detailed elsewhere [20]. Suffice to say,
263 the general pattern of seasonality in river flow in the UK is well established and reported [22] with
264 higher flows during winter months (December to February) compared with summer (June to August)
265 although regional variations occur. A degree of dilution of wastewater may occur within the sewer
266 system after periods of rain owing to some sewer catchments collecting both domestic and industrial
267 wastewater as well as runoff from roofs and roads (termed combined sewers). In fact, within some
268 catchments there is a mix of both combined and separated sewerage within the same urban
269 catchment, with combined sewers within the older urban centres and separated systems in newer
270 satellite housing estates [20]. Furthermore, some temperature trends across the UK could have also
271 impacted on works efficiency but have not been allowed for because the point of this data analysis
272 exercise has been to use a sufficiently large chemical analysis dataset to absorb these influences
273 and therefore to determine seasonal trends which are over and above such variables.

274

275

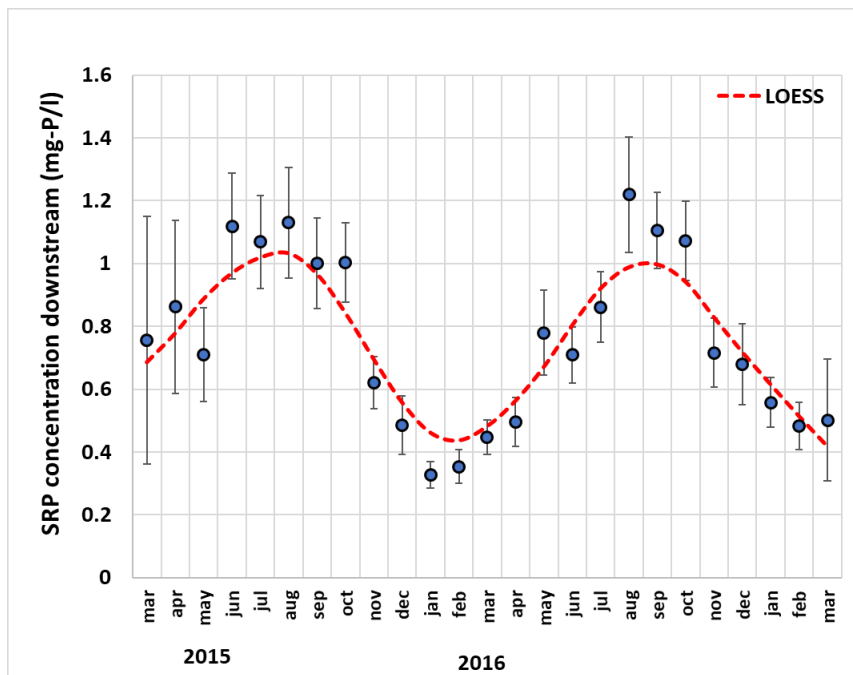
276

277 **3.1 Type A: Seasonal trends determined by dilution**

278

279 This is illustrated with reference to phosphorus concentrations. WwTW sources, along with diffuse
280 agricultural runoff, are the principal phosphorus inputs to surface waters [20]. Elevated
281 concentrations are a major cause of Environmental Quality Standard (EQS) exceedances under the

282 WFD [23]. Understanding relative contributions and seasonality is vital as phosphorus
 283 concentrations and standards are linked to biological activity which is itself seasonally mediated.
 284 Figure 2 provides a LOESS fit for SRP in river samples downstream of effluent discharge over two
 285 years.
 286



287
 288 **Figure 2 Soluble reactive phosphorus in river samples downstream of effluent discharge**
 289 **over two years (averages with a 90% confidence interval)**
 290

291 Soluble reactive phosphorus concentrations show marked seasonality within downstream receiving
 292 waters. Highest concentrations were observed in later summer and lowest in later winter. This picture
 293 is consistent with relatively constant emission of phosphorus from WwTW over an annual period,
 294 with mean monthly concentrations for all 170 WwTW effluents only varying between 1.7 and 2.5 mg-
 295 P/l over the sampling period, compared with a variation of a factor of 3 (ca. 0.4 to 1.2 mg-P/l) for
 296 observed downstream river concentrations (Figure S2).

297
 298 Some of the observed limited variability of WwTW SRP concentrations reflects that a large proportion
 299 of the WwTW (in this case approximately two thirds of the 170 sampled) have discharge permits
 300 applied to their effluents; restricting concentrations to an annual average of typically 1 or 2 mg-P/l.
 301 Works without explicit measures for phosphorus removal, have effluents of concentration of around
 302 5 mg-P/l [24]. The lower concentration of P present in the WwTW effluent during winter months is
 303 most likely to reflect the increased proportion of surface water runoff low in P from combined sewers
 304 entering the WwTW during wetter times of the year (e.g. Figure S3) rather than within WwTW

305 efficiency variation (see Type B below) because there is an excess of P entering WwTW over and
306 above that required to maintain works performance [25,26].

307

308 Recent trend analyses have been carried out for P in the UK [7-9] using long term datasets. They
309 have assessed the wider catchment influences including WwTW, which also recognise the
310 asynchronous relationship between river flow and observed concentrations associated with
311 predominantly low flows in summer and higher flows in winter (for example see Thames river flows
312 in Figure S3). Changes in amplitude of the seasonality and slight shifts in synchronisation were
313 attributed to changes in WwTW effluent quality and long term decline in fertiliser use on agricultural
314 land. It may be concluded therefore that variation in available dilution of effluent derived P in receiving
315 waters significantly exceeds variation in seasonal effluent concentrations.

316

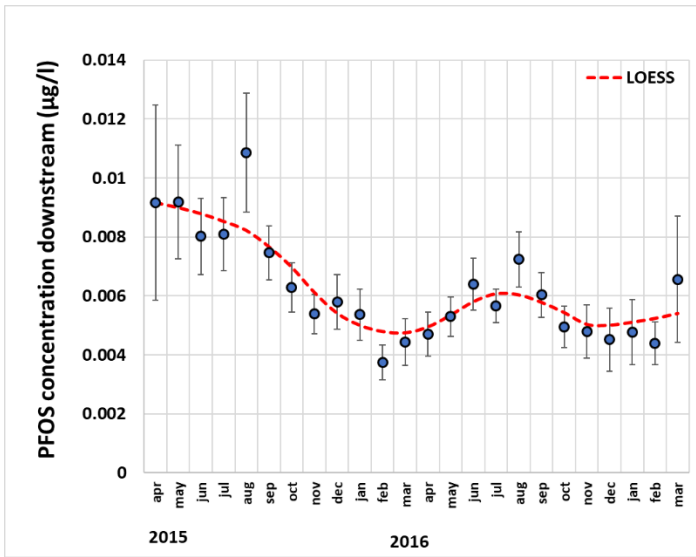
317 Analysis in-river data downstream of WwTW effluent discharges for priority chemicals regulated
318 under the WFD there is evidence that perfluorinated octane sulphonic acid (PFOS), perfluorinated
319 octanoic acid (PFOA) and hexabromocyclododecane (HBCDD) fall into Type A patterns. Figure 3
320 shows PFOS, PFOA and HBCDD averages by calendar month respectively. Prior to extensive
321 source control, all three compounds were used extensively in products and as flame retardants
322 owing to their thermal stability, which is an important factor in their persistence in the environment,
323 leading to bioaccumulation and concerns regarding toxicity and food chain transfer.

324

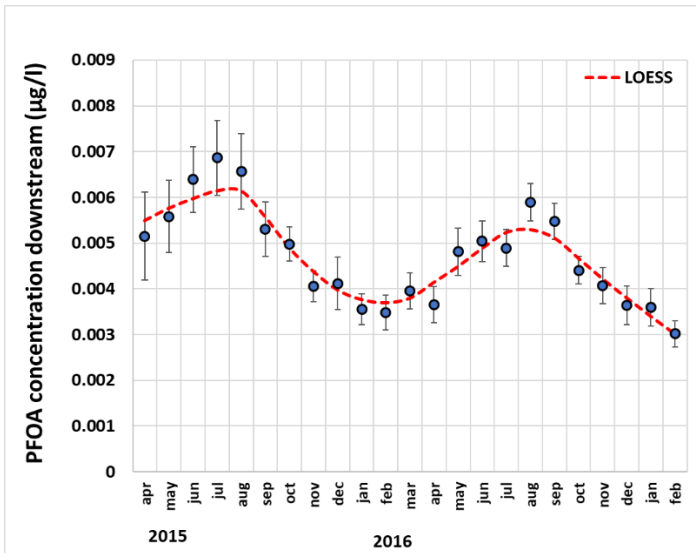
325 PFOS was originally included in REACH annex xvii restricted substances list. After PFOS was added
326 to the Annex B of the Stockholm Convention in 2009, the European Commission removed PFOS
327 from REACH annex xvii and added it to the annex I of the Regulation (EC) No 850/2004 of the
328 European Parliament and of the Council on persistent organic pollutants. PFOS is now regulated as
329 a persistent organic pollutant (POP) in EU [27]. Consequently, it is limited to less than <10 mg/kg in
330 products and preparations, <0.1 % by weight calculated with reference to the mass of structurally or
331 micro-structurally distinct parts that contain PFOS, <1 µg/m² of the coated material in textiles or other
332 coated materials. Exemptions occur for photoresists or anti reflective coatings for photolithography
333 processes, photographic coatings, provided certain conditions are met.

334

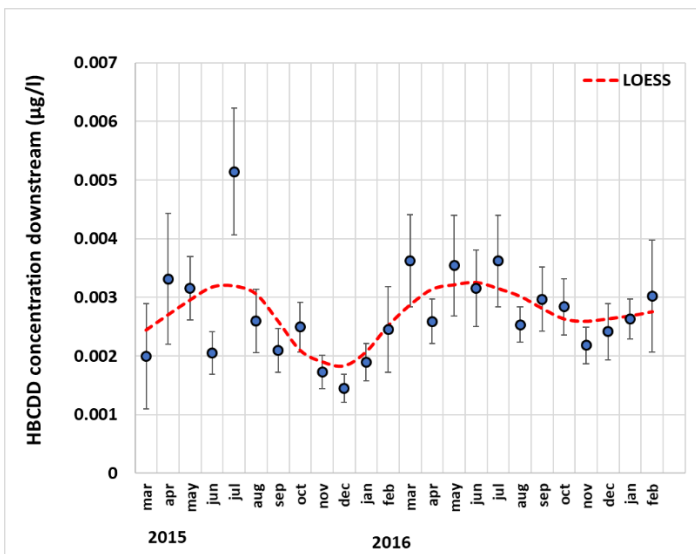
335



336



337



338 **Figure 3 PFOS (top graph), PFOA (middle graph) and HBCDD (bottom graph) in river**
339 **samples downstream of effluent discharge over two years with LOESS plot**
340 **(averages with a 90% confidence interval)**

341 Perfluorooctanoic acid (PFOA) and its salts are suspected to have a similar hazard profile to PFOS,
342 estimates of 100's to low 1,000's of tonnes per year use in the EU have been calculated with a high
343 degree of uncertainty [28,29], which appear to be less than that for PFOS. PFOA was added to
344 REACH annex XVII restricted substances (entry 68) by Commission Regulation (EU) 2017/1000 on
345 14 June 2017. Requirements include that it shall not be manufactured, or placed on the market as
346 substances on their own from 4 July 2020; shall not, from 4 July 2020, be used in the production of,
347 or placed on the market in (a) another substance, as a constituent; (b) a mixture; (c) an article, in a
348 concentration equal to or above 25 µg/kg of PFOA including its salts or 1000 µg/kg of one or a
349 combination of PFOA-related substances. A number of exemptions apply through to 2032 [30].
350 Control over the production and use of these substances means that concentrations should be
351 decreasing in the environment, although sources are most likely to be associated with WwTW with
352 the exception of inputs from release of firefighting foams directly into the environment, as was the
353 case with the Buncefield fire in the UK in 2005 [31].

354

355 The prevalence of these compounds in the products and their persistence means that they are still
356 detectable, and the fact that they are resistant to degradation means they will be less impacted by
357 seasonal changes in WwTW efficiency and observed river concentrations will be controlled by river
358 dilution. Two-year trends for samples collected downstream of WwTW for PFOS (Figure 3) show
359 minima during December and January for the two years. The EQS for PFOS is 6.5×10^{-4} µg/l as an
360 annual average [32] and so concentrations in the river downstream of the WwTW are still of the order
361 of 10 times the compliance target, at any given time of the year (across all sites in England and
362 Wales downstream of WwTW). Consequently, any observed seasonality combined with frequency
363 of compliance monitoring schemes, will not impact on the observed compliance for this substance.

364

365 PFOS has been reported in river samples downstream of WwTW in other countries such as Japan
366 and USA where concentrations range from low ng/l as reported here up to 100's of ng/l, which is
367 significantly higher [33-35]. The reported higher concentrations may be resulting from lower dilution,
368 the fact that the data reported elsewhere is at least 10 years old (and so pre any possible restrictions)
369 or potential contributions from surface runoff [35].

370

371 PFOA concentrations downstream of WwTW are of similar concentrations, but marginally lower,
372 likely to reflect the lower volumes used within Europe. The PNEC assigned to PFOA is the same as
373 the EQS value for PFOS (6.5×10^{-4} µg/l) and so observed levels across England and Wales are just
374 under 10 times the PNEC for any given waterbody at any time of the year. Seasonality shows the
375 same trend (Figure 3) but with an amplitude that varies by about a factor of two, and is better defined
376 than that for PFOS. For the same reasons of source and persistence, the observed concentrations

377 downstream are driven by dilution. As for PFOS, other reported concentrations in Japan and USA
378 range from ng/l to 1000's of ng/l downstream of manufacturing facilities or sewage treatment works
379 [33,34]. There was however, no assessment of seasonal patterns to compare with the UK data
380 reported here.

381

382 For HBCDD concentrations across all sites sampled throughout England and Wales are lower than
383 PFOS or PFOA monthly concentrations, averaging around 0.0025 µg/l downstream of the 172
384 WwTW (Figure 3). The lower concentrations may reflect reduced production and use compared with
385 PFOS/PFOA although a seasonal trend still is evident, the winter minimum in 2016 is less
386 pronounced than that for 2015. The annual average EQS set for identified sites within waterbodies
387 is 0.0016 µg/l and so again, seasonality and monitoring frequency/pattern will not impact on
388 compliance assessments for these sites as observed concentrations are almost exclusively greater
389 than the EQS. The limited data reported from other sources shows HBCDD levels are similar, for
390 example, effluent concentrations ranged from 0.4 to 12 ng/l in WwTW effluents and 0.19 to 14 ng/l
391 in river samples, therefore of the same order as reported here for the UK [36].

392

393 **3.2 Type B: Seasonal trends determined by treatment efficiency**

394

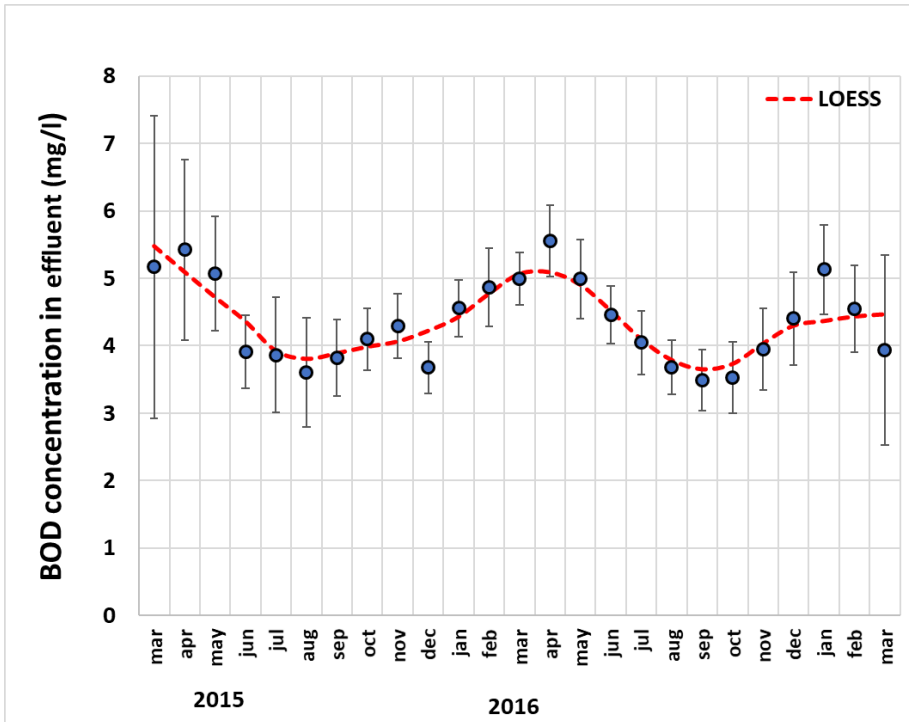
395 Before discussing trends in treatment efficiency, it is important to note that the statistical analysis
396 has been undertaken using all CIP WwTW for which data are available. There has been no attempt
397 to split WwTW into different treatment types for a number of reasons. Firstly, sub dividing the dataset
398 weakens the power of the statistical analysis and so detracts from the objective of determining
399 statistically seasonal trends based on big datasets and secondly previous data has shown that any
400 variation between works was not shown to be statistically significant [6].

401

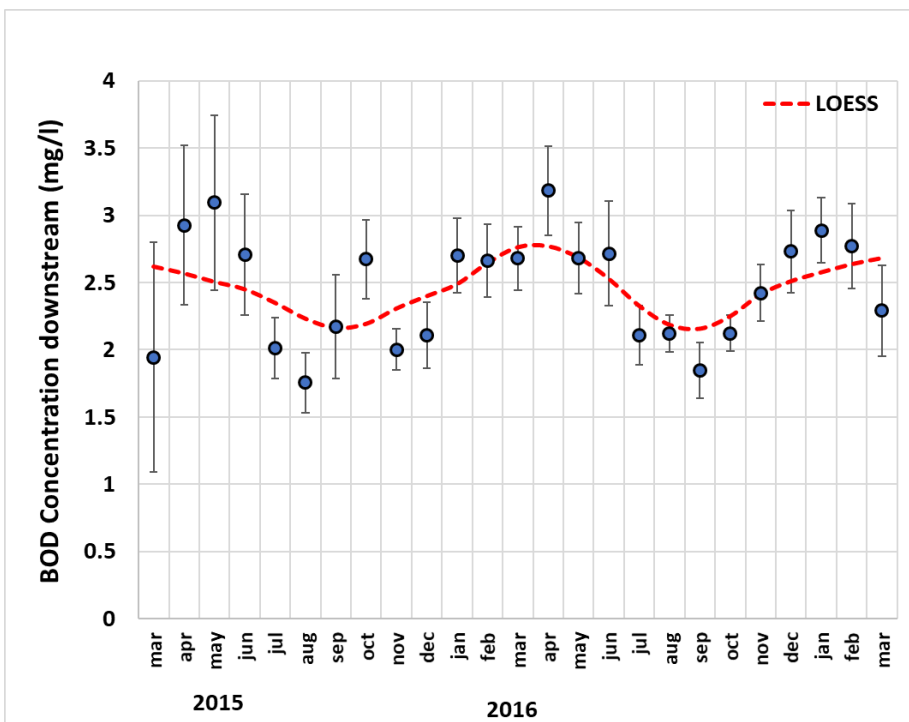
402 Biochemical Oxygen Demand (BOD) is a key metric for water quality (Figure 4). The seasonal
403 profiles for BOD are almost in complete opposition to those seen for SRP. Although clear seasonality
404 is observed, its phase, with minima in early autumn and maxima in late winter, is the reverse of that
405 for SRP. Furthermore, the amplitude of the variability is considerably greater in effluent than in river
406 samples (again opposite to the behaviour observed for SRP), indicating a source of variation in the
407 wastewater treatment process, and one that is powerful enough to reverse the effect of in-river
408 dilution. This source of variation is proposed as the temperature dependence of the biological
409 treatment process. During the warmer late summer/early autumn period the temperature and hence
410 efficiency of BOD removal is at its highest, compared with winter where the opposite is the case [37].
411 This assumption is supported by data from further north, where under more Arctic conditions winter
412 temperatures drop significantly below zero Celsius and impacts on WwTW efficiency has also been

413 reported [38]. There are unlikely to be significant variation across the English geographic regions,
414 because winter temperatures between the extreme north and south of the UK only vary by 2 degrees
415 Celsius (Met Office data).
416

417



418



419

420

421

422

423

424

425

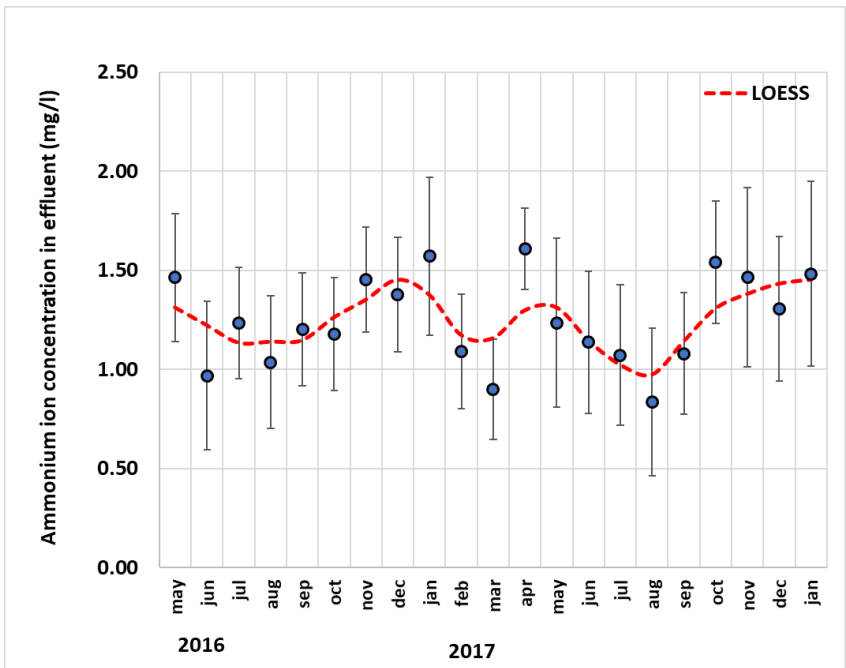
Figure 4 BOD in WwTW effluent (top graph) and downstream (bottom graph) over two years (averages with a 90% confidence interval)

426 Ammonia also exhibits a Type B behaviour similar to that for BOD, where reduced treatment
427 efficiency in winter leads to higher concentrations observed downstream even when greater dilution
428 occurs through the winter months (Figure 5). For good status under the WFD depending on typology
429 (upland, lowland, high and low alkalinity) 90th percentile concentrations range from 0.3 to 0.6 mg/l
430 total ammonia (0.25 mg-N/l and 0.49 mg-N/l respectively). It is not possible to compare these values
431 directly with an EQS because of the aforementioned aggregation of England and Wales data and
432 the fact that compliance is based on a river typology and reported 90th percentile concentrations.
433 The influence of WwTW effluents on downstream concentrations is obvious for the UK, however, in
434 rural environments where effluents are not a significant source of river flow, then observed
435 concentrations tend to reflect a flow-based pattern, such is the case for the North Saskatchewan
436 River, Canada [39].

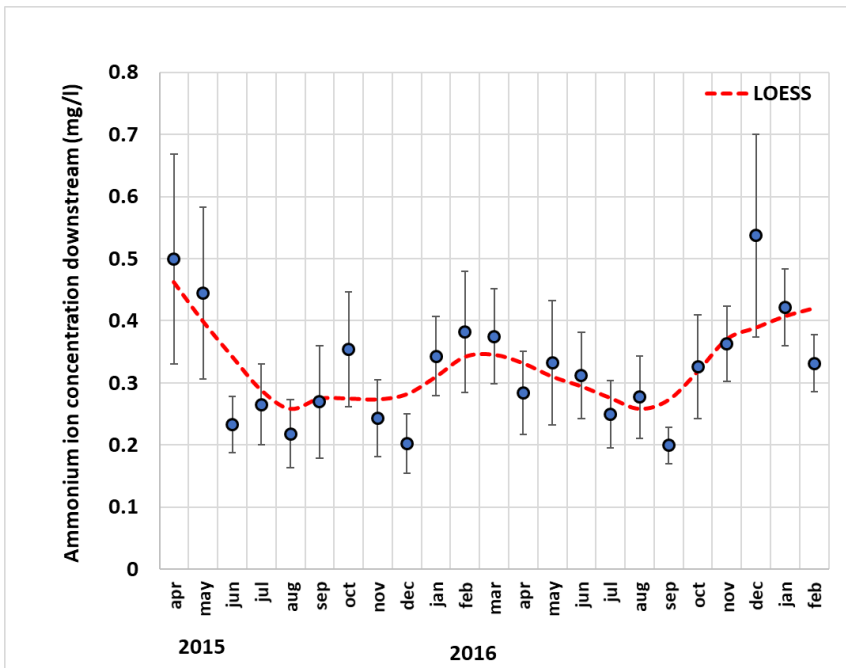
437

438

439
440
441
442
443
444



445



446

447

448

449

450

Figure 5 Ammonium ion concentrations in effluent (top graph) and in downstream river samples (bottom graph) over two years with LOESS plot (averages with a 90% confidence interval)

451 **3.3 Type C: Little seasonal variation**

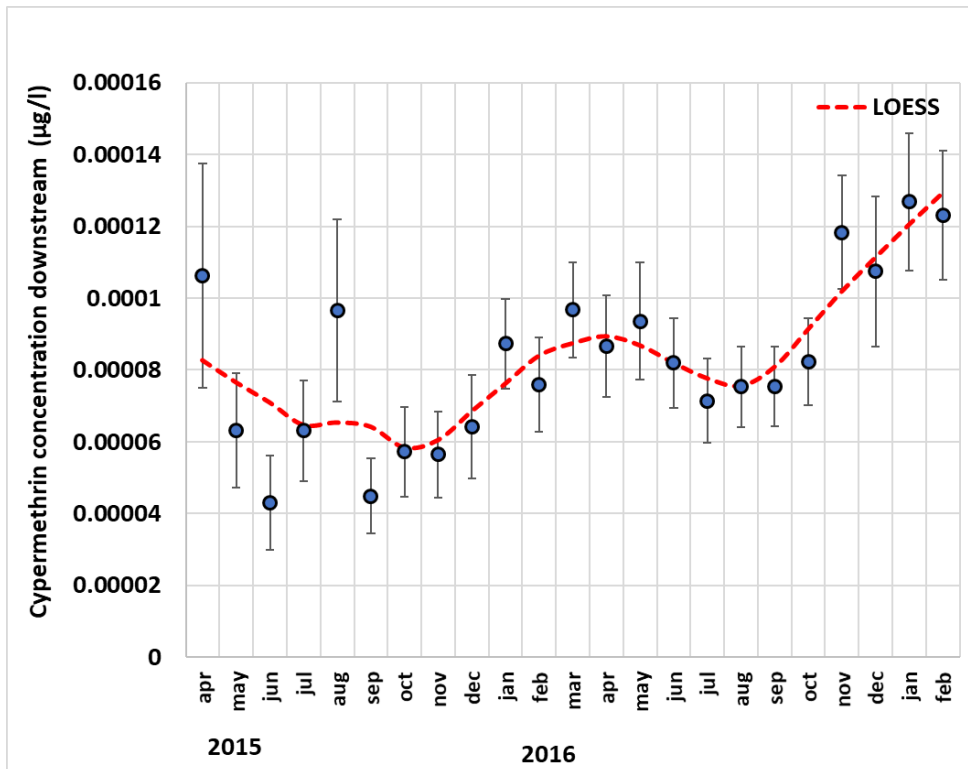
452

453 Other priority substances exhibited limited seasonal variation (Type C) in terms of obvious and
454 statistically robust conclusions. Cypermethrin for example (Figure 6) showed no statistically relevant
455 trends at 90% confidence level.

456

457

458



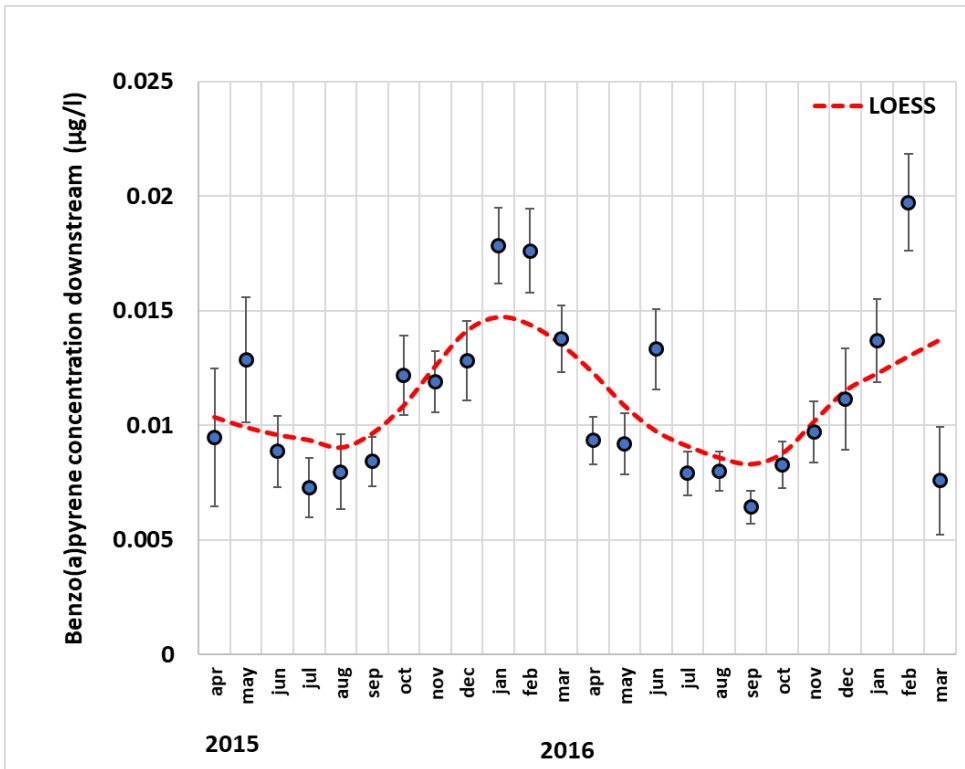
459

460 **Figure 6 Cypermethrin in river samples downstream of effluent discharge over two years**
461 **with LOESS plot (averages with a 90% confidence interval)**

462

463 A further potential driver of seasonality, illustrated below by benzo(a)pyrene (Figure 7), should not
464 be neglected. This is the case of substances for which the inputs to surface waters might vary, but
465 for which WwTW effluent is not the primary source. Low concentration in the summer months are
466 not related to sewage inputs and could probably be ascribed to seasonally reduced rainfall and
467 consequent more limited influence of run-off as an input to rivers [40]. The EQS is 1.7×10^{-4} µg/l and
468 so observed concentrations exceed the EQS by over 50 times largely as a result of diffuse runoff
469 sources [41].

470



471

472

473 **Figure 7 Benzo(a) pyrene in river samples downstream of effluent discharge over two years**
 474 **with LOESS plot (averages with a 90% confidence interval)**
 475

476 The CIP monitoring has shown that sewage effluents are not the principal sources of PAHs. Current
 477 opinion is that the main source in the UK is related to soils and surface waters contaminated by
 478 combustion products [42]. Given this, it might be proposed that run-off from soils and urban surfaces
 479 might be the main source and that lower volumes of run-off in the drier summer months could explain
 480 the seasonal effect illustrated above.

481

482
483
484

3.4 Seasonal trends in influent and effluent for pharmaceuticals

485 There is a dearth of data on seasonal trends for pharmaceutical concentrations within the
486 environment. The ability to analyse the CIP2 data provides vital information for wastewater
487 undertakers and regulators in terms of being able to plan future management strategies. Figure 8
488 below shows seasonal assessments for four pharmaceuticals representative of three large classes
489 of popular medicines: a steroid oestrogen (ethinyloestradiol - EE2) where inputs to works may be
490 expected to be constant year-round; two non-steroidal anti-inflammatory drugs (NSAIDs - ibuprofen
491 and diclofenac) where again seasonality would not be expected in use [38] and an antibiotic
492 (erythromycin) which could be expected to be more prescribed during winter months [43]. These
493 substances were determined in both wastewater influent and effluent (but not in receiving river
494 water). The volume of data for pharmaceuticals was not as substantial as for the determinands
495 discussed above; results were obtained for 45 sites instead of 170. Figure 8 illustrates, by the
496 differences in concentration in influent and effluent, the overall extent by which wastewater treatment
497 reduces concentrations of each determinand and provide an indication that seasonality is not a
498 particularly important factor in determining the concentrations of these substances either in influent
499 or effluent. This suggests the assumption that NSAIDs and steroid hormones are consumed at a
500 fairly constant rate throughout the year with few peaks or troughs in influent concentrations appears
501 to hold true. There was, however, no significant pattern in the influent concentrations observed for
502 erythromycin, which as an antibiotic, may lead to the assumption that there would be more
503 prescription in winter than summer and hence increased influent concentrations during the winter
504 months. Prescription data for macrolides such as erythromycin in America have shown seasonal
505 trends in prescriptions of macrolide drugs [44]. In the UK, erythromycin is not used as a flu vaccine
506 that is widely administered and is predominantly used for bacterial infections and is not effective
507 against colds, flu or other viral infections and so may not necessarily be expected to follow a seasonal
508 trend. Examination of effluent concentrations of the pharmaceuticals also fail to show a seasonal
509 trend. This may be owing to the fact that many pharmaceuticals are either readily biodegradable
510 such as EE2 and ibuprofen or poorly degradable such as diclofenac and erythromycin and so
511 temperature has only a limited impact on removal. In colder climates such as Finland, a distinct
512 reduction in removal has been reported for pharmaceuticals such as ibuprofen, diclofenac and
513 naproxen in the winter months [38]. However average winter temperature in Finland are sub-zero
514 Celsius compared with 6.8 Celsius for the UK (Met Office data).

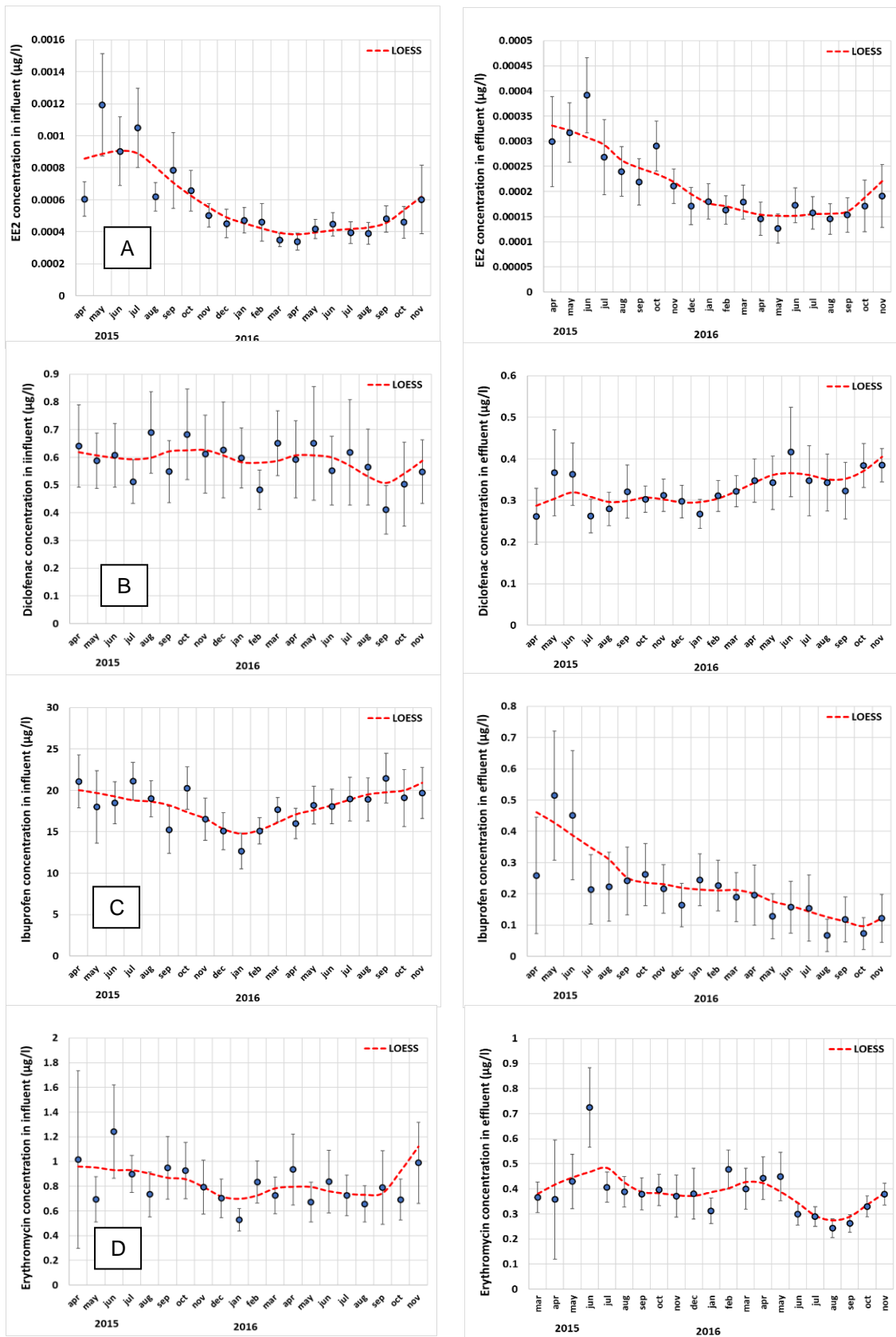
515

516 The notable feature of data for all four substances is that there is little seasonal variation; certainly,
517 there is little that might be of practical importance. The real-time (sequential) results for ibuprofen in
518 effluents appear to be influenced by some high measured values early in the monitoring programme.

519 There is no indication of any seasonality for erythromycin either by calendar month or over the 2-
520 year monitoring period. Finally, the time / concentration profile of the synthetic steroid EE2 is unusual
521 in that the data for early 2015 appear to be higher than subsequent values, but there is a striking
522 correspondence in the differences between the influent and effluent data; indicating a consistent
523 reduction in concentration of two thirds during treatment.

524

525



581
582
583
584

Figure 8 Ethinylestradiol (A), diclofenac (B), ibuprofen (C) and erythromycin (D) in WwTW influent (left hand side) and effluent (right hand side) over two years with LOESS plot (averages with a 90% confidence interval)

585 **4. Conclusions**

586 An analysis of over 6,000 samples has been completed to determine if it is possible to discern
587 seasonal trends in observed receiving water concentrations and/or effluent and influent wastewater
588 in the case of 4 pharmaceuticals. This has been the first time such a large dataset has been analysed
589 for these substances, many of which are not routinely determined. Furthermore, it has been possible
590 to show impacts that WwTW effluent has on downstream water quality irrespective of flow or climatic
591 conditions. Seasonality has been observed in data for several determinands reported here. Two
592 specific patterns driving seasonal variation within receiving waters are proposed:

- 593 a. Variation of riverine concentrations likely to be dominated by seasonal fluctuations in
594 river flow (sewage concentration being relatively consistent). This appears to be
595 responsible for a cyclic variation in riverine phosphate concentrations characterised
596 by high concentrations in late summer and low concentrations in late winter;
- 597 b. Variation attributable to the performance of wastewater treatment rather than river
598 flow and therefore subsequent dilution. Consequently higher concentrations are
599 observed in colder months owing to less efficient wastewater treatment which is
600 sufficiently to counteract any increase in dilution within the receiving water.

601 Seasonality for trace contaminants is more difficult to characterise than that of sanitary parameters
602 owing to the higher variability in effluent concentrations and the significantly lower concentrations of
603 the substances of interest leading to lower analytical precision. However, there is clear statistical
604 evidence for in-river dilution on observed concentrations of PFOS and hexabromocyclododecane.

605 For pharmaceutical concentrations measured within WwTW (influent and effluent) no such seasonal
606 cycling was observed, even for an antibiotic.

607 Overall, the data show not only the existence of seasonality (or lack of it), but also provide an insight
608 into the amplitude of such variation. This makes it possible to use this type of mathematical modelling
609 approach to assess the likely effects of seasonality in a wider context of regulation and potential
610 impact on aquatic life. For example, the existence of seasonality (perhaps due only to dilution effects)
611 might be demonstrated, but the amplitude might be too small to have any significant impact on either
612 compliance monitoring bias or possible ecological effects.

613
614

615 **References**

- 616 [1] Defra, Wastewater Treatment in the UK – 2012a: *UK Implementation of the EC Urban Waste*
617 *Water Treatment Directive*. Defra, London, UK.
- 618 [2] EU, European Union, *Dangerous Substances Directive (67/548/EEC)*, 1967.

- 619 [3] EU, European Union, *Urban Wastewater Treatment Directive (91/271/EEC)* COUNCIL
620 DIRECTIVE of 21 May 1991 concerning urban waste water treatment, 1991.
- 621 [4] EU, European Union, *Water Framework Directive (2000/60/EC) of the European Parliament and*
622 *of the Council establishing a framework for the Community action in the field of water policy*, 2000.
- 623 [5] EU, *European Union Directive Of The European Parliament And Of The Council Amending*
624 *Directives 2000/60/EC AND 2008/105/EC as regards priority substances in the field of water policy*,
625 2013.
- 626 [6] M. Gardner, V. Jones, S. Comber, M. Scrimshaw, T. Coello-Garcia, E. Cartmell, J. Lester and B.
627 Ellor B., Performance of UK wastewater treatment works with respect to trace contaminants.
628 *Sci.Total Environ.*, 2013, 456-457, 359-369.
- 629 [7] C. Svensson, Seasonal river flow forecasts for the United Kingdom using persistence and
630 historical analogues. *Hydrolog. Sci. J.*, 2014, 61, 19-35.
- 631 [8] B. Abbott, F. Moatar, O. Gauthier, O. Fovet, V. Antoine and O. Ragueneau, Trends and
632 seasonality of river nutrients in agricultural catchments: 18 years of weekly citizen science in France.
633 *Sci. Total Environ.*, 2018, 624, 845-858.
- 634 [9] A. Civan, F Worrall, H. Jarvie, N. Howden and T. Burt, Forty-year trends in the flux and
635 concentration of phosphorus in British rivers. *J. of Hydrol.*, 2018, 558, 314-327.
- 636 [10] M. Gardner, S. Comber, M. Scrimshaw, E. Cartmell, J. Lester and B. Ellor, The significance of
637 hazardous chemicals in wastewater treatment works effluents. *Sci. Total Environ.*, 2012a, 437, 363-
638 372.
- 639 [11] S. Comber M. Gardner, V. Jones, and B. Ellor Source Apportionment of Trace Contaminants in
640 Urban Sewer Catchments. *Environ. Technol.*, 2014, 36(5), 573-587.
- 641 [12] UKWIR, UK Water Industry Research, *The Chemical Investigations Programme Phase 2, 2015-*
642 *2020 – Initial Findings Volumes 1-4*, ISBN 1 84057 851 3, 2018.
- 643 [13] G. Jirka, T. Bleninger, R Burrows and T. Larsen. Management of point source discharges into
644 rivers: where do environmental quality standards in the new EC-water frame-work directive apply?
645 *International Journal of River Basin Management*, 2004, 2-3, 225-234.
- 646 [14] M. J. Gardner, S. Comber, D. Leverett, and A Gravell, Sample Stability of Trace Priority
647 Substances in Wastewater. *Analyt. Lett.*, 2012b, 45, 1686-1694.
- 648 [15] L. Keith. Environmental sampling and analysis: A practical guide. Lewis Publishers, 1991, ISBN
649 13: 978-0-87371-381-8.
- 650 [16] M. Thompson and S.L.R. Ellison, Towards an uncertainty paradigm of detection capability.
651 *Analyt. Methods*, 2013, 5, 5857-61.
- 652 [17] EC, European Commission, *Technical Specifications for Chemical Analysis and Monitoring of*
653 *Water Status*. Directive 2009/90/EC, 2009.
- 654 [18] S. Squire, M Ramsay, M Gardner and D Lister. Sampling proficiency test for the estimation of
655 uncertainty in the spatial delineation of contamination. *The Analyst*, 2000, 125, 11, 2026-2031.
- 656 [19] W.S. Cleveland and S.J. Devlin, Locally Weighted Regression: An Approach to Regression
657 Analysis by Local Fitting, *J. Am. Stat. Ass.*, 1988, 83, 596-610.
- 658 [20] S. Comber, R. Smith, P. Daldorph, M. Gardner, C. Constantino and B. Ellor Development of a
659 chemical source apportionment decision support framework for catchment management. *Environ.*
660 *Sci. Technol.*, 2013a, 47, 9824-9832.
- 661 [21] Met Office (2019) UK Meteorological Office data. Regional values for 2016. Accessed from
662 <https://www.metoffice.gov.uk/climate/uk/summaries/2016/annual/regional-values>, on 14 Jan 2019.

- 663 [22] J. Hannaford and G. Buys, Trends in seasonal river flow regimes in the UK. *J of Hydrol.*, 2012,
664 475, 158-174.
- 665 [23] UKTAG, UK Technical Advisory Group, *A revised approach to setting Water Framework*
666 *Directive phosphorus standards*. UK Technical Advisory Group, October 2012.
- 667 [24] S. Comber, M. Gardner, J. Darmovzalova and B. Ellor, Determination of the forms and stability
668 of phosphorus in wastewater effluent from a variety of treatment processes. *J. Environ. Chem. Eng.*,
669 2015, 3, 4, 2924-2930. [doi:10.1016/j.jece.2015.10.002](https://doi.org/10.1016/j.jece.2015.10.002).
- 670 [25] C. Karpf and P. Krebs, Quantification of groundwater infiltration and surface water inflows in
671 urban sewer networks based on a multiple model approach. *Wat. Res.*, 2011, 45, 3129-3136.
- 672 [26] S. Comber, M. Gardner, K. Georges, D. Blackwood and D. Gilmour Domestic source of
673 phosphorus to sewage treatment works. *Environ. Technol.*, 2013b, 34 (9-12), 1349-58.
- 674 [27] EC, *COMMISSION REGULATION (EU) No 757/2010 of 24 August 2010 amending Regulation*
675 *(EC) No 850/2004 of the European Parliament and of the Council on persistent organic pollutants*
676 *as regards Annexes I and III*. 2010.
- 677 [28] ECHA, *Annex xv restriction report proposal for a restriction substance name: Perfluorooctanoic*
678 *acid (PFOA), PFOA salts and PFOA-related substances*. 2014.
- 679 [29] ECHA, Committee for Risk Assessment (RAC) *Opinion on an Annex XV dossier proposing*
680 *restrictions on Perfluorooctanoic acid (PFOA), its salts and PFOA-related substances*.
681 ECHA/RAC/RES-O-0000006229-70-02/F. 2015.
- 682 [30] EC, *Commission Regulation (EU) 2017/1000 of 13 June 2017 amending Annex XVII to*
683 *Regulation (EC) No 1907/2006*, 2017.
- 684 [31] Environment Agency. *Investigation of PFOS and other perfluorochemicals in groundwater and*
685 *surface water in England and Wales*. Environment Agency, Bristol, 2007.
- 686 [32] EU, European Union, *Commission Regulation (EU) 2016/293 of 1 March 2016 amending*
687 *Regulation (EC) No 850/2004 of the European Parliament and of the Council on persistent organic*
688 *pollutants as regards Annex I* (Text with EEA relevance), 2016.
- 689 [33] K.J. Hansen, H.O. Johnson, J.S. Eldridge, J.L. Butenhoff and L.A. Dick, Quantitative
690 Characterization of Trace Levels of PFOS and PFOA in the Tennessee River. *Environ. Sci. Technol.*,
691 2002, 36, 1681-1685.
- 692 [34] N.P.H. Lien, S. Fuji, S. Tanaka, N. Nozoe and H. Tanaka, Contamination of perfluorooctane
693 sulfonate (PFOS) and perfluorooctanoate (PFOA) in surface water of the Yodo River basin (Japan).
694 *Desalination*, 2008, 226, 338-347.
- 695 [35] Y. Zushi, T. Takeda and S. Masunaga, Existence of nonpoint source of perfluorinated
696 compounds and their loads in the Tsurumi River basin, Japan. *Chemosphere*, 2008, 71, 1566-1573.
- 697 [36] M. Ichihara, A. Yamamoto, K.I. Takakura, N. Kakutani and M. Sudo, Distribution and pollutant
698 load of hexabromocyclododecane (HBCD) in sewage treatment plants and water from Japanese
699 Rivers. *Chemosphere*, 2014, 110, 78-84.
- 700 [37] A. Neville, The ecology and function of Protozoa in sewage purification. *Annals of Appl. Biol.*,
701 1946, 33, 314-325.
- 702 [38] N.M. Vieno, T. Tuhkanen and L. Kronberg, Seasonal variation in the occurrence of
703 pharmaceuticals in effluents from a sewage treatment plant and in the recipient water. *Environ. Sci.*
704 *Technol.*, 2005, 39, 8220-8226.
- 705 [39] T. Hebben, *Analysis of water quality trends for the long term river network: North Sakatchewan*
706 *River, 1977-2002*. Alberta Environment, December, 2005.

- 707 [40] C.C. Johnson, E.L. Ander, M.R. Cave and B. Palumbo-Roe, *Normal background concentrations*
708 *(NBCs) of contaminants in English soils: Final project report*. British Geological Survey
709 Commissioned Report, CR/12/035. 40pp, 2012.
- 710 [41] EU, European Union, *Cypermethrin EQS dossier*. A dossier prepared by the Sub-Group on
711 Review of the Priority Substances List (under Working Group E of the Common Implementation
712 Strategy for the Water Framework Directive), 2011.
- 713 [42] Defra, *Technical Guidance Sheet (TGS) on normal levels of contaminants in English soils.*
714 *Benzo(a) pyrene*. Technical Guidance Sheet Supplementary Information TGS04s, 2012b, July 2012.
- 715 [43] S. Caucci, A. Karkman, D. Carace, M. Rybicki, P. Timpel, V. Voolaid, R. Gurke, M. Virta and
716 T.U. Berendonk, Seasonality of antibiotic prescriptions for outpatients and resistance genes in
717 sewers and wastewater treatment plant outflow. *FEMS Microbiol. Ecol.*, 2016, 92(5) fiw060.
- 718 [44] L. Sun, E.Y. Klein and R. Laxminarayan, Seasonality and temporal correlation between
719 community antibiotic use and resistance in the United States. *Clinical Infectious Diseases*, 2012, 55,
720 687–694.
- 721